GRB BOOKS

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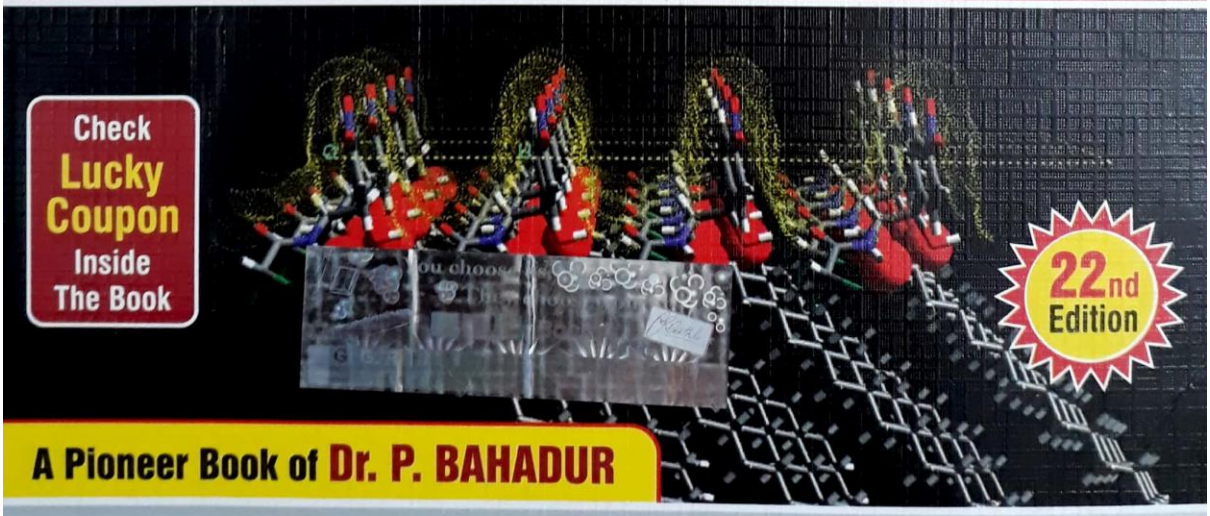
GRB

NUMERICAL CHEMISTRY

A New Pattern Book for

JEE (Main & Advanced)

& All Other Engineering Entrance Examinations

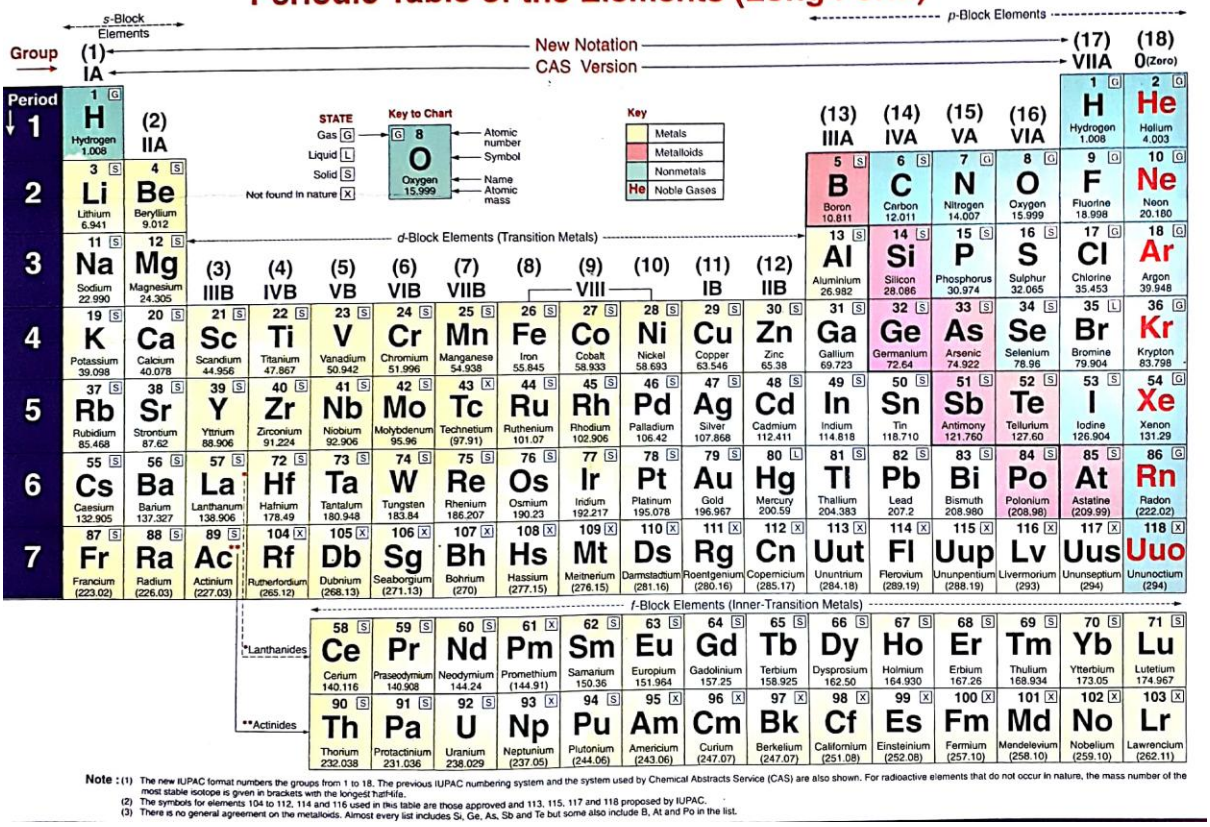


A Pioneer Book of Dr. P. BAHADUR

G. R. BATHLA PUBLICATIONS PVT. LTD.

DELHI

Periodic Table of the Elements (Long Form)



Period	(1) IA	(2) IIA	(3) IIIB	(4) IVB	(5) VB	(6) VIB	(7) VIIB	(8)	(9) VIII	(10)	(11) IB	(12) IIB	(13) IIIA	(14) IVA	(15) VA	(16) VIA	(17) VIIA	(18) 0(Zero)
1	1 G H Hydrogen 1.008																	2 G He Helium 4.003
2	3 S Li Lithium 6.941	4 S Be Beryllium 9.012											5 S B Boron 10.811	6 S C Carbon 12.011	7 G N Nitrogen 14.007	8 G O Oxygen 15.999	9 G F Fluorine 18.998	10 G Ne Neon 20.180
3	11 S Na Sodium 22.990	12 S Mg Magnesium 24.305											13 S Al Aluminium 26.982	14 S Si Silicon 28.086	15 S P Phosphorus 30.974	16 S S Sulphur 32.065	17 G Cl Chlorine 35.453	18 G Ar Argon 39.948
4	19 S K Potassium 39.098	20 S Ca Calcium 40.078	21 S Sc Scandium 44.956	22 S Ti Titanium 47.867	23 S V Vanadium 50.942	24 S Cr Chromium 51.996	25 S Mn Manganese 54.938	26 S Fe Iron 55.845	27 S Co Cobalt 58.933	28 S Ni Nickel 58.693	29 S Cu Copper 63.546	30 S Zn Zinc 65.38	31 S Ga Gallium 69.723	32 S Ge Germanium 72.64	33 S As Arsenic 74.922	34 S Se Selenium 78.96	35 L Br Bromine 79.904	36 G Kr Krypton 83.798
5	37 S Rb Rubidium 85.468	38 S Sr Strontium 87.62	39 S Y Yttrium 88.906	40 S Zr Zirconium 91.224	41 S Nb Niobium 92.906	42 S Mo Molybdenum 95.96	43 X Tc Technetium (97.91)	44 S Ru Ruthenium 101.07	45 S Rh Rhodium 102.906	46 S Pd Palladium 106.42	47 S Ag Silver 107.868	48 S Cd Cadmium 112.411	49 S In Indium 114.818	50 S Sn Tin 118.710	51 S Sb Antimony 121.760	52 S Te Tellurium 127.60	53 S I Iodine 126.904	54 G Xe Xenon 131.29
6	55 S Cs Caesium 132.905	56 S Ba Barium 137.327	57 S La Lanthanum 138.906	72 S Hf Hafnium 178.49	73 S Ta Tantalum 180.948	74 S W Tungsten 183.84	75 S Re Rhenium 186.207	76 S Os Osmium 190.23	77 S Ir Iridium 192.217	78 S Pt Platinum 195.078	79 S Au Gold 196.967	80 L Hg Mercury 200.59	81 S Tl Thallium 204.383	82 S Pb Lead 207.2	83 S Bi Bismuth 208.980	84 S Po Polonium (208.98)	85 S At Astatine (209.99)	86 G Rn Radon (222.02)
7	87 S Fr Francium (223.02)	88 S Ra Radium (226.03)	89 S Ac Actinium (227.03)	104 X Rf Rutherfordium (265.12)	105 X Db Dubnium (268.13)	106 X Sg Seaborgium (271.13)	107 X Bh Bohrium (270)	108 X Hs Hassium (277.15)	109 X Mt Meitnerium (276.15)	110 X Ds Darmstadtium (281.16)	111 X Rg Roentgenium (280.16)	112 X Cn Copernicium (285.17)	113 X Uut Ununtrium (284.18)	114 X Fl Flerovium (289.19)	115 X Uup Ununpentium (288.19)	116 X Lv Livermorium (293)	117 X Uus Ununseptium (294)	118 X Uuo Ununoctium (294)

*Lanthanides	58 S Ce Cerium 140.116	59 S Pr Praseodymium 140.908	60 S Nd Neodymium 144.24	61 X Pm Promethium (144.91)	62 S Sm Samarium 150.36	63 S Eu Europium 151.964	64 S Gd Gadolinium 157.25	65 S Tb Terbium 158.925	66 S Dy Dysprosium 162.50	67 S Ho Holmium 164.930	68 S Er Erbium 167.26	69 S Tm Thulium 168.934	70 S Yb Ytterbium 173.05	71 S Lu Lutetium 174.967
**Actinides	90 S Th Thorium 232.038	91 S Pa Protactinium 231.036	92 S U Uranium 238.029	93 X Np Neptunium (237.05)	94 S Pu Plutonium (244.06)	95 X Am Americium (243.06)	96 X Cm Curium (247.07)	97 X Bk Berkelium (247.07)	98 X Cf Californium (251.08)	99 X Es Einsteinium (252.08)	100 X Fm Fermium (257.10)	101 X Md Mendelevium (258.10)	102 X No Nobelium (259.10)	103 X Lr Lawrencium (262.11)

Note : (1) The new IUPAC format numbers the groups from 1 to 18. The previous IUPAC numbering system and the system used by Chemical Abstracts Service (CAS) are also shown. For radioactive elements that do not occur in nature, the mass number of the most stable isotope is given in brackets with the longest half-life.
(2) The symbols for elements 104 to 112, 114 and 116 used in this table are those approved and 113, 115, 117 and 118 proposed by IUPAC.
(3) There is no general agreement on the metalloids. Almost every list includes Si, Ge, As, Sb and Te but some also include B, At and Po in the list.

GRB

NUMERICAL CHEMISTRY

For JEE (Main & Advanced)
& All Other Engineering Entrance Examinations

By :

Dr. Prakash Bahadur

M.Sc., Ph.D.

Retd., Head of Chemistry Department,
D.A.V. (P.G.) College, Muzaffarnagar (U.P.)

Edited by :

Shalabh Saxena

B. Tech. (Chemical Engg.), Gold Medalist

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9 Colligative Properties and Solutions

Colligative Properties

The properties of a solution which depend on the number of particles present in solution, *e.g.*, osmotic pressure, lowering in vapour pressure, elevation in boiling point and depression in freezing point.

1. Osmosis and Osmotic pressure

(a) Spontaneous movement of solvent particles from dilute solution to concentrate solution through semipermeable membrane (SPM) is known as **osmosis.**

(b) The osmotic pressure is defined as the hydrostatic pressure developed in a **vertical** column as a result of osmosis, when a solution is separated with its solvent by SPM.

i.e., Osmotic pressure $(\pi) = h \times d \times g$

where h is height developed

	In CGS cm	In MKS metre
d is density of final solution	g /cm^3	kg / m^3
g is gravitational acceleration	981 cm /sec^2	9.8 cm /sec^2

(c) Osmotic pressure is given by solution equation proposed by van't Hoff as

$$\pi V = nST \quad ...(1)$$

or $$\pi = \frac{n}{V} ST \quad ...(2)$$

or $$\pi V = \frac{w}{m} ST \quad ...(3)$$

or $$\pi = CST \quad ...(4)$$

Conditions for validity of Eqs. (1) to (4).

(1) Dilute solutions.

(2) Solute neither dissociate nor associate.

	Litre atm	CGS	MKS
where π is osmotic pressure	atm	dyne /cm^2 Newton /m^2	
V is volume of solution	litre	cm^3	m^2
n is no. of mole of solute	—	—	—
w is mass of solute	g	g	kg
m is M. mass of solute	g	g	kg
S is solution constant	0.0821 litre atm K^{-1} mol^{-1}	8.314×10^7 erg K^{-1} mol^{-1}	8.314 joule K^{-1} mol^{-1}
T is temperature	Kelvin	Kelvin	Kelvin
C is concentration	mol litre^{-1}	mol / cm^3	mol / cm^3

Isotonic or iso-osmotic solutions: Two solutions of different substances having same osmotic pressure at same temperature are known as isotonic solutions.

For isotonic solutions

$\pi_1 = \pi_2$ Primary Condition ...(5)

Also, $C_1 = C_2$ Secondary Conditions ...(6)

Eq. (6) holds good only for those solutes which neither possess the tendency to get associate nor dissociate in solution NaCl, Na_2SO_4 etc.

2. Vapour Pressure Lowering

(a) The pressure exerted by the vapours of a solvent when they are in equilibrium with its liquid at a temperature is known as **vapour pressure.**

(b) Vapour pressure varies with:

(1) Temperature—Increases with increase in temperature.

(2) Nature of solvent—High boiling point liquid has low vapour pressure and *vice-versa*.

(3) Addition of a non-volatile solute—Addition of a non-volatile solute to a solvent always lowers the vapour pressure, *i.e.*,

$$\underset{(P^\circ)}{\text{V.P. of solvent}} > \underset{(P_s)}{\text{V.P. of solution}}$$

(c) The decrease in V.P. of a solvent on addition of a non-volatile solute (*i.e.*, $P^\circ - P_s$) is known as lowering in vapour pressure.

$$\Delta P = P^\circ - P_s$$

(d) Raoult's law for mixture of volatile liquids: The vapour pressure of a mixture obtained by mixing two or more volatile liquids is equal to the sum of partial vapour pressure of each component in mixture.

$$P_M = P'_A + P'_B + \ldots \quad \ldots(7)$$

where partial vapour pressure (P') of a component in a mixture is equal to the product of V.P. of pure component and its mole fraction in liquid mixture, *i.e.*,

$$P'_A = P^\circ_A \cdot X_A \; ; \quad P'_B = P^\circ_B \cdot X_B \text{; and so on}$$

$$\therefore \quad P_M = P^\circ_A \cdot X_A + P^\circ_B \cdot X_B + \ldots \quad \ldots(8)$$

$$\text{or} \quad P_M = P^\circ_A \cdot \frac{n_A}{n_A + n_B + \ldots} + P^\circ_B \cdot \frac{n_B}{n_A + n_B + \ldots} + \ldots \quad \ldots(9)$$

where, X is mole fraction of that component in mixture

and n is no. of mole of components, *i.e.*, w/m

$$\therefore \quad P_M = P^\circ_A \cdot \frac{w_A/m_A}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \ldots} + P^\circ_B \cdot \frac{w_B/m_B}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \ldots} + \ldots \quad \ldots(10)$$

(e) Raoult's law for non-volatile solute-liquid system: For non-volatile solute-solvent systems, the vapour pressure of a solution $P(s)$ is directly proportional to mole fraction of solvent.

$$P_s \propto \frac{N}{n+N} = P^\circ \times \frac{N}{n+N} \quad \ldots(11)$$

where, P° is vapour pressure of pure solvent

$$1 - \frac{P_s}{P^\circ} = 1 - \frac{N}{n+N}$$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} \quad \ldots(12)$$

Thus, the relative lowering in vapour pressure is equal to mole fraction of solute in solution,

where, $\frac{P^\circ - P_s}{P^\circ}$ = Relative lowering in vapour pressure.

$\therefore$ By Eq. (12) $\quad \frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} \quad \ldots(13)$

For dilute solutions: $n << N$

$$\therefore \quad n + N \approx N$$

$$\therefore \quad \frac{P^\circ - P_s}{P^\circ} = \frac{n}{N} = \frac{w \times M}{m \times W} \quad \ldots(14)$$

Note: (i) It is to be noted that use of Eq. (14) should be made only when solution is reported to be dilute.

(ii) In case dilute solutions are not reported, use Eq. (13) for calculating relative lowering in V.P. and if any other factor is to be calculated, an alternative derivation for Raoult's law given below (a simplified form for the numericals) should be used.

Alternative derivation: According to Raoult's law:

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} \quad \text{or} \quad \frac{P^\circ}{P^\circ - P_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

$$\text{or} \quad \frac{P^\circ}{P^\circ - P_s} - 1 = \frac{N}{n} \quad \text{or} \quad \frac{P^\circ - P^\circ + P_s}{P^\circ - P_s} = \frac{N}{n}$$

$$\text{or} \quad \frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{w \times M}{m \times W} \quad \ldots(15)$$

Eq. (15) gives accurate results whether solution is dilute or concentrated one.

(f) Raoult's law in combination with Dalton's law of partial pressure: Suppose X_A mole fraction of A and X_B mole fraction of B are present in a liquid mixture.

According to Raoult's law for liquid mixtures:

$$P'_A = P^\circ_A \cdot X_A$$

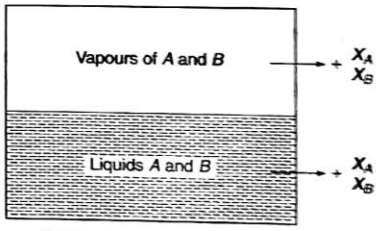
$$P'_B = P^\circ_B \cdot X_B \quad \text{and} \quad P_M = P'_A + P'_B$$

According to Dalton's law of partial pressure:

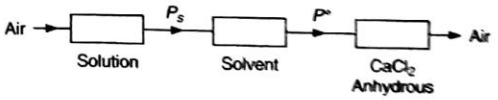
$$P'_A = P_M \cdot X'_A$$

$$P'_B = P_M \cdot X'_B$$

$$\therefore \quad P_M \cdot X'_A = P^\circ_A \cdot X_A \quad \ldots(16)$$



(g) Ostwald-Walker method for determination of vapour pressure: The method is based on the principle—when air is allowed to pass through a solvent or solution it takes up solvent vapours with it to get itself saturated with vapours at that temperature.



Loss in mass of solution $\propto P_s$

Loss in mass of solvent $\propto P^\circ - P_s$

Gain in mass of $CaCl_2 \propto P^\circ$

(h) Partial pressure of two immiscible liquids : According to Dalton's law :

$$P'_A = P_M \cdot X'_A = P_M \times \frac{n'_A}{n'_A + n'_B}$$

$$P'_B = P_M \cdot X'_B = P_M \times \frac{n'_B}{n'_A + n'_B}$$

where, X'_A and X'_B are mole fractions of A and B in gaseous phase.

$$\therefore \quad \frac{P'_A}{P'_B} = \frac{n'_A}{n'_B} \qquad ...(17)$$

3. Elevation in boiling point

(a) B. pt. of a liquid is a characteristic temperature at which its vapour pressure becomes equal to 1 atm pressure or 76 cm or 760 mm pressure.

(b) Addition of a non-volatile solute in a solvent lowers its vapour pressure and thus more heat is required to increase the V.P. of solution up to 1 atm. That is why b. pt. of solution increases. This increase in b. pt. is known as elevation in b. pt.

Elevation in b. pt. $= \Delta T_b = T_1 - T_0$

where, T_1 = b. pt. of solution and T_0 = b. pt. of solvent

(c) The elevation in b. pt. of solution is given by

$$\Delta T_b = K'_b \times \text{molality} = \frac{1000 K'_b w}{mW} = \frac{100 K_b w}{mW} \qquad ...(18)$$

where, K'_b = molal elevation constant in K mol^{-1} kg

K_b = molecular elevation constt. in K mol^{-1} 100 kg

and w = mass of solute

W = mass of solvent

m = molar mass of solute

4. Depression in freezing point

(a) F. pt. of a liquid is a characteristic temperature at which vapour pressure of solvent in its liquid and solid phase becomes same.

(b) Addition of a non-volatile solute to a solvent lowers the freezing point. The decrease in freezing point is known as depression in freezing point.

Depression in f. pt. $= \Delta T_f = T_0 - T_1$

where, T_1 = f. pt. of solution

T_0 = f. pt. of solvent

(c) The depression in f. pt. of solution is given by

$$\Delta T_f = K'_f \times \text{molality} = \frac{1000 K'_f w}{mW} = \frac{100 K_f w}{mW} \qquad ...(19)$$

where, K'_f = molal depression constant in K mol^{-1} kg

K_f = molecular depression constant in K mol^{-1} 100 g

Rest all terms have usual meanings.

5. Thermodynamic derivation for molal constants

$$K' = \frac{RT^2}{1000l} = \frac{0.002T^2}{l\,(\text{in cal/g})} = \frac{RT^2 \times M}{1000\,\Delta H} = \frac{RT \cdot M}{1000\,\Delta S} \qquad ...(20)$$

where, K' is molal elevation or depression constant

T is boiling point or freezing point of solvent

l is latent heat of vaporisation or latent heat of fusion in cal/g

R is molar gas constant

ΔH_V is heat of vaporisation or fusion in cal/mole $= l \times M$

ΔS_V is entropy change of vaporisation or fusion $= \frac{\Delta H}{T}$

Note : (1) Put R in the units of latent heat.

(2) Thus, $K'(K'_b$ or $K'_f)$ are characteristic constants for given solvent and are independent of nature of solute.

(3) K'_b is also known as molal ebullioscopic constant.

(4) K'_f is also known as molal cryoscopic constant.

Abnormal colligative properties

The experimental values of C.P. (*i.e.*, π, ΔP, ΔT_b and ΔT_f) of many solutes in solution resemble to calculated values of C.P.

However, in some cases, the experimental values of C.P. differ widely than those obtained by calculations. Such experimental values of C.P. are known as abnormal values of C.P.

Thus, Exp. values of C.P. $\lessgtr$ Calculated values of C.P.

or — or

Observed value — Normal values or Theoretical values

The abnormal behaviour of C.P. has been observed in following cases.

(1) Solutes having dissociation nature: Such solutes, which dissociate in solvent (water), *i.e.*, electrolytes show, an increase in the no. of particles present in solution. This gives rise to higher experimental values since,

C.P. $\propto$ No. of particles in solution

$\therefore$ Exp. C.P. > Normal C.P.

or Exp. π, ΔP, ΔT_b or ΔT_f > Normal π, ΔP, ΔT_b or ΔT_f

Also $\because$ $\text{C.P.} \propto \frac{1}{\text{Molar mass}}$

$\therefore$ Exp. Molar mass < Normal Molar mass

Consider an electrolyte say $A_X B_Y$ in water

$$A_X B_Y\ (aq.) \rightleftharpoons XA^{(+Y)}(aq.) + YB^{(-X)}(aq.)$$

Mole before dissociation	1	0	0
Mole after dissociation	$1-\alpha$	$X \cdot \alpha$	$Y \cdot \alpha$

Let α is degree of dissociation $= \frac{\text{Mole dissociated}}{\text{Total mole added}}$

$\therefore$ Normal C.P. $\propto$ No. of particles before dissociation

$\propto 1$

$\therefore$ Exp. C.P. $\propto$ No. of particles after dissociation

$\propto 1 - \alpha + X \cdot \alpha + X \cdot \alpha$

$\propto 1 - \alpha + X \cdot \alpha + X \cdot \alpha$

$$(i) = \frac{\text{Exp. C.P.}}{\text{Normal C.P.}} = 1 - \alpha + X \cdot \alpha + Y \cdot \alpha$$

$$= \frac{\text{Normal Molar mass}}{\text{Exp. Molar mass}} \qquad ...(21)$$

where (i) is van't Hoff factor. Also $i > 1$ for electrolytes

$$\therefore \quad \alpha = \frac{i-1}{(X+Y)-1} = \frac{i-1}{n-1} \quad [\text{where } n = (X+Y)] \quad ...(22)$$

$$\text{Further, van't Hoff coefficient } (g) = \frac{i}{n} = \frac{i}{(X+Y)} \quad ...(23)$$

where n is no. of particles furnished by 1 molecule of electrolyte assuming its 100% ionisation.

(2) Solutes showing association nature: Such solutes, which associate in solvent show a decrease in the no. of particles present in solution. This gives rise to lower experimental values of C.P.

$\therefore$ Exp. C.P. < Normal C.P.

or Exp. π, ΔP, ΔT_b, ΔT_f < Normal π, ΔP, ΔT_b, ΔT_f

and Exp. Molar mass > Normal Molar mass

consider a solute having association nature as,

$$nA \rightleftharpoons (A)_n$$

Mole before association	1	0
Mole after assocaition	$1-\alpha$	$\frac{\alpha}{n}$

where α is degree of association and n is no. of associated molecules.

$\therefore$ Normal C.P. $\propto$ No. of particles before association

$\propto 1$

$\therefore$ Exp. C.P. $\propto$ No. of particles after association

$$\propto 1-\alpha+\frac{\alpha}{n}$$

$$\therefore \quad (i) = \frac{\text{Exp. C.P.}}{\text{Normal C.P.}} = 1-\alpha+\frac{\alpha}{n} = \frac{\text{Normal Molar mass}}{\text{Exp. Molar mass}} \quad ...(24)$$

where i is van't Hoff factor; also $i < 1$ to such solutes.

Note : (1) For solutes having neither dissociation nor association, $i = 1$ because

Experimental C.P. = Normal C.P.

(2) General formulae for any C.P. may be written as

C.P. $\propto$ concentration $\times (1-\alpha+X\cdot\alpha+Y\cdot\alpha)$

$$\propto \frac{w\times 1000}{m\times V}(1-\alpha+X\cdot\alpha+Y\cdot\alpha)$$

(for dissociation)

or C.P. $\propto$ concentration $\left(1-\alpha+\frac{\alpha}{n}\right)$ (for association)

Henry's law : Amount of gas (a) dissolved per unit volume of solvent is directly proportional to pressure of gas (P)

$$a \propto P, \qquad a = K_H \cdot P \quad ...(25)$$

where K_H is Henry's law constant in g/atm

Also, $P \propto X_{gas}$, $P = K_H \cdot X_{gas}$ ...(26)

where X_{gas} is mole fraction of gas dissolved at pressure P of gas. K_H is expressed in atm.

• NUMERICAL PROBLEMS •

1. Calculate the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose per 150 mL solution.
2. The osmotic pressure of a non-volatile solute in C_6H_6 at 25°C is 20.66 Nm^{-2}. If the solution had a concentration of 2 g / dm^3, what is molar mass of solute?
3. At 27°C, 36 g of glucose per litre has an O.P. of 4.92 atm. If the osmotic pressure of solution is 1.5 atm at the same temperature, what should be its concentration?
4. 2.5 g of a substance is present in 200 mL of solution showing the osmotic pressure of 60 cm Hg at 15°C. Calculate the molar mass of substance. What will be the osmotic pressure if temperature is raised to 25°C?
5. Calculate O.P. of a solution obtained by mixing 100 mL of 3.4% solution (mass/vol.) of urea (molar mass 60) and 100 mL of 1.6% solution (mass/vol.) of cane-sugar (molar mass 342) at 20°C.
6. A 10 g mixture of glucose and urea present in 250 mL solution shows the osmotic pressure of 7.4 atm at 27°C. Calculate % composition of mixture.
7. At 25°C, a solution containing 0.2 g of polyisobutylene in 100 mL of benzene developed a rise of 2.4 mm at osmotic equilibrium. Calculate the molar mass of polyisobutylene if the density of solution is 0.88 g/mL.
8. A tube of uniform cross-sectional area 1 cm^2 is closed at one end with semipermeable membrane. A solution of 5g glucose per 100 mL is placed inside the tube and is dipped in pure water at 27°C. What equilibrium is established, calculate:
   (a) Osmotic pressure of solution.
   (b) Height developed in vertical column.
   Assume density of final glucose solution 1 g/mL.
9. A beaker containing 20 g sugar in 100 g water and another containing 10 g sugar in 100 g water are placed under a bell-jar and allowed to stand until equilibrium is reached. How much water will be transferred from one beaker to other?
10. At 300 K, two solutions of glucose in water of concentration 0.01 *M* and 0.001 *M* are separated by semipermeable membrane with respect to water. On which solution, the pressure need be applied to prevent osmosis? Calculate magnitude of this applied pressure.
11. 100 mL of 1.0 g sample of a drug having the compound $C_{21}H_{23}O_5N$ as drug is coated with sugar lactose (molar mass 342) exerts the osmotic pressure of 0.70 atm at 27°C. What is the drug percentage in sample.
12. A 5% solution (mass/vol.) of cane-sugar is isotonic with 0.877% (mass/vol.) of urea solution. Find molar mass of urea, if molar mass of sugar is 342.
13. How many g of glucose must be present in 0.5 litre of a solution for its osmotic pressure to be same as that of solution of 9.2 g glucose per litre?
14. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.
15. At 300 K, the vapour pressure of an ideal solution containing one mole of *A* and 3 mole of *B*, is 550 mm of Hg. At the same temperature, if one mole of *B* is added to this solution, the vapour pressure of solution increases by 10 mm of Hg. Calculate the V.P. of *A* and *B* in their pure state.
16. Cyclohexane and ethanol at a particular temperature have vapour pressure of 280 mm and 168 mm respectively. If these two solutions having mole fraction value of cyclohexane equal to 0.32 are mixed and the mixture has a total vapour pressure of 376 mm, will the mixture be an ideal solution?
17. The vapour pressure of benzene and toluene at 20°C are 75 mm of Hg and 22 mm of Hg respectively. 23.4 g of benzene and 64.4 g of toluene are mixed. If two form ideal solution, calculate the mole fraction of benzene in vapour phase when vapours are in equilibrium with liquid mixture.
18. Benzene and toluene form two ideal solutions *A* and *B* at 313 K. Solution *A* contains 4 mole of toluene and one mole of C_6H_6. Solution *B* contains equal masses of toluene and benzene. Calculate total pressure in each case. The vapour pressure of C_6H_6 and toluene are 160 and 60 mm respectively at 313 K.
19. The vapour pressures of pure ethylene bromide and propylene bromide are 170 and 127 mm of Hg at a temperature. Find out the vapour pressure of ethylene bromide in a 60% by mass solution of ethylene bromide in propylene bromide at same temperature. Also report the vapour pressure of propylene bromide as well as total vapour pressure of solution.
20. An aqueous solution containing liquid *A* (Molar mass = 128) 64% by mass has a V.P. of 145 mm. Find the V.P. of *A*, if that of water is 155 mm at the same temperature.
21. A mixture of ethyl alcohol and propyl alcohol has a V.P. of 290 mm at 27°C. If mole fraction of ethyl alcohol is 0.65, calculate the vapour pressure of ethyl alcohol, if vapour pressure of propyl alcohol is 210 mm.
22. A solution of *A* and *B* with 30% mole in solution is in equilibrium with its vapour which contains 60% mole of *A*. Assuming ideal nature, calculate the ratio of the vapour pressure of pure *A* to that of pure *B*.
23. The mole fraction of $CCl_4(g)$ in the vapour in equilibrium with liquid mixture of CCl_4 and $SiCl_4$ is

0.3474. The vapour pressure of $SiCl_4$ and CCl_4 is 238.3 and 114.9 mm respectively at the same temperature. Calculate % by mass of CCl_4 in liquid mixture.

24. The molar volume of liquid benzene (density $= 0.877\ g\ mL^{-1}$) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density $0.867\ g\ mL^{-1}$) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution. **(IIT 1996)**

25. At 90°C, the vapour pressure of toluene is 400 mm and that of xylene is 150 mm. What is the composition of liquid mixture that will boil at 90°C when the pressure of mixture is 0.5 atm?

26. An organic liquid *A*, is immiscible with water. When boiled together with water, the boiling point is 90°C at which the partial vapour pressure of water is 526 mm Hg. The superincumbent (atmospheric) pressure is 736 mm Hg. The mass ratio of the liquid and water collected is 2.5 : 1. What is the molar mass of the liquid?

27. A mixture of two immiscible liquids nitrobenzene and water boiling at 99°C has a partial vapour pressure of water 733 mm and that of nitrobenzene 27 mm. Calculate the ratio of the mass of nitrobenzene to the water in distillate.

28. A mixture of chlorobenzene and water (immiscible) boils at 90.3°C at an external pressure of 740.2 mm. The vapour pressure of pure water at 90.3°C is 530.1 mm. Calculate the % composition of distillate.

29. Dichlorodifluoro methane, CCl_2F_2, one of the chlorofluoro refrigerant responsible for destroying part of the earth's ozone layer has $P_{(vap)} = 40.0$ mm Hg at −81.6°C and $P_{(vap)} = 400$ mm Hg at −43.9°C. What is the normal boiling point of CCl_2F_2 in °C?

30. The vapour pressure of pure water at 25°C is 23.62 mm. What will be the vapour pressure of a solution of 1.5 g of urea in 50 g of water? **(Roorkee 2001)**

31. Calculate the vapour pressure of solution having 3.42 g of cane-sugar in 180 g water at 40°C and 100°C. Given that boiling point of water is 100°C and heat of vaporisation is 10 kcal mol^{-1} in the given temperature range. Also calculate the lowering in vapour pressure of 0.2 molal cane-sugar at 40°C.

32. The vapour pressure of pure benzene at 25°C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.9 mm of Hg. Calculate molality of solution.

33. What mass of solute (Molar mass 60) is required to dissolve in 180 g of water to reduce the vapour pressure to 4/5th of pure water?

34. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molar mass of solid substance? **(IIT 1990)**

35. The vapour pressure of an aqueous solution of glucose is 750 mm of Hg at 373 K. Calculate molality and mole fraction of solute. **(IIT 1989)**

36. The vapour pressure of water is 92.5 mm at 300 K. Calculate V.P. of 1 molal solution of a solute in it.

37. A solution containing 30 g of a non-volatile solute in exactly 90 g water has a vapour pressure of 21.85 mm of Hg at 25°C. Further 18 g of water is then added to solution, the new vapour pressure becomes 22.15 mm of Hg at 25°C. Calculate,

(a) Molar mass of solute.

(b) Vapour pressure of water at 25°C.

38. The vapour pressure of an aqueous solution at 20°C is 17 mm and that of pure water at same temperature is 17.39 mm. Calculate, (i) Density of water vapours at this temperature, (ii) Osmotic pressure of solution assuming molarity and molality be same.

39. The vapour pressure of water at 293 K is 2338 Pa and the vapour pressure of an aqueous solution is 2295.8 Pa. If density of solution is 1010 kg / m^3 at 313 K, calculate the osmotic pressure at 313 K. Molar mass of solute = 60.

40. Calculate the relative lowering in V.P. if 10 g of a solute (molar mass 100) are dissolved in 180 g water.

41. At 50°C the vapour pressure of pure water and ethyl alcohol are 92.5 and 219.9 mm of Hg respectively. If 6g of non-volatile solute of molar mass 120 are dissolved in 150 g of each of these solvent, what will be the ratio of relative vapour pressure lowering in two solvents?

42. 0.1 *M* solution of glucose was found to be isotonic with a solution of *X* in 100 g water. Calculate relative lowering in vapour pressure of solution of *X* in water.

43. Calculate the mass of a non-volatile solute (molar mass 40), which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

44. What mass of non-volatile solute, urea (NH_2CONH_2) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of solution?

45. Dry air was successively passed through a solution of 5 g solute in 80 g water and then through pure water. The loss in mass of solution was 2.5 g and that of pure water was 0.04 g. What is molar mass of solute?

46. Calculate the vapour pressure lowering of a 0.10 m aqueous solution of non-electrolyte at 75°C.

47. A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour

pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene? **(IIT May 1997)**

48. An aqueous solution of glucose containing 12 g in 100 g of water was found to boil at 100.34°C. Calculate K_b for water in K mol^{-1} kg.

49. 20 mL of ethanol (density 0.7893 g/mL) and 40 mL of H_2O (density 0.9971 g/mL) at 25°C are mixed to have a mixture (density 0.9571 g/mL). Calculate the per cent change in volume after mixing. Also report molality and molarity of alcohol and deviation from Raoult's law.

50. The boiling point of $CHCl_3$ was raised by 0.323°C when 0.5143 g of anthracene was dissolved in 35 g $CHCl_3$. Calculate the molar mass of anthracene. K_b' for $CHCl_3$ = 3.9 K mol^{-1} kg.

51. What will be the boiling point of bromine when 174.5 mg of octa atomic sulphur is added to 78 g of brsomine? K_b' for Br_2 is 5.2 K mol^{-1} kg and *b*. pt. of Br_2 is 332.15 K.

52. 0.48 g of a substance was dissolved in 10.6 g C_6H_6. The freezing point of benzene was lowered by 1.8°C. Calculate molar mass of the substance. Molecular depression constant for benzene is 50 K mol^{-1} 100 g.

53. One mole of triphenyl methanol lowers the freezing point of 1000 g of 100% sulphuric acid twice as much as one mole of methanol. Why?

54. Menthol is a crystalline substance with a peppermint taste. A 6.2% (mass/mass) solution of menthol in cyclohexane freezes at −19.5°C. Determine molar mass of menthol. The freezing point and molal depression constant of cyclohexane are 6.5°C and 20.2 K molality^{-1}.

55. How much ethyl alcohol must be added to 1.00 litre of water so that the solution will freeze at 14° F ? (K_f for water = 1.86°C / mol)

56. An aqueous solution containing 5% by mass of urea and 10% by mass of glucose. What will be its freezing point? K_f' for H_2O is 1.86° mol^{-1} kg.

57. An aqueous solution of glucose boils at 100.01°C. The molal elevation constant for water is 0.5 K mol^{-1} kg. What is the number of glucose molecules in the solution containing 100 g water?

58. 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 178.4 K. 2.8 g of a solid (*A*) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molar mass of (*A*). **(Roorkee 2000)**

59. Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g C_6H_6, 1 g of AB_2 lowers the f. pt. by 2.3°C whereas 1.0 g of AB_4 lowers it by 1.3°C. The K_f for C_6H_6 is 5.1 K mol^{-1} kg. Calculate atomic mass of *A* and *B*.

60. The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g of water is found to −34°C. Assuming ideal behaviour calculate the density of ethylene glycol.
(K_f' for water = 1.86 K kg mol^{-1}) **(Roorkee 1999)**

61. A solution of 0.643 g of an organic compound in 50 mL of benzene (density 0.879 g/mL) lowered its freezing point from 5.51°C to 5.03°C. Calculate the molar mass of solid. K_f for benzene is 5.12 K mol^{-1} kg.
(IIT 1992)

62. A motor vehicle radiator was filled with 8 litre of water to which 2 litre of methyl alcohol (density 0.8 g/mL) were added. What is the lowest temperature at which the vehicle can be parked out doors without a danger that the water in radiator will freeze? K_f' for H_2O = 1.86 K mol^{-1} kg.

63. A mixture which contains 0.550 g of camphor and 0.090 g of an organic solute melts at 161°C. The solute contains 93.75% C and 6.25% H by mass. What is the molecular formula of compound? K_f' for camphor is 37.5°C mol^{-1} kg. The m. pt. of camphor is 209°C.

64. If boiling point of an aqueous solution is 100.1°C. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

65. Calculate the freezing point of an aqueous solution having mole fraction of water 0.8. Latent heat of fusion of ice is 1436.3 cal mol^{-1}.

66. Two solutions of non-volatile solutes *A* and *B* having molar mass ratio of *A* and *B* (M_A / M_B) as 1/3 are prepared by dissolving 5% (mass/vol.) of each in water. Calculate the ratio of freezing point depression. If the two solutions are mixed to prepare a new solution (S_1) by mixing in the ratio 2 : 3 by volume and another new solution (S_2) is obtained by mixing in the ratio 3 : 2, find out $\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}}$. Assume density of solution *A* and *B* equal to one.

67. Calculate the entropy change for vaporisation of water if latent heat of vaporisation for water is 540 cal/g. Given K_b for H_2O = 0.51 K / molality.

68. Match the following if the molar masss of *X*, *Y* and *Z* are same. **[IIT 2003]**

	b.pt.	K_b
X	100	0.68
Y	27	0.53
Z	253	0.98

69. Calculate the amount of ice that will separate out on cooling *a* solution containing 50 g of ethylene glycol in 200 g water to −9.3°C. (K_f for water = 1.86 K mol^{-1} kg) **(Roorkee 1995)**

70. 1000 g of 1 m sucrose solution in water is cooled to −3.534°C. What mass of ice would be separated out at this temperature? K'_f H_2O = 1.86 K mol^{-1} kg.

71. 100 g of sucrose solution in water is cooled to −0.5°C. What mass of ice would be separated out at this temperature, if solution started to freeze at −0.38°C ? K'_f for H_2O = 1.86 K mol^{-1} kg.

72. Calculate the freezing point of an aqueous solution of non-electrolyte having an osmotic pressure 2.0 atm at 300 K. K'_f = 1.86 K mol^{-1}kg and S = 0.0821 litre atm K^{-1} mol^{-1}. Assume molarity and molality same. **(Roorkee 1993)**

73. An aqueous solution of urea has freezing point of −0.52°C. Calculate the osmotic pressure of solution at 27°C. Assume molarity and molality be same. K'_f for H_2O is 1.86 K mol^{-1} kg.

74. The osmotic pressure of an aqueous solution of sucrose is 2.47 atm at 303 K and the molar volume of the water present is 18.10 cm^3. Calculate the elevation in boiling point of the solution. Given $\Delta H_{Vap.}$ = 540 cal / g. Assume volume of solvent equal to volume of solution.

75. The molar mass of an organic compound is 58 g / mol. 24 g of this is dissolved in 600 g of water, calculate its boiling point when vapour pressure of water becomes 760 mm at 99.725°C. K_b of H_2O is 0.513 K kg mol^{-1}.

76. A solution of a non-volatile solute in water freezes at −0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K. **(IIT 1998)**

77. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate osmotic pressure of the solution. Given S = 8.314 JK^{-1} mol^{-1}. **(Roorkee 1991)**

78. A 1% (mass/vol.) KCl solution is ionised to the extent of 82%. What would be its osmotic pressure at 18°C ?

79. Calculate the osmotic pressure of 0.1N Na_3PO_4 solution at 300 K.

80. Arrange the osmotic pressures of given solution in increasing order assuming complete ionisation of each salt.

(a) 0.1 N glucose (b) 0.1 N KNO_3

(c) 0.1 N K_2SO_4 (d) 0.1 N K_3PO_4

81. A 0.001 molal solution of a complex represented as Pt $(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054°C. Given K_f for H_2O = 1.86 K molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

82. Calculate the osmotic pressure of 20% (mass/vol.) anhydrous $CaCl_2$ solution at 0°C assuming 100% ionisation.

83. A solution of KCl containing 7.45 g of it per litre solution has osmotic pressure 4.68 atm at 300 K. Calculate van't Hoff factor, degree of dissociation and osmotic coefficient (g).

84. A certain mass of a substance when dissolved in 100 g C_6H_6 lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100 g of water lowers the freezing point by 1.40°C. If the substance has normal molar mass in benzene and is completely dissociated in water, into how many ions does it dissociate in water? K'_f for H_2O and C_6H_6 are 1.86 and 5.12 K mol^{-1} kg respectively.

85. X g of a non-electrolyte compound (molar mass = 200) are dissolved in 1.0 litre of 0.05 M NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of X. Assume complete dissociation of NaCl and ideal behaviour of this solution. (R = 0.082 litre atm mol^{-1} K^{-1}) **(Roorkee 1998)**

86. Calculate osmotic pressure of a decinormal solution of $BaCl_2$ at 27°C showing 80% degree of ionisation.

87. A 1.2% solution (mass/volume) of NaCl is isotonic with 7.2% solution (mass/volume) of glucose. Calculate degree of ionisation and van't Hoff factor of NaCl.

88. The vapour pressure of a solution containing 2 g of an electrolyte BA in 100 g water, which dissociates in one B^+ and one A^- ion in water, is 751 mm, at 100°C. Calculate degree of ionisation of BA if its molar mass is 56.

89. When 11.7 g of NaCl are dissolved in 200 g of water the depression in freezing point is doubled than the depression caused by 342 g of cane-sugar in 1000 g of water. From this information what do you infer about the nature of solute particles of NaCl in solution?

90. A storage battery contains a solution of H_2SO_4 38% by mass. At this concentration, van't Hoff factor is 2.50. At what temperature will the battery contents freeze? (K'_f = 1.86° mol^{-1} kg)

91. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7 g of salt per 100 g of water at 100°C is 70%. Calculate the vapour pressure of solution. **(IIT 1991)**

92. 1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168°C. If 0.2 g of same acid requires 15.1 mL of N / 10 alkali for complete neutralization, calculate degree of dissociation of acid. K'_f for H_2O is 1.86 K mol^{-1} kg.

93. 1 g of a mixture containing NaCl and $CaCl_2$ is dissolved in water. Sodium oxalate on addition to this solution completely converts $CaCl_2$ to CaC_2O_4. The CaC_2O_4 is filtered and dissolved in dil. H_2SO_4. The clear solution requires 22 mL of 0.1 M $KMnO_4$. Calculate freezing point of an aqueous solution prepared by dissolving 5 g of same mixture containing $CaCl_2$ and NaCl in 100 g water. K_f of water is 1.86 K kg^{-1} mol^{-1}. Assume complete dissociation of $CaCl_2$ and NaCl.

94. What will be the osmotic pressure of 0.1 *M* monobasic acid if its pH is 2 at 25°C?

95. A complex is represented as $CoCl_3xNH_3$. Its 0.1 molal solution in water shows $\Delta T_f = 0.558°$. K_f for H_2O is 1.86 K molality^{-1}. Assuming 100% ionisation of complex and coordination number of Co as six, calculate formula of complex.

96. What is the ratio by mass of NaF and NaI which when dissolved in water produces the same osmotic effects as 0.1 molar solution of urea in water at same temperature? The mass of residue obtained on evaporation of the salt solution is 0.48 gram per 100 mL of solution evaporated. Assume complete dissociation of the salts.

97. A 0.025*M* solution of monobasic acid had a freezing point of −0.06°C. Calculate K_α for the acid. K_f for $H_2O = 1.86°$ molality^{-1}. Assume molality equal to molarity.

98. 0.01 *M* aqueous solution of weak acids H*A* and H*B* shows osmotic pressures equal to 0.30 atm and 0.35 atm respectively at 25°C. Calculate the ratio of their degree of dissociation.

99. Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and 2.3 K kg mol^{-1}.

(Roorkee 1997)

100. 1.22 g of benzoic acid is dissolved in 100 g each of acetone and benzene separately. Boiling point of mixture with acetone increase by 0.17°C and boiling point of mixture with benzene increases by 0.13°C. K_b for acetone and benzene are 1.7 and 2.6 K kg mol^{-1} respectively. Find the molar mass of benzoic acid in acetone and benzene. Justify your answer with structure. **(IIT 2004)**

101. To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3} respectively. **(IIT 2000)**

102. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene. Assume acetic acid dimerizes in benzene. K_f for benzene = 5.12 K mol^{-1} kg. **(Roorkee 1994)**

103. 2 g of benzoic acid dissolved in 25 g of C_6H_6 shows a depression in freezing point equal to 1.62 K. Molal depression constant of C_6H_6 is 4.9 K mol^{-1} kg. What is the percentage association of acid if it forms double molecule in solution? **(Roorkee 1990)**

104. 75.2 g C_6H_5OH (phenol) is dissolved in 1 kg of solvent of $K_f = 14$ K molality^{-1}. If depression in freezing point is 7K, then find the % dimerisation of phenol.

[IIT 2006]

105. The freezing point of 0.02 mole fraction of acetic acid in benzene is 277.4 K. Acetic acid exists partly as dimer. Calculate the equilibrium constant for dimerisation. Freezing point of benzene is 278.4 K and heat of fusion of benzene is 10.042 kJ mol^{-1}. Assume molarity and molality same.

106. A solution containing 28 g phosphorus in 315 g CS_2 (b.pt. 46.3°C) boils at 47.98°C. K_b' for CS_2 is 2.34 K mol^{-1} kg. Calculate molar mass of phosphorus and deduce its molecular formula. Assume its complete association.

107. Calculate the molal lowering of vapour pressure for H_2O at 100°C.

108. The freezing point of 0.08 molal $NaHSO_4$ is −0.345°C. Calculate the percentage of HSO_4^- ions that transfers a proton to water. Assume 100% ionisation of $NaHSO_4$ and K_f for $H_2O = 1.86$ K molality^{-1}.

109. The vapour pressure of two miscible liquids (*A*) and (*B*) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (*A*) is mixed with 12 mole of (*B*). However, as soon as (*B*) is added, (*A*) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. **(IIT 2001)**

110. The vapour pressure of a very dilute aqueous solution and pure water are 17 and 17.39 mm at 20°C. Calculate the osmotic pressure at 20°C and density of water vapours at 20°C.

111. A 10% (mass/mass) solution of cane-sugar undergoes partial conversion into glucose and fructose to show inversion of cane-sugar as:

$$\text{Sucrose} + \text{Water} \longrightarrow \text{Glucose} + \text{Fructose}.$$

If the solution boils at 100.27°C at this state, calculate the average mass of the dissolved material. What fraction of the sugar has inverted? Given K_b for H_2O is 0.512 K mol^{-1} kg.

112. The vapour pressure of a certain liquid is given by the equation:

$$\log_{10} P = 3.54595 + \frac{313.7}{T} + 1.40655 \log_{10} T,$$

where P is the vapour pressure in mm and T is temperature in K. Determine molar latent heat of vaporisation as a function of temperature and calculate its value at 80K.

113. Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 4 atm over the liquid at 25°C. The Henry's law constant for CO_2 in water at 25°C is 3.1×10^{-2} mol / litre - atm.

114. If N_2 gas is bubbled through water at 293 K, how many milli miles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given, that Henry's law constant for N_2 at 293 K is 76.48 l bar.

SOLUTIONS (Numerical Problems)

1. Given that, $w = 1.75\,g$, $m = 342$

$V = \frac{150}{1000}$ litre, $T = 290\,K$

$\pi V = nST = \frac{w}{m}ST$

$\pi \times \frac{150}{1000} = \frac{1.75}{342} \times 0.0821 \times 290$

$\pi = \mathbf{0.812\ atm}$

2. Given that,

$\pi = 20.66\,Nm^{-2}$,

$\frac{w}{V} = 2\,g/dm^3 = \frac{2\times10^{-3}}{10^{-3}}\,kg/m^3$

$S = 8.314\,J\,K^{-1}\,mol^{-1}$, $T = 273+25 = 298\,K$

$\pi V = \frac{w}{m}ST \quad \therefore \quad m = \frac{w}{V}\frac{ST}{\pi}$

$m = \frac{2\times10^{-3}\times8.314\times298}{10^{-3}\times20.66} = \mathbf{239.84\ kg\ mol^{-1}}$

3. Given that, $\pi_1 = 4.92\,atm$, $\pi_2 = 1.5\,atm$

$C_1 = \frac{36}{180\times1}$ $\left(\because C = \frac{w}{m\times V}\right)$ $C_2 = ?$

$\pi_1V_1 = n_1ST_1$, $\pi_2V_2 = n_2ST_2$

At same temperature,

$\frac{\pi_1}{\pi_2} = \frac{n_1}{V_1}\times\frac{V_2}{n_2} = \frac{C_1}{C_2} \quad \therefore \quad \frac{4.92}{1.5} = \frac{36}{180\times C_2}$

$\therefore \quad C_2 = \mathbf{0.061\ mol/L}$

4. Given that, $w = 2.5\,g$, $V = \frac{200}{1000}$ litre, $\pi = \frac{60}{76}$ atm, $T = 288\,K$

$\because \quad \pi V = \frac{w}{m}ST \quad \frac{60}{76}\times\frac{200}{1000} = \frac{2.5}{m}\times0.0821\times288$

$\therefore \quad m = \mathbf{374.38\ g\ mol^{-1}}$

Also, $\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$

$\because \quad \frac{60}{\pi_2} = \frac{288}{298}$

$\therefore \quad \pi_2 = \mathbf{62.08}$

5. $\pi_1V_1 = \frac{w_1}{m_1}ST_1$ for urea

$\pi_2V_2 = \frac{w_2}{m_2}ST_2$ for sugar

Since, 100 mL of urea solution are mixed with 100 mL of cane-sugar solution and thus, total volume becomes 200 mL in which 3.4 g urea and 1.6 g sugar is present

$\therefore \quad \pi_1 \times \frac{200}{1000} = \frac{3.4}{60}\times0.0821\times293$

$\pi_1 = \mathbf{6.82\ atm}$

$\pi_2 \times \frac{200}{1000} = \frac{1.6}{342}\times0.0821\times293$

$\therefore \quad \pi_2 = \mathbf{0.56\ atm}$

$\therefore \quad \pi_{Total} = \pi_1 + \pi_2 = 6.82+0.56 = \mathbf{7.38\ atm}$

6. Let mixture contains a g glucose and b g urea.

$\therefore \quad a+b = 10$ ...(1)

From $\pi V = nST$

Also, $7.4\times\frac{250}{1000} = \left[\frac{a}{180}+\frac{b}{60}\right]\times0.0821\times300$

$3a+b = 13.52$ ...(2)

Solving Eqs. (1) and (2), $a = 1.76g$

$b = 8.24g$

$\therefore \quad$ % of glucose $= \frac{1.76}{10}\times100 = \mathbf{17.6}$

% of urea $= \frac{8.24}{10}\times100 = \mathbf{82.4}$

7. Height developed = 2.4 mm

$\therefore$ Osmotic pressure $= h\cdot d\cdot g = \frac{2.4}{10}\times0.88\times981$

$= 207.187\,dyne\,cm^{-2}$

Now, $\pi V = nST$

$207.187\times100 = \frac{0.2}{m}\times8.314\times10^7\times298$

(R in erg; V in mL, using CGS system)

$\therefore \quad m = \mathbf{2.39\times10^5\ g\ mol^{-1}}$

8. (a) $\pi V = \frac{w}{m}ST$

Given that, $w = 5\,g$, $V = \frac{100}{1000}$ litre

$T = 300\,K$, $m = 180$

$\pi = \frac{5\times1000\times0.0821\times300}{180\times100} = \mathbf{6.842\ atm}$

(b) $\pi = hdg$

$6.841\times1.01\times10^5 = h\times10^3\times9.81$

$h = \frac{6.841\times1.01\times10^5}{9.81\times10^3}$

$= \mathbf{70.43\ m}$

$\pi = 6.841\,atm$

$= 6.841\times1.01\times10^5\ Nm^{-2}$

$d = 1\,g/cm^3$

$= 10^3\ kg/m^3$

$g = 9.81\,m/sec^2$

9. 1. At equilibrium the solutions occupy same vapour pressures as well as same concentrations since both are non-electrolyte.

2. Let w g of water passes from dilute solution to concentrate one to attain equilibrium.

Since, $P_s \propto$ mole fraction of solvent and $\frac{P°-P_s}{P_s} = \frac{n}{N}$

$\frac{P°-P_s}{P_s}$ for I $= \frac{P°-P_s}{P_s}$ for II

$\frac{20\times18}{342\times(100+w)} = \frac{10\times18}{342\times(100-w)}$

$\therefore \quad w = \mathbf{33.3\ g}$

10. For 0.01M solution,

$\pi_1 V_1 = n_1 S T_1$ | $n_1 / V_1 = 0.01$

$\therefore \ \pi_1 = 0.01 \times 0.0821 \times 300$ | $T = 300$ K

$= \mathbf{0.2463\ atm}$

For 0.001M solution,

$\pi_2 V_2 = n_2 S T_2$ | $n_2 / V_2 = 0.001$

$\therefore \pi_2 = 0.001 \times 0.0821 \times 300$ | $T = 300$ K

$= \mathbf{0.02463\ atm}$

The movement of solvent particles occurs from dilute to concentrate solution, *i.e.*, 0.001M to 0.01M solution. Thus, pressure should be applied on concentrated solution, *i.e.*, on **0.01M** solution to prevent osmosis.

Also, magnitude of external pressure

$= 0.2463 - 0.0246 = 0.2217$ atm pressure on 0.01M solution.

11. Let a, b g be the amount of drug (molar mass 369) and sugar (molar mass 342) respectively.

$$a + b = 1.0 \qquad ...(1)$$

$$\therefore \quad \pi V = (n_1 + n_2) \cdot ST$$

$$0.70 \times \frac{100}{1000} = \left[\frac{a}{369} + \frac{b}{342}\right] \times 0.0821 \times 300$$

$$\therefore \quad 342a + 369b = 358.66 \qquad ...(2)$$

By Eqs. (1) and (2) $a = 0.617$ g

$b = 0.383$ g

$$\therefore \quad \%\text{ of drug} = \frac{0.617}{1} \times 100 = \mathbf{61.7\%}$$

12. For iostonic solutions, having neither dissociation nor association nature of solutes.

$$C_1 = C_2 \quad \text{or} \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

For sugar For urea

$$\frac{5}{\frac{342 \times 100}{1000}} = \frac{0.877}{\frac{m \times 100}{1000}}$$

$$\therefore \quad m = \frac{0.877 \times 342}{5} = \mathbf{59.99\ g\ mol^{-1}}$$

13. For isotonic solutions of non-electrolytes;

$$C_1 = C_2$$

$$\text{or} \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2} \quad \text{or} \quad \frac{w_1}{180 \times 0.5} = \frac{9.2}{180 \times 1}$$

$$\therefore \quad w = \mathbf{4.60\ g}$$

14. For initial solution, $\because \ \pi = \frac{500}{760}$ atm, $T = 283$ K

$$\frac{500}{760} \times V_1 = n \times S \times 283 \qquad ...(1)$$

After dilution, let volume becomes V_2 and temperature is raised to 25° C, *i.e.*, 298 K.

$$\pi = \frac{105.3}{760} \text{ atm}$$

$$\frac{105.3}{760} \times V_2 = n \times S \times 298 \qquad ...(2)$$

$\therefore$ By Eqs. (1) and (2), we get $\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500}$

$$\frac{V_1}{V_2} = \frac{1}{5}$$

$$\therefore \quad V_2 = \mathbf{5} V_1$$

i.e., Solution was **diluted to 5 times.**

15. Initially, $P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$

$$550 = P_A^\circ \cdot \frac{1}{1+3} + P_B^\circ \cdot \frac{3}{1+3}$$

or $P_A^\circ + 3P_B^\circ = 2200 \qquad ...(1)$

When, one mole of B is further added to it

$$P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$$

$$560 = P_A^\circ \cdot \frac{1}{1+4} + P_B^\circ \cdot \frac{4}{1+4}$$

$$\therefore \quad P_A^\circ + 4P_B^\circ = 2800 \qquad ...(2)$$

Solving Eqs. (1) and (2), we get

$P_A^\circ = \mathbf{400\ mm}$, $P_B^\circ = \mathbf{600\ mm}$.

16. Mole fraction of cyclohexane = 0.32

$\therefore$ Mole fraction of ethanol $= 1 - 0.32 = 0.68$

Thus, $P_M = P_C^\circ \cdot X_C + P_E^\circ \cdot X_E$

$P = 280 \times 0.32 + 168 \times 0.68 = 203.84$ mm

For the solution to be an ideal one, the vapour pressure should be 203.84 but the given value of vapour pressure is 376 mm, the **solution is non-ideal.**

17. Mole of $C_6H_6 = \frac{23.4}{78} = 0.3$

Mole of $C_7H_8 = \frac{64.4}{92} = 0.7$

Mole fraction of $C_6H_6 = \frac{0.3}{0.3+0.7} = 0.3$

Mole fraction of $C_7H_8 = \frac{0.7}{0.3+0.7} = 0.7$

According to Raoult's law for liquid mixtures

P_M = Partial V.P. of C_6H_6 + Partial V.P. of C_7H_8

$= 75 \times 0.3 + 22 \times 0.7 = 22.5 + 15.4 = 37.9$ mm

Now from Dalton's law of partial pressure,

Partial V.P. of $C_6H_6 = P_M \times$ Mole fraction of C_6H_6 in vapour phase

$22.5 = 37.9 \times$ Mole fraction of C_6H_6 in vapour phase

$\therefore$ Mole fraction of C_6H_6 in vapour phase $= \frac{22.5}{37.9} = \mathbf{0.59}$

$\therefore$ Mole fraction of C_7H_8 in vapour phase $= \mathbf{0.41}$

18. *A*: $P_M = P_B' + P_T' = P_B^\circ \cdot X_B + P_T^\circ \cdot X_T$ | $X_B = \frac{1}{1+4}$

$= 160 \times \frac{1}{1+4} + 60 \times \frac{4}{1+4} = 32 + 48$ | $X_T = \frac{4}{1+4}$

$= \mathbf{80\ mm}$

B: $P_M = 160 \times \frac{w/78}{\frac{w}{78} + \frac{w}{92}} + 60 \times \frac{w/92}{\frac{w}{78} + \frac{w}{92}}$

(Given, equal masss are mixed)

$= 160 \times \frac{92}{170} + 60 \times \frac{78}{170} = 86.588 + 27.529$

$= \mathbf{114.117\ mm}$

19. Given that,

Molar mass of $C_2H_4Br_2 = 188$, M. mass of $C_3H_6Br_2 = 202$

Mass of $C_2H_4Br_2 = 60\,g$, Mass of $C_3H_6Br_2 = 40\,g$

$$P'_{C_2H_4Br_2} = P° \times \text{Mole fraction of } C_2H_4Br_2$$

$$= 170 \times \frac{60/188}{\frac{60}{188}+\frac{40}{202}} = \mathbf{104.9\ mm}$$

$$P'_{C_3H_6Br_2} = 127 \times \frac{40/202}{\frac{60}{188}+\frac{40}{202}} = \mathbf{48.63\ mm}$$

$$P_M = 104.9 + 48.63 = \mathbf{153.53\ mm}$$

20. According to Raoult's law for liquid mixtures:

$$P_M = P'_A + P'_B$$

$$\therefore \quad P_M = P_A^\circ \times \frac{\frac{w_A}{m_A}}{\frac{w_A}{m_A}+\frac{w_B}{m_B}} + P_B^\circ \times \frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A}+\frac{w_B}{m_B}}$$

Given that,

$$w_A = 64\,g, \quad w_{H_2O} = 36\,g, \quad P_M = 145\ mm$$

$$P_{H_2O} = 155\ mm, \quad m_A = 128, \quad m_{H_2O} = 18$$

$$\therefore \quad P_M = 145 = P_A^\circ \times \frac{\frac{64}{128}}{\frac{64}{128}+\frac{36}{18}} + 155 \times \frac{\frac{36}{18}}{\frac{64}{128}+\frac{36}{18}}$$

$$\therefore \quad P_A^\circ = \mathbf{105\ mm}$$

21.

$$P_M = P_{EA}^\circ \times MF_{EA} + P_{PA}^\circ \times MF_{PA}$$

$$= P_{EA}^\circ \times X_{EA} + P_{PA} \times X_{PA}$$

$$290 = P_{EA}^\circ \times 0.65 + 210 \times 0.35$$

$$P_{EA}^\circ = \mathbf{333.1\ mm}$$

Given that,

$P_{PA}^\circ = 210\ mm$

$X_1 = MF_{EA} = 0.65$

$\therefore \quad X_1 + X_2 = 1$

$X_2 = MF_{PA} = 0.35$

$P_M = 290\ mm$

22.

$$P_A^\circ \cdot X_{A(LP)} = P_M \cdot X'_{A(VP)}$$

$$P_A^\circ \cdot \frac{30}{100} = P_M \times \frac{60}{100}$$

$$P_B^\circ \cdot \frac{70}{100} = P_M \times \frac{40}{100}$$

$$\therefore \quad \frac{P_A^\circ}{P_B^\circ} \times \frac{30}{70} = \frac{60}{40}$$

$$\therefore \quad \frac{P_A^\circ}{P_B^\circ} = \frac{60 \times 70}{30 \times 40} = \mathbf{3.5}$$

23.

$$X_{CCl_4(g)} = 0.3474$$

$$X_{SiCl_4(g)} = 0.6526$$

$$P_{SiCl_4}^\circ = 238.3\ mm$$

$$P_{CCl_4}^\circ = 114.9$$

$$P'_{CCl_4} = P_{CCl_4}^\circ \cdot X_{CCl_4(l)} = P_M \times X_{CCl_4(g)}$$

$$\therefore \quad 114.9 \times X_{CCl_4(l)} = P_M \times 0.3474 \quad ...(1)$$

Also, $\quad 238.3 \times X_{SiCl_4(l)} = P_M \times 0.6526 \quad ...(2)$

By Eqs. (1) and (2) $\quad \frac{X_{CCl_4(l)}}{X_{SiCl_4(l)}} = \frac{0.3474}{0.6526} \times \frac{238.3}{114.9} = 1.104$

Let a g CCl_4 and b g $SiCl_4$ be present in liquid and ratio of mole fraction is the ratio of their mole.

Then $\quad \frac{\frac{a}{154}}{\frac{b}{170}} = 1.104 \quad \therefore \quad \frac{a}{b} = \mathbf{1}$

Thus 50% by mass of CCl_4 liquid is present in mixture.

24. In vapour phase

1 mole or 78 g benzene has volume at 20° C

$$= \frac{78 \times 1}{0.877} \times 2750\ mL$$

Similarly,

1 mole or 92 g toluene has volume at 20° C

$$= \frac{92 \times 1}{0.867} \times 7720\ mL$$

Thus, from $\quad PV = nRT$

$$\therefore \quad \frac{P_B^\circ}{760} \times \frac{78 \times 2750}{0.877 \times 1000} = 1 \times 0.0821 \times 293$$

$$P_B^\circ = 74.74\ mm$$

Similarly, $\quad \frac{P_T^\circ}{760} \times \frac{92 \times 7720}{0.867 \times 1000} = 1 \times 0.0821 \times 293$

$$P_T^\circ = 22.37\ mm$$

$$\because \quad P_M = P_B^\circ X_B + P_T^\circ X_T$$

$$\therefore \quad P_M = P_B^\circ X_B + P_T^\circ (1 - X_B)$$

or $\quad 46 = 74.74\, X_B + 22.37\,(1 - X_B)$

$$\therefore \quad X_B = 0.45 \quad \text{(in liquid phase)}$$

$$\because \quad X_B + X_T = 1$$

$$\therefore \quad X_T = 0.55 \quad \text{(in liquid phase)}$$

Also, $\quad P'_B = P_B^\circ \cdot X_B = P_M \cdot X'_B$

or $\quad 74.74 \times 0.45 = 46 \cdot X'_B$

$$\therefore \quad X'_B \text{ (in gas phase)} = \mathbf{0.73}$$

25. The solution boils at 0.5 atm and thus,

$$\text{V.P. of mixture} = \frac{760}{2}\ mm = 380\ mm$$

$$\because \quad P_M = P_T^\circ \cdot X_T + P_{xylene}^\circ \cdot X_{xylene}$$

$$380 = 400(X_T) + 150(1 - X_T) \quad (\because \ X_T + X_{xylene} = 1)$$

$$\therefore \quad X_{toluene} = \mathbf{0.92} \text{ and } X_{xylene} = \mathbf{0.08}$$

26. At boiling point $P_{Mixture} = 736\ mm$

Thus, at boiling point $P'_{H_2O} = 526\ mm$

$$\therefore \quad P'_l = 736 - 526 = 210\ mm$$

Also, $\quad P' = P_m \times \text{m. f. in vapour phase} \quad ...(1)$

Let a g of liquid and water is collected or this is the amount of vapours at equilibrium

Thus, $\quad \text{mass of liquid vapours} = \frac{2.5 \times a}{3.5}$

$$\text{mass of water vapours} = \frac{a}{3.5}$$

Now for liquid, from Eq. (1)

$$210 = 736 \times \frac{\frac{2.5a}{3.5 \times m}}{\frac{a}{3.5 \times 18}+\frac{2.5a}{3.5 \times m}} \quad ...(2)$$

where m is molar mass of liquid

For H_2O, from Eq. (1)

$$526 = 736 \times \frac{\frac{a}{3.5\times 18}}{\frac{a}{3.5\times 18}+\frac{2.5a}{3.5\times m}} \quad ...(3)$$

Thus, from Eqs. (2) and (3) $\frac{210}{526} = \frac{18\times 2.5}{m}$

$\therefore$ $m = \mathbf{112.7}$

27. $P' = P_M \cdot X_A$

where X_A is mole fraction in gaseous phase

$\therefore$ $27 = 760 \cdot \frac{\frac{w_2}{123}}{\frac{w_1}{18}+\frac{w_2}{123}}$ (for nitrobenzene)

and $733 = 760 \cdot \frac{w_1/18}{\frac{w_1}{18}+\frac{w_2}{123}}$ (for water)

$\therefore$ $\frac{w_1}{w_2} = \mathbf{4}$

28. At boiling point $P'_M = 740.2$ mm

$P'_{H_2O} = 530.1$ mm

$\therefore$ $P'_{\text{chlorobenzene}} = 740.2 - 530.1 = 210.1$ mm

Also, $P' = P_M \times$ mole fraction

$530.1 = 740.2 \times$ mole fraction of H_2O

$\therefore$ mole fraction of $H_2O = 0.716$

$\therefore$ mole fraction of $C_6H_5Cl = 0.284$

Let a g H_2O and b g chlorobenzene be present in distillate

or $\frac{w_{H_2O}/18}{\frac{w_{CB}}{112.5}+\frac{w_{H_2O}}{18}} = 0.716$ ...(1)

and $\frac{w_{CB}/112.5}{\frac{w_{CB}}{112.5}+\frac{w_{H_2O}}{18}} = 0.284$ ...(2)

By Eqs (1)/(2)

or $\frac{a}{18}\times\frac{112.5}{b} = \frac{0.716}{0.284}$ or $\frac{a}{b} = \frac{12.89}{31.95} = 0.403$ ...(3)

Let total mass of distillate be 100 g, than

$a + b = 100$ ...(4)

By Eqs. (3) and (4) $a = \mathbf{28.73}$

$b = \mathbf{71.27}$

29. $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$\therefore$ $2.303 \log \frac{400}{40} = \frac{\Delta H}{2}\left[\frac{229.1-191.4}{229.1\times 191.4}\right]$

$\therefore$ $\Delta H_{vap} = 5357.35$ cal

Again $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$2.303 \log \frac{760}{400} = \frac{5357.35}{2}\left[\frac{T-229.1}{T\times 229.1}\right]$

$\therefore$ $\frac{T-229.1}{T} = 0.055$

$\therefore$ $T = 242.43$ K $= \mathbf{-30.57°C}$

30. $\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$

$\frac{23.62-P_s}{P_s} = \frac{1.5\times 18}{60\times 50}$

$\therefore$ $P_s = \mathbf{23.41\ mm}$

31. **At 100° C:** Vapour pressure of pure water ($P°$) = 760 mm

$\because$ $\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$ ...(1)

$\therefore$ $\frac{760-P_s}{P_s} = \frac{3.42\times 18}{342\times 180}$

$\therefore$ $P_s = \mathbf{759.2\ mm}$

Also we have, $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R}\frac{[T_2 - T_1]}{T_1 T_2}$ ...(2)

$\because$ $P_2 = 760$ mm; $T_2 = 373$ K; $T_1 = 313$ K

and $\Delta H = 10$ kcal mol^{-1}

$\therefore$ From Eq. (2)

$$2.303 \log \frac{760}{P_1} = \frac{10}{2\times 10^{-3}} \times \frac{[373-313]}{373\times 313}$$

$\therefore$ $P_1 = \mathbf{58.2\ mm}$

Now at 40° C: $\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$

For 0.2 molal solution $P°_{H_2O} = 58.2$ mm at 40° C

$\because$ $\frac{w}{m} = 0.2$ and $W = 1000$ g; $M = 18$

$\therefore$ $\frac{58.2-P_s}{P_s} = \frac{0.2\times 18}{1000}$

$\therefore$ $P_s = \mathbf{57.99\ mm}$

$\Delta P = P° - P_s = 58.20 - 57.99 = \mathbf{0.21\ mm}$

32. $\because$ $\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$

$\therefore$ Molality $= \frac{w}{m\times W}\times 1000 = \frac{P°-P_s}{P_s\times M}\times 1000$

$= \frac{639.7-631.9}{631.9\times 78}\times 1000$

$= \mathbf{0.158\ mol\ /\ kg\ of\ solvent}$

33. $\because$ $\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$

$P_s = \frac{4P°}{5}$, $m = 60$ g mol^{-1}, $w = ?$, $W = 180$ g, $M = 18$

$\therefore$ $\frac{P° - \frac{4P°}{5}}{\frac{4P°}{5}} = \frac{w\times 18}{60\times 180}$

$\therefore$ $w = \frac{60\times 180}{4\times 18} = \mathbf{150\ g}$

34. Given that,

$P° = 640$ mm, $P_s = 600$ mm, $w = 2.175$ g, $W = 39.0$ g, $M = 78$ g mol^{-1}

$\because$ $\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$

$\therefore$ $\frac{640-600}{600} = \frac{2.175\times 78}{m\times 39}$

$\therefore$ $m = \mathbf{65.25\ g\ mol^{-1}}$

35. Given that, temperature is 373 K and b. pt. of H_2O = 373 K

$\therefore$ Vapour pressure of H_2O = 76 cm

We have, $\frac{P°-P_s}{P_s} = \frac{w \times M}{m \times W}$

$\therefore$ Molality $= \frac{w}{m \times W} \times 1000 = \frac{P°-P_s}{P_s} \times \frac{1}{M} \times 1000$

$= \frac{760-750}{750} \times \frac{1}{18} \times 1000$

$=$ **0.741 mol / kg of solvent**

Also we have, $\frac{P°-P_s}{P°} = \frac{n}{n+N}$

$\therefore$ Mole fraction $= \frac{P°-P_s}{P°} = \frac{760-750}{760} = \frac{10}{760} =$ **0.013**

36. $\frac{P°-P_s}{P_s} = \frac{w \times M}{m \times W} = \frac{w \times M \times 1000}{m \times W \times 1000} =$ Molality $\times \frac{M}{1000}$

$\therefore$ $\frac{92.5-P_s}{P_s} = 1 \times \frac{18}{1000}$

$\therefore$ $P_s =$ **90.84 mm**

37. We have, $\frac{P°-21.85}{21.85} = \frac{30 \times 18}{90 \times m}$ for I case ...(1)

Now, Mass of solvent = 90 + 18 = 108 g

$\frac{P°-22.15}{22.15} = \frac{30 \times 18}{108 \times m}$ for II case ...(2)

$\therefore$ By Eq. (1) $P_M^\circ - 21.85m = 21.85 \times 6 = 131.1$

By Eq. (2) $P_M^\circ - 22.15m = 22.15 \times 5 = 110.75$

$- \quad + \quad -$

$\therefore$ $0.30m = 20.35$

$\therefore$ $m = \frac{20.35}{0.30} = 67.83 \text{ g mol}^{-1}$

On substituting the value of m in Eq. (1),

$\frac{P°-21.85}{21.85} = \frac{30 \times 18}{90 \times 67.83}$

$\therefore$ $P° =$ **23.78 mm**

38. For water vapours : $PV = \frac{w}{m}RT$

$\therefore$ $\frac{w}{V} = (d) = \frac{Pm}{RT} = \frac{17.39 \times 18}{760 \times 0.0821 \times 293} = 0.0171 \text{ g / litre}$

Also, $\frac{P°-P_s}{P_s} = \frac{w \times M \times 1000}{m \times W \times 1000}$

$\therefore$ molality $\left(\frac{w}{m \times W} \times 1000\right) = \frac{17.39-17}{17} \times \frac{1000}{18} = 1.275$

$=$ molarity $\left(\frac{n}{V}\right)$

$\therefore$ $P = \frac{n}{V} \times S \times T = 1.275 \times 0.0821 \times 293 =$ **30.67 atm**

39. At 293 K; $\frac{P°-P_s}{P_s} = \frac{n}{N} = \frac{n \times 18}{W}$

$\therefore$ $\frac{2338-2295.8}{2295.8} = \frac{n \times 18}{W}$

$\therefore$ $\frac{n}{W} = \frac{42.2}{2295.8} \times \frac{1}{18}$ or $W = 979.25 \times n$ g

$\therefore$ Mass of solution = 979.25n + mass of solute

$= 979.25n + 60n = 1039.25n$ g $= 1.0393n$ kg

$\therefore$ Volume of solution $\underset{\text{(at 313K)}}{=} \frac{\text{Mass}}{\text{Density}} = \frac{1.0393n}{1010}$ m^3

Now, $PV = nST$

$P \times \frac{1.0393n}{1010} = n \times 8.314 \times 313$

$\therefore$ $P =$ **2.53 × 10^6 Pa**

40. $\frac{P°-P_s}{P°} = \frac{n}{n+N} = \frac{w/m}{\frac{w}{m}+\frac{W}{M}} = \frac{10/100}{\frac{10}{100}+\frac{180}{18}} =$ **0.0099**

41. $\frac{P°-P_s}{P°} = \frac{n}{n+N} = \frac{w/m}{\frac{w}{m}+\frac{W}{M}}$

For H_2O $\frac{P°-P_s}{P°} = \frac{6/120}{\frac{6}{120}+\frac{150}{18}}$

For C_2H_5OH $\frac{P°-P_s}{P°} = \frac{6/120}{\frac{6}{120}+\frac{150}{46}}$

$\therefore$ Ratio of $\left(\frac{P°-P_s}{P°}\right)$ for H_2O and C_2H_5OH

$= \frac{6/120}{\frac{6}{120}+\frac{150}{18}} \times \frac{6/120+150/46}{\frac{6}{120}} =$ **0.3949**

42. Given that 0.1 M glucose is isotonic with solution of X in 100 g water.

Thus, Conc. of solution of X = 0.1 mol per litre

For dilute solution:

Volume of solution = volume of solvent (H_2O)

= weight of H_2O

$\therefore$ Mole of X = 0.1; Mole of water $= \frac{1000}{18}$

$\frac{P°-P_s}{P°} = \frac{n}{n+N} = \frac{0.1}{0.1+\frac{1000}{18}} =$ **0.0018**

43. Given that, $P_s = \frac{80}{100}P°$, $w = ?$, $m = 40$, $W = 114$ g, $M = 114$

$\because$ $\frac{P°-P_s}{P_s} = \frac{w \times M}{m+W}$

$\frac{P° - \frac{80}{100}P°}{\frac{80}{100}P°} = \frac{w \times 114}{40 \times 114}$

$w = \frac{40}{4} =$ **10 g**

44. According to Raoult's law:

$\frac{P°-P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$

Given if $P° = 100$, then $P_s = 75$ mm, $m = 60$, $M = 18$, $W = 100$ g

$\frac{100-75}{75} = \frac{w \times 18}{60 \times 100}$

$\therefore$ $w =$ **111.11 g**

Also molality of solution,

$$= \frac{\text{mass of solute}}{\text{molar mass of solute} \times \text{mass of solvent (in kg)}}$$

$$= \frac{111.11}{60 \times \frac{100}{1000}} = \mathbf{18.52\ m}$$

45. $\because$ Loss in mass of solution $\propto P_s$

Loss in mass of solvent $\propto P^\circ - P_s$

$$\therefore \quad \frac{P^\circ - P_s}{P_s} = \frac{\text{Loss in mass of solvent}}{\text{Loss in mass of solution}} \qquad ...(1)$$

Also, $$\frac{P^\circ - P_s}{P_s} = \frac{w \times M}{m \times W} \qquad ...(2)$$

$\therefore$ By Eqs. (1) and (2), we get $\frac{0.04}{2.5} = \frac{5 \times 18}{80 \times m}$

$$\therefore \quad m = \mathbf{70.31\ g\ mol^{-1}}$$

46. At 100° C: $P_2 = 760$ mm; $\Delta H_{\text{vap.}} = 540 \times 18$ cal / mol

$= 9720$ cal / mol

$$\therefore \quad 2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

$$\log \frac{P_2}{P_1} = \frac{9720}{1.987 \times 2.303} \times \frac{[373-348]}{373 \times 348}$$

$$\therefore \quad \frac{P_2}{P_1} = 2.57$$

$$\therefore \quad P_1 = \frac{760}{2.57} = 295.7 \text{ mm (or } P^\circ)$$

Now, $$\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{0.1}{1000/18}$$

$$\frac{P^\circ}{P_s} - 1 = \frac{1.8}{1000} \qquad \therefore \quad \frac{P^\circ}{P_s} = \frac{1001.8}{1000}$$

$$\therefore \quad P_s = \frac{P^\circ \times 1000}{1001.8} = \frac{295.7 \times 1000}{1001.8} = 295.17$$

$$\therefore \quad \Delta P = 295.7 - 295.17 = \mathbf{0.53\ mm}$$

47. $\frac{P^\circ - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$, $\therefore$ $\frac{100 - 98.88}{98.88} = \frac{w \times 78 \times 1000}{m \times W \times 1000}$

or $$\text{molality} \left(\frac{w \times 1000}{m \times W}\right) = \frac{1.12 \times 1000}{78 \times 98.88} = 0.1452$$

Also, $\Delta T = K'_f \times$ molality

$0.73 = K'_f \times 0.1452$

$$\therefore \quad K'_f = \mathbf{5.028\ K\ molality^{-1}}$$

48. Given, b. pt. of water $= 100^\circ$ C, b.pt. of solution $= 100.34^\circ$ C

$\therefore$ Elevation in b. pt., $\Delta T = 0.34$, $w = 12$ g, $W = 100$ g, $m = 180$

$$\Delta T = \frac{1000 K'_b\, w}{mW}$$

$$0.34 = \frac{1000 \times K'_b \times 12}{180 \times 100}$$

$$\therefore \quad K'_b = \mathbf{0.51\ K\ mol^{-1}\ kg}$$

49. $w_{EA} = 20 \times 0.7893 = 15.786$ g

$w_{H_2O} = 40 \times 0.9971 = 39.884$

$\therefore$ $w_{\text{mixture}} = 55.670$ g $\therefore$ $V_{\text{mixture}} = \frac{55.67}{0.9571} = 58.165$ mL

$\therefore$ % change in volume $= \frac{[60 - 58.165]}{60} \times 100 = 3.058$

molality of alcohol $= \frac{15.786}{46 \times \frac{39.884}{1000}} = \mathbf{8.6\ m}$

molarity of alcohol $= \frac{15.786}{46 \times \frac{58.165}{1000}} = \mathbf{5.90\ M}$

$\Delta V_{\text{mixing}} = (58.165 - 60) = -1.835$ mL

$\therefore$ –ve deviation from Raoult's law.

50. Given that, $w = 0.5143$ g, $W = 35$ g

$K'_b = 3.9$ K mol^{-1} kg, $\Delta T = 0.323^\circ$ C

$\because$ $$\Delta T = \frac{1000 K'_b\, w}{mW}$$

$$\therefore \quad 0.323 = \frac{1000 \times 3.9 \times 0.5143}{m \times 35}$$

$$m = \mathbf{177.42\ g\ mol^{-1}}$$

51. Given, $w = 174.5 \times 10^{-3}$ g, $W = 78$ g

$m = 8 \times 32 = 256$ ($\because$ Octa atomic), $K'_b = 5.2$

$$\because \quad \Delta T = \frac{1000 K'_b\, w}{Wm} = \frac{1000 \times 5.2 \times 174.5 \times 10^{-3}}{78 \times 256} = 0.045$$

$\therefore$ Boiling pt. of Br_2 solution $= 332.15 + \Delta T$

$= 332.15 + 0.045 = \mathbf{332.195\ K}$

52. $\because$ $$\Delta T = \frac{100 K_f\, w}{mW}$$

$\because$ $w = 0.48$ g, $W = 10.6$ g, $\Delta T_f = 1.8$, $K_f = 50$

$$\therefore \quad 1.8 = \frac{100 \times 50 \times 0.48}{m \times 10.6}$$

$$\therefore \quad m = \mathbf{125.79\ g\ mol^{-1}}$$

53. $MeOH + H_2SO_4 \rightleftharpoons MeOH_2^+ + HSO_4^-$ (two ions)

$Ph_3C{\cdot}OH + H_2SO_4 \rightleftharpoons Ph_3COH_2^+ + HSO_4^-$

$Ph_3COH_2^+ \rightleftharpoons Ph_3C^+ + H_2O$

$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$

$Ph_3COH + 2H_2SO_4 \rightleftharpoons Ph_3C^+ + H_3O^+ + 2HSO_4^-$ (four ions)

Since, number of ions are doubled in Ph_3COH and so depression is two times more for same number of mole of each.

54. Given, $W_{\text{menthol}} = 6.2$ g; $w_{\text{cyclohexane}} = 100 - 6.2 = 93.8$ g

$\Delta T_f = 6.5 - (-19.5) = 26.0$; $K = 20.2$ K molality^{-1}

$$\therefore \quad \Delta T_f = \frac{1000 \times K_f \times w}{W \times m}$$

or $$m = \frac{1000 \times 20.2 \times 6.2}{93.8 \times 26.0} = \mathbf{51.35\ g\ mol^{-1}}$$

55. $\frac{F - 32}{9} = \frac{C}{5}$ (For conversion of ° F scale to ° C scale)

$$\frac{14 - 32}{9} = \frac{C}{5}$$

$$\therefore \quad C = -10^\circ \text{ C} \qquad \therefore \quad \Delta T = 10$$

Now, $\Delta T = K_f \times$ molality

$$10 = 1.86 \times \frac{w}{46 \times 1}$$

$\therefore$ $w = \mathbf{247.31\ g}$

56. $\because$ Solution has 5% by mass urea and 10% by mass glucose

$\because$ $$\%\ \text{By mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

$\therefore$ Mass of water = 85 g; mass of urea = 5 g; mass of glucose = 10 g

$$\Delta T = \Delta T_{\text{Urea}} + \Delta T_{\text{Glucose}}$$

$$\Delta T = \frac{1000 \times 1.86 \times 5}{60 \times 85} + \frac{1000 \times 1.86 \times 10}{180 \times 85}$$

$$= 1.824 + 1.216 = \mathbf{3.04}$$

$\therefore$ Freezing point $= 0 - 3.04 = \mathbf{-3.04^\circ C}$

57. $\because$ $$\Delta T = \frac{1000 K_b' w}{mW}$$

$$0.01 = \frac{1000 \times 0.5 \times w}{180 \times 100} \quad \therefore \quad w = 0.36\,\text{g}$$

$\because$ 180 g glucose contains $= 6.023 \times 10^{23}$ molecules

$\therefore$ 0.36 g glucose contains

$$= \frac{6.023 \times 10^{23} \times 0.36}{180}$$

$$= \mathbf{1.2 \times 10^{21}\ molecules}$$

58. For acetone + Benzene mixture:

$$\Delta T = \frac{K_f' \times 1000 \times w}{m \times W}$$

$$(278.40 - 277.12) = \frac{1000 \times K_f \times 1.4}{100 \times 58}$$

or $$1.28 = \frac{1000 \times K_f \times 1.4}{100 \times 58} \qquad \ldots(1)$$

For solute (A) + Benzene mixture (Let m be the molar mass of A)

$$(278.40 - 277.76) = \frac{1000 \times K_f \times 2.8}{100 \times m}$$

or $$0.64 = \frac{1000 \times K_f \times 2.8}{100 \times m} \qquad \ldots(2)$$

By Eqs. (1) and (2), $m = \mathbf{232\ g\ mol^{-1}}$

59. $$\Delta T = \frac{1000 \times K_f' w}{mW}$$

For AB_2 $$2.3 = \frac{1000 \times K_f' \times 1}{m_1 \times 20} = \frac{1000 \times 5.1 \times 1}{m_1 \times 20}$$

For AB_4 $$1.3 = \frac{1000 \times K_f' \times 1}{m_2 \times 20} = \frac{1000 \times 5.1 \times 1}{m_2 \times 20}$$

$\therefore$ $m_1 = 110.87\ \text{g mol}^{-1}$; and $m_2 = 196.15\ \text{g mol}^{-1}$

Now, m_1 is molar mass of AB_2 $\therefore$ $a + 2b = 110.87$

m_2 is molar mass of AB_4 $\therefore$ $a + 4b = 196.15$

where a and b are atomic mass of A and B

$\therefore$ $a = \mathbf{25.59\ g/mol}$

$b = \mathbf{42.64\ g/mol}$

60. Given ethylene glycol $= 50\,\text{cm}^3$; $K_f' = 1.86\ \text{K mol}^{-1}$ kg

$\therefore$ mass of glycol $= 50 \times d$, where d is density of glycol

mass of water = 50 g

$$\Delta T_f = 34^\circ\text{C}$$

Now, $$\Delta T_f = \frac{1000 \times K_f' \times w}{m \times W}$$

$$34 = \frac{1000 \times 1.86 \times 50 \times d}{62 \times 50}$$

$\therefore$ $d = \mathbf{1.133\ g/cm^3}$

61. [Ans. $m = 156.06\ \text{g mol}^{-1}$]

62.

$$\Delta T = \frac{1000 \times K_f' \times w}{m \times W}$$

$\therefore$ $$\Delta T = \frac{1000 \times 1.86 \times 2000 \times 0.8}{32 \times 8000}$$

$$= 11.625$$

$\therefore$ F. pt. of solution $= 0 - 11.625 = -11.625$

Given,

$w = 2000 \times 0.8\,\text{g}$

$W = 8000 \times 1\,\text{g}$

$K_f' = 1.86\ \text{K mol}^{-1}$ kg

$m = 32$ for CH_3OH

$\therefore$ Vehicle may be parked out door not below $\mathbf{-11.625^\circ C}$.

63.

$$\Delta T = \frac{1000 \times K_f' \times w}{m \times W}$$

$$48 = \frac{1000 \times 37.5 \times 0.09}{m \times 0.55}$$

$\therefore$ $m = \mathbf{127.84\ g\ mol^{-1}}$

Given,

$\Delta T = 209 - 161 = 48^\circ\text{C}$

$w = 0.09\,\text{g}$

$W = 0.55\,\text{g}$

$K_f' = 37.5^\circ\text{C mol}^{-1}$ kg

Now %	$\frac{\%}{\text{Atomic mass}}$ **value**	**Value/Lowest value**
C = 93.75	$\frac{93.75}{12} = 7.8125$	$\frac{7.8125}{6.25} = 1.25$
H = 6.25	$\frac{6.25}{1} = 6.25$	$\frac{6.25}{6.25} = 1$

$\therefore$ C : H :: 1.25 : 1 or 5 : 4

$\therefore$ Empirical formula is C_5H_4 and empirical formula mass = 64

$\therefore$ Molecular formula is $(C_5H_4)_n$ and $n = \frac{127.84}{64} \approx 2$

$\therefore$ Molecular formula of solute is $(C_5H_4)_2 = \mathbf{C_{10}H_8}$

64. For a given aqueous solution

$$\Delta T_b = K_b' \times \text{molality}$$

$$\Delta T_f = K_f' \times \text{molality}$$

$\therefore$ $$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b'}{K_f'} = \frac{RT_b^2}{1000 l_v} \times \frac{1000 l_f}{RT_f^2}$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times l_f}{T_f^2 \times l_v}$$

$\because$ $T_b = 100 + 273 = 373\ \text{K}$

$T_f = 0 + 273 = 273\ \text{K}$

$l_f = 80\,\text{cal g}^{-1}$

$l_v = 540\,\text{cal g}^{-1}$

$\therefore$ $$\frac{0.1}{\Delta T_f} = \frac{373 \times 373 \times 80}{273 \times 273 \times 540} \quad \therefore \quad \Delta T_f = 0.362$$

$\therefore \quad T_f = 0.0 - 0.362 = -0.362°C$

65. Given, $l_f = 1436.3 \text{ cal/mole} = \frac{1436.3}{18} \text{ cal/g}$

$$K_f' = \frac{RT^2}{1000 l_f} = \frac{2\times273\times273}{1000\times\frac{1436.3}{18}}$$

$$K_f' = \frac{2\times273\times273\times18}{1000\times1436.3} = 1.87$$

Now, Mole fraction of $H_2O = 0.8 = \frac{N}{n+N}$

$\therefore$ Now, Mole fraction of solute $= 0.2 = \frac{n}{n+N}$

$\therefore \quad \frac{n}{N} = \frac{0.2}{0.8} = \frac{1}{4}$

or $\quad \frac{w\times M}{m\times W} = \frac{1}{4}$ or $\frac{w}{m\times W} = \frac{1}{4\times18}$

$\therefore \quad \Delta T = \frac{1000\times K_f'\times w}{m\times W} = 1000\times1.87\times\frac{1}{4\times18}$

$= 25.97°C$

$\therefore$ F. pt. $= 0 - 25.97 = \mathbf{-25.97°C}$

66. **For 5% solution of A :**

$$(\Delta T_f)_A = \frac{K_f\times5\times1000}{m_A\times95} \quad ...(1)$$

For 5% solution of B :

$$(\Delta T_f)_B = \frac{K_f\times5\times1000}{m_B\times95} \quad ...(2)$$

By Eqs. (1) and (2), $\therefore \quad \frac{(\Delta T_f)_A}{(\Delta T_f)_B} = \frac{m_B}{m_A} = \frac{3}{1} \left(\because \frac{m_A}{m_B} = \frac{1}{3}\right)$

For solution S_1 : Let $2V$ mL solution of A is mixed with $3V$ mL solution of B.

Mass of A in $2V$ mL or $2V$ g $= \frac{5\times2V}{100}$ g $= \frac{10V}{100}$ g

Mass of B in $3V$ mL or $3V$ g $= \frac{5\times3V}{100}$ g $= \frac{15V}{100}$ g

Total mass of solution $= 5V$ g

$$(\Delta T_f)_{S_1} = \frac{K_f\times1000\times\left[\frac{0.1V}{m_A}+\frac{0.15V}{m_B}\right]}{\left[5V-\frac{10V}{100}\right]}$$

$$= \frac{1000K_f[0.1m_B+0.15m_A]}{4.9\times m_A\times m_B}$$

For solution S_2 : Similarly, we have

$$(\Delta T_f)_{S_2} = \frac{1000\times K_f[0.15m_B+0.10m_A]\times0.9898}{4.85\times m_A\times m_B}$$

Thus, $\quad \frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}} = \frac{(0.1m_B+0.15m_A)\times0.9898}{(0.10m_A+0.15m_B)}$

$$= \frac{(0.1\times3m_A+0.15m_A)\times0.9898}{(0.10m_A+0.15\times3m_A)}$$

$$= \frac{0.45\times0.9898}{0.55} = \mathbf{0.81}$$

67. $$K_b = \frac{RT_b^2\cdot M}{1000\Delta H_V} = \frac{RT_bM}{1000\Delta S_V} \quad \left(\because \Delta S_V = \frac{\Delta H_V}{T_b}\right)$$

$\therefore \quad \Delta S_V = \frac{RT_b^2\cdot M}{1000\Delta K_b} = \frac{2\times373\times18}{1000\times0.51} = \mathbf{26.33 \text{ cal/mol}}$

68. $$K_b = \frac{RT_b^2}{1000 l_V} = \frac{RT_b\cdot M}{1000\Delta H_V} = \frac{RT_b^2\cdot M}{1000\Delta S_V}$$

Where, ΔS_V is change in entropy during vaporisation at T_b. Since, during vaporisation entropy increases because randomness increases. Also ΔS_V may be taken as almost constant as for liquid $\rightleftharpoons$ vapour even if the extent of disorderness varies from liquid to liquid since, entropy in vapour state is abnormally higher. Thus, $S_V - S_L = \Delta S_V$ is almost constant. If M and R are constant, $K_b \propto T_b$.

Thus, values reported in table are in accordance with X, Y and Z.

69. Given, $\Delta T = 9.3$, $w = 50$ g; K_f for $H_2O = 1.86$ K mol^{-1} kg, $m_{\text{Glycol}} = 62$

$\because \quad \Delta T = \frac{1000\times K_f\times w}{m\times W} \quad \therefore \; 9.3 = \frac{1000\times1.86\times50}{62\times W}$

$\therefore \quad W_{\text{Water}} = 161.29$ g

Thus, mass of ice separated $= 200 - 161.29 = \mathbf{38.71 \text{ g}}$

70. $\Delta T = K_f' \times$ molality $= 1.86\times1 = 1.86$

$\therefore$ Solution starts freezing at $-1.86°C$. Thus, on cooling up to $-3.534°C$, freezing continues,

Let molality of solution left at $-3.534°C$ be m'

$\therefore \quad \Delta T = K_f'\times m'$

$\therefore \quad m' = \frac{3.534}{1.86} = 1.9$ m

Initially 1000 g solvent contains 342 g Sucrose

or 1342 g solution contains 342 g Sucrose

$\therefore$ 1000 g solution contains

$$= \frac{342\times1000}{1342} \text{ g sucrose} = 254.84 \text{ g sucrose}$$

Finally,

$\therefore \quad$ Mass of water $= 1000 - 254.84 = 745.16$ g

Since, sucrose remains same in solution before and after freezing

Now, 1.9×342 g sucrose is in 1000 g water $(\because m' = 1.9)$

254.84 g sucrose should be in

$$\frac{1000\times254.84}{1.9\times342} = 392.18 \text{ g } H_2O$$

Thus, mass of ice separated out

$= 745.16 - 392.18$ g $= \mathbf{352.98 \text{ g}}$

Alternate Solution

$$\Delta T_f = \frac{1000\times K_f'\times w}{W\times m} \quad ...(1)$$

or $\quad \Delta T_f = K_f'\times$ molality $\quad ...(2)$

$\Delta T_f = 1.86\times1 = 1.86$

Now using Eq. (1) again to obtain $\frac{w}{W}$ for sucrose

$$\frac{w}{W} = \frac{1.86\times 342}{1.86\times 1000} = 0.342 \quad ...(3)$$

Also, $w + W = 1000$ ...(4)

(mass of solution = 1000 g)

$\therefore$ By Eqs. (3) and (4), we get $w = 254.84$ g

$W = 745.16$ g

(*i.e.*, mass of water)

Now if solution has been freezed up to –3.534, the mass of sucrose remains same and therefore, using Eq. (1) again

$$3.534 = \frac{1.86\times 1000\times 254.84}{342\times W_1}$$

$\therefore$ $W_1 = 392.18$ g (*i.e.*, new mass of water)

Thus, Ice separated = 745.16 – 392.18

= 352.98 g

71. Let 100 g solution contains w g solute in W g solvent

$\therefore$ $w + W = 100$ ...(1)

Now, $$\Delta T_f = \frac{1000\times K_f'\times w}{W\times m}$$

$$0.38 = \frac{1000\times 1.86\times w}{W\times 342} \quad \therefore \quad \frac{w}{W} = 0.07 \quad ...(2)$$

Solving Eqs. (1) and (2), we get

$w = 6.6$ g

$W = 93.40$ g

Now at –0.5° C, some water separates out as ice and solute exists as 6.6 g.

$\therefore$ $$0.5 = \frac{1000\times 1.86\times 6.6}{W\times 342} \quad \therefore \quad W = 71.78 \text{ g}$$

$\therefore$ Mass of ice separated out is (93.40 – 71.78) g **= 21.62 g**

72. $\because$ $\pi V = nST$

$$\therefore \frac{n}{V} = \frac{\pi}{ST} = \frac{2}{0.0821\times 300}$$

Given, $\pi = 2$ atm; $S = 0.0821$ litre atm K^{-1} mol^{-1} and $T = 300$ K

$\therefore$ Molarity $\left(\frac{n}{V}\right) = 0.0812$ mol litre^{-1}

Since, $\Delta T = K_f' \times$ molality

$\because$ molarity = molality

and thus, molality = 0.0812

$\therefore$ $\Delta T = 1.86\times 0.0812 = 0.151$

$\therefore$ Freezing point = $T_0 - \Delta T$ ($\because T_0 = 0°$ C)

$= 0 - 0.151 = -$ **0.151° C**

73. $\because$ $$\Delta T = \frac{1000\times K_f'\times w}{m\times W} = K_f' \times \text{molality}$$

$\therefore$ $0.52 = 1.86\times$ molality

$\therefore$ Molality $= \frac{0.52}{1.86} =$ molarity $\left(\frac{n}{V}\right)$ (given)

Now, $\pi V = nST$

$\therefore$ $$\pi = \frac{n}{V}\cdot ST = \frac{0.52}{1.86}\times 0.0821\times 300 = \mathbf{6.886 \text{ atm}}$$

74. $\pi = CST$

$2.47 = C\times 0.0821\times 303$

$\therefore$ $C = 9.93\times 10^{-2}$ M

Thus, 1 litre solution of sucrose contains 9.93×10^{-2} mole of sucrose or $9.93\times 10^{-2}\times 342$ g of sucrose.

$\because$ Volume of solution = Volume of solvent = 1000 mL

$\therefore$ Mole of water $= \frac{1000}{18.10}$

$\therefore$ Mass of water $= \frac{1000}{18.10}\times 18 = 994.475$ g

Thus, molality of solution $= \frac{9.93\times 10^{-2}}{994.475\times 10^{-3}}$

$= 9.985\times 10^{-2}$ M

$$\Delta T_b = K_b \times \text{molality} = \frac{RT_b^2}{1000l}\times \text{molality}$$

$$= \frac{2\times 373\times 373}{1000\times 540}\times 9.985\times 10^{-2}$$

$$= \mathbf{5.145\times 10^{-2}}$$

75. b.pt. of $H_2O = 99.725°$ C

Given, $w_{\text{organic compound}} = 24$ g, $w_{H_2O} = 600$ g,

$m_{\text{organic compound}} = 58$

Also, $$\Delta T_b = \frac{1000\times K_b\times w}{W\times m} = \frac{1000\times 0.513\times 24}{600\times 58} = 0.354$$

$\therefore$ b.pt. of solution = 99.725 + 0.354 **= 100.079° C**

76. We have, $\Delta T = K_f \times$ molality

Also from Raoult's law,

$$\frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W} = \frac{w\times 1000\times M}{m\times W\times 1000}$$

$$\frac{P°-P_s}{P_s} = \text{molality}\times \frac{M}{1000}$$

$$\frac{P°-P_s}{P_s} = \frac{\Delta T}{K_f}\times \frac{M}{1000}$$

Given, $P° = 23.51$ mm of Hg; $\Delta T = 0.3$

$K_f = 1.86$ K molality^{-1}; $M = 18$

$\therefore$ $$\frac{23.51 - P_s}{P_s} = \frac{0.3}{1.86}\times \frac{18}{1000} \quad \therefore \quad P_s = \mathbf{23.44 \text{ mm Hg}}$$

77. Given, Molarity $= \frac{n}{V} = 0.1$ mol litre^{-1}

$$= \frac{0.1}{10^{-3}} \text{ mol m}^{-3} = 10^2 \text{ mol m}^{-3}$$

$\because$ $\pi_N \times V = nST$

$\pi_N = \frac{n}{V}ST$

$\pi_N = 10^2\times 8.314\times 300$ Nm^{-2}

For $$\underset{1}{K_4Fe(CN)_6} \rightleftharpoons \underset{0}{4K^+} + \underset{0}{Fe(CN)_6^{4-}}$$

$$\underset{1-\alpha}{} \qquad \underset{4\alpha}{} \qquad \underset{\alpha}{}$$

where 'α' is degree of dissociation.

Given, $\alpha = 0.5$

$$\frac{\pi_{exp}}{\pi_N} = 1 + 4\alpha \quad \therefore \quad \pi_{exp} = \pi_N\,(1 + 4\alpha)$$

$$= 10^2\times 8.314\times 300\times (1 + 4\times 0.5)$$

$$= 10^2\times 8.314\times 300\times (1 + 2)$$

$$= \mathbf{7.483\times 10^5 \text{ Nm}^{-2}}$$

78. Given, $w = 1\,g$, $m = 74.5$, $V = \frac{100}{1000}$ litre,

$T = 18 + 273 = 291\,K$

$\because \quad \pi_N = \frac{n}{V}ST = \frac{w}{m \cdot V}ST$

$= \frac{1 \times 1000}{74.5 \times 100} \times 0.0821 \times 291 = 3.21\,atm$

For $KCl \rightleftharpoons K^+ + Cl^-$

Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore \quad \frac{\pi_{exp}}{\pi_N} = 1 + \alpha$

$\therefore \quad \pi_{exp} = 3.21(1 + 0.82) = \mathbf{5.842\ atm}$

79. Given, $N_{Na_3PO_4} = 0.1$

$\therefore \quad$ Molarity of $Na_3PO_4 = \frac{0.1}{3}M \qquad \left(\because M = \frac{N}{V}\right)$

Thus, using $\pi V = nST$

or $\pi = \frac{n}{V}ST = \frac{0.1}{3} \times 0.0821 \times 300 = \mathbf{0.821\ atm}$

80. $\because$ Molarity = Normality × Valence factor

$\therefore \quad M_{Glucose} = \frac{0.1}{1} = 0.1$

$M_{KNO_3} = \frac{0.1}{1} = 0.1$

$M_{K_2SO_4} = \frac{0.1}{2} = 0.05$

$M_{K_3PO_4} = \frac{0.1}{3} = 0.033$

Also $\quad \pi \propto$ Molarity $\times (1 - \alpha + x\alpha + y\alpha)$

$\therefore \quad \pi_{Glucose} \propto 0.1 \propto 0.1$

$\pi_{KNO_3} \propto 0.1 \times 2 \propto 0.2$

$\pi_{K_2SO_4} \propto 0.05 \times 3 \propto 0.15$

$\pi_{K_3PO_4} \propto 0.033 \times 4 \propto 0.132$

$\therefore \quad \pi_{order}$ is : $\pi_{KCl} > \pi_{K_2SO_4} > \pi_{K_3PO_4} > \pi_{Glucose}$

81. Let n atoms of Cl be acting as ligand. Then formula of complex and its ionisation is :

$$\underset{1}{[Pt(NH_3)_4Cl_n]}\underset{0}{Cl_{(4-n)}} \rightarrow \underset{0}{[Pt(NH_3)_4Cl_n]^{+(4-n)}} + \underset{0}{(4-n)Cl^-}$$
$$\qquad\qquad\qquad

Now, $\frac{\pi_{exp}}{\pi_N} = 1+2\alpha$

$\therefore \quad \pi_{exp} = \pi_N \times (1+2\alpha) = 1.2315\times(1+2\times0.8)$
$= 1.2315\times2.6 = \mathbf{3.20\ atm}$

87. $\because$ % of mass/volume $= \frac{\text{mass of solute}}{\text{volume of solution}} \times 100$

$\therefore$ Mass of glucose = 7.2 g
Volume of solution = 100 mL

For glucose: π_{exp} or $\pi_N = \frac{w}{m\times V}\times ST$ (V in litre)

$\because \quad \pi_{exp}$ or $\pi_N = \frac{7.2\times1000\times0.0821\times T}{180\times100}$

For NaCl: $\pi_N = \frac{w}{m\times V}\times ST = \frac{1.2\times1000\times0.0821\times T}{58.5\times100}$

Now, since two solutions are isotonic and therefore,

$\pi_{exp_{NaCl}} = \pi_{N_{Glucose}}$

$\therefore$ **For NaCl:** $\frac{\pi_{exp}}{\pi_N} = 1+\alpha$

$\frac{7.2\times1000\times0.0821\times T}{180\times100}\times\frac{58.5\times100}{1.2\times1000\times0.0821\times T} = 1+\alpha = (i)$

$\therefore \quad \alpha = 0.95$ and $i = \mathbf{1.95}$

88. $\because \quad \frac{P°-P_s}{P_s} = \frac{w\times M}{m\times W}$

$\frac{760-751}{751} = \frac{2\times18}{m\times100} \quad \therefore \quad m_{exp} = 30.04$

For

	$BA \rightleftharpoons B^+ + A^-$		
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

Now, $\frac{m_n}{m_{exp}} = 1+\alpha$

$\therefore \quad \frac{56}{30.04} = 1+\alpha$

$\therefore \quad \alpha = \mathbf{0.8641}$ or **86.41%**

89. For NaCl:

Given, $2\Delta T = \frac{1000\times K'_f\times11.7}{200\times m}$

(Let depression in f. pt. for sugar = ΔT)

For Sugar: $\Delta T = \frac{1000\times K'_f\times342}{1000\times342}$

($\therefore$ depression in f. pt. for NaCl = $2\times\Delta T$)

$\therefore \quad m_{NaCl} = 29.25$ (experimental)

Now m_{Normal} for NaCl = 58.5 g mol^{-1}

For NaCl:

	$NaCl \rightleftharpoons Na^+ + Cl^-$		
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore \quad \frac{m_{Normal}}{m_{exp}} = 1+\alpha$

$\frac{58.5}{29.25} = 1+\alpha \quad \therefore \quad \alpha = 1$

That is NaCl is 100% ionised in solution.

90. Given, $w_{H_2SO_4} = 38$ g, $W_{H_2O} = 100-38 = 62$ g

$\therefore \quad \Delta T = \frac{1000\times K'_f\times w}{mW}$

$\Delta T = \frac{1000\times1.86\times38}{98\times62} \quad \therefore \quad \Delta T_{Normal} = 11.633$

Now, $\frac{\Delta T_{exp}}{\Delta T_N} = i = 2.50$

$\therefore \quad \Delta T_{exp} = 11.633\times2.50 = 29.08$

$\therefore$ f. pt. = 273 − 29.08 = **243.92 K**

91.

	$Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3^-$		
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	2α

$\therefore$ Total mole at equilibrium = $(1+2\alpha) = (1+2\times0.7) = 2.4$
($\because \alpha = 0.7$)

For $Ca(NO_3)_2$: $\frac{m_N}{m_{exp}} = 1+2\alpha$

$\therefore \quad m_{exp} = \frac{m_N}{(1+2\times0.7)} = \frac{164}{2.4} = 68.33$

Also at 100° C, $P°_{H_2O} = 760$ mm, $w = 7$ g, $W = 100$ g

Now, $\frac{P°-P_s}{P_s} = \frac{7\times18}{68.33\times100} = 0.0184$

or $\frac{P°}{P_s} - 1 = 0.0184$

$\therefore \quad P_s = \frac{760}{1.0184} = \mathbf{746.27\ mm}$

92. $\because \quad \Delta T = \frac{1000\times K'_f\times w}{m\cdot W}$

and $\Delta T = 0.168$, $w = 1$g, $W = 100$g and $K'_f = 1.86$

$\therefore \quad m_{acid} = 110.71$ (This is exp. molar mass)

Now, Meq. of acid = Meq. of alkali

$\frac{0.2}{E}\times1000 = 15.1\times\frac{1}{10}$

$\therefore$ Eq. mass of acid $= \frac{0.2\times1000\times10}{15.1} = 132.45$

$\therefore$ Normal Molar mass of acid = 132.45×1
(Since monobasic)

	$HA \rightleftharpoons H^+ + A^-$		
Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

Now, $\frac{m_N}{m_{exp}} = \frac{132.45}{110.71} = 1+\alpha \quad \therefore \quad \alpha = \mathbf{19.6\%}$

93. Let NaCl and $CaCl_2$ be a, b g respectively in 1 g mixture

$\therefore \quad a+b = 1$

Also, Meq. of $CaCl_2$ = Meq. of CaC_2O_4
= Meq. of $KMnO_4$ = 22 × 0.1 × 5 = 11

$\therefore$ mass of $CaCl_2 = 11\times\frac{111}{2}\times\frac{1}{1000} = 0.61$ g

$\therefore$ mass of NaCl = 0.39 g

$\therefore$ mass of $CaCl_2$ in 5 g mixture = 0.61 × 5 = 3.05 g
mass of NaCl in 5 g mixture = 0.39 × 5 = 1.95 g

Now, $\Delta T = \dfrac{1000 K_b}{W}\left[\underset{\text{for NaCl}}{(1+\alpha)\dfrac{w}{m}} + \underset{\text{for } CaCl_2}{(1+2\alpha)\dfrac{w}{m}}\right]$

$= \dfrac{1000\times 1.86}{100}\left[(1+1)\times\dfrac{1.95}{58.5}+(1+2)\times\dfrac{3.05}{111}\right]$

$= \dfrac{1000\times 1.86}{100}\times 0.149 = 2.77\ \text{K}$

$\therefore$ Freezing point $= 273 - 2.77 = \mathbf{270.23\ K}$

94. $HA \rightleftharpoons H^+ + A^-$

$[H^+] = C\alpha = 10^{-2}$

$\therefore \quad \alpha = \dfrac{10^{-2}}{0.1} = 10^{-1} = 0.1$

$\therefore$ Total particles in solution $= 1+\alpha = 1+0.1 = 1.1$

Now, $P = CST(1+\alpha)$

$= 0.1\times 0.0821\times 298\times 1.1 = \mathbf{2.69\ atm}$

95. $\underset{1}{CoCl_3\cdot x NH_3} \longrightarrow \underset{0}{CoCl_{3-n}\cdot x NH_3} + \underset{n\alpha}{n Cl^-}$

$\quad\quad\quad

Now for $2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

Before association: 1, 0

After association: $(1-\alpha)$, $\frac{\alpha}{2}$

where α is degree of association

$\therefore \quad \frac{m_{normal}}{m_{observed}} = 1-\alpha+\frac{\alpha}{2}$

or $\quad \frac{60}{113.78} = 1-\alpha+\frac{\alpha}{2}$

or $\quad \alpha = \mathbf{0.945}$ or $\mathbf{94.5\%}$

103. Given, $w = 2\,g$, $W = 25\,g$, $\Delta T = 1.62$, $K_f' = 4.9$

$\because \quad \Delta T = \frac{1000\times K_f'\times w}{m\times W}$

$1.62 = \frac{1000\times 4.9\times 2}{25\times m}$

$\therefore \quad m_{exp} = 241.98\,g\,mol^{-1}$

$nC_6H_5COOH \rightleftharpoons (C_6H_5COOH)_n$

Before association: 1, 0

After association: $(1-\alpha)$, $\frac{\alpha}{n}$

$\therefore$ Total number of mole at equilibrium $= 1-\alpha+\frac{\alpha}{n}$

$\frac{m_N}{m_{exp}} = 1-\alpha+\frac{\alpha}{n}$

For dimer formation $n = 2$

$\frac{122.0}{241.98} = 1-\alpha+\frac{\alpha}{2}$ ($m_N = 122.0$ for C_6H_5COOH)

or $\quad 1-\frac{\alpha}{2} = 0.504$

$\therefore \quad \alpha = \mathbf{0.992}$ or $\mathbf{99.2\%}$

104. $2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$

$\underset{(1-\alpha)}{1}$, $\underset{\frac{\alpha}{2}}{0}$

$\because \quad \Delta T_f = \frac{1000K_f\times w}{m\times W}\left(1-\alpha+\frac{\alpha}{2}\right)$

$7 = \frac{1000\times 14\times 75.2}{94\times 1000}\left(1-\frac{\alpha}{2}\right)$

$\therefore \quad \alpha = \mathbf{0.75}$ **or** $\mathbf{75\%}$

105. For benzene $K_f' = \frac{RT^2}{1000l_{f(cal/g)}} = \frac{8.314\times(278.4)^2}{1000\times\frac{10.042\times10^3}{78}}$

$= 5.0$ K molality

Also, $\quad \Delta T = 278.4 - 277.4 = 1$

For acetic acid in benzene

$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

Before association: C, 0

After association: $C(1-\alpha)$, $\frac{C\alpha}{2}$

$\therefore K_C = \frac{\frac{C\alpha}{2}}{C^2(1-\alpha)^2}$; where α is degree of association ...(1)

Also, $\quad \Delta T = K_f' \times \text{molality} \times \left(1-\frac{\alpha}{2}\right)$ ...(2)

$\left(\because \text{total particles at equilibrium} = 1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}\right)$

Given mole fraction of acetic acid $= 0.02 = \frac{n}{n+N}$

$\therefore \quad$ Mole fraction of benzene $= 0.98 = \frac{N}{n+N}$

$\frac{n}{N} = \frac{0.02}{0.98}$

$\therefore$

$\text{molality} = \frac{n}{W}\times 1000 = \frac{n\times 1000}{N\times M} = \frac{0.02\times 1000}{0.98\times 78} = 0.262\,m$

$\therefore$ From Eq. (2), $\quad 1 = 5\times 0.262\times\left(1-\frac{\alpha}{2}\right) \quad \therefore \quad \alpha = 0.48$

From Eq. (1), Assuming molarity = molality

$K_C = \frac{0.262\times 0.48}{2\times(0.262)^2\times(1-0.48)^2} = \mathbf{3.39}$

106. $\Delta T = \frac{1000\times K_b'\times w}{m\times W}$

$1.68 = \frac{1000\times 2.34\times 28}{m\times 315}$

$\therefore \quad m_{exp} = 123.80\,g\,mol^{-1}$

$\frac{m_N}{m_{exp}} = 1-\alpha+\frac{\alpha}{n}$

$\because \alpha = 1 \therefore \quad \frac{m_N}{m_{exp}} = \frac{1}{n}$ (m_N of $P = 31$)

$\therefore \quad \frac{31}{123.80} = \frac{1}{n}$

$\therefore \quad n \approx \mathbf{4}$, *i.e.*, $\mathbf{P_4}$

107. $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N}$

$P^\circ - P_s = P^\circ\left[\frac{n}{n+N}\right]$

Let 1 mole of solute is dissolved in 1000 g solvent water.

Thus, $\quad n = 1$ and $N = \frac{1000}{18}$

Also, $P^\circ = 760$ mm for water at 100° C

$\therefore \quad P^\circ - P_s = \left[\frac{1}{1+\frac{1000}{18}}\right]\times 760$

$= \mathbf{13.43\ mm}$

108. $NaHSO_4 \longrightarrow \underset{0}{\overset{1}{Na^+}} + \underset{1}{\overset{0}{HSO_4^-}}$

$\underset{1-h}{\overset{1}{HSO_4^-}} + H_2O \longrightarrow \underset{h}{\overset{0}{H_3O^+}} + \underset{h}{\overset{0}{SO_4^{-2}}}$

$\therefore$ Total particles after dissolution of $NaHSO_4$

$= 1+1-h+h+h = 2+h$

Now, $\quad \Delta T_f = K_f \times \text{molality} \times (i)$

$0.345 = 1.86\times 0.08\times(2+h)$

$\therefore \quad 2+h = 2.319$

$\therefore \quad h = \mathbf{0.319}$

i.e., 31.9% of HSO_4^- shows proton transfer to H_2O.

109. $A(l)+B(l) \longrightarrow \underset{\text{Insoluble}}{(A)_n}+B(l)$

$$P_M = P_A^{\circ}\cdot X_A + P_B^{\circ}\cdot X_B$$

$$P_M = 300\left(\frac{a}{12+a}\right)+500\left(\frac{12}{12+a}\right) \quad ...(1)$$

where a mole of A are left after polymerisation after 100 minute

Also rate constant, $K = \frac{2.303}{t}\log\frac{10}{a}$

$$K = \frac{2.303}{100}\log\frac{10}{a} \quad ...(2)$$

after 100 minute polymerisation is checked

After 100 minute solute is added and final vapour pressure is 400 (*i.e.*, $P_s = 400$)

$$\therefore \quad \frac{P_M - 400}{400} = \frac{0.525}{(a+12)} \quad ...(3)$$

Solving Eqs. (1) and (3), $a = 9.9$

Using this value of a in Eq. (2),

$$K = \frac{2.303}{100}\log\frac{10}{9.9}$$

$$K = \mathbf{1.0\times10^{-4}}$$

110. $$\frac{P^{\circ}-P_s}{P_s} = \frac{n}{N} = \frac{n\times M\times 1000}{W\times 1000}$$

$$\frac{17.39-17.0}{17.0} = \frac{\text{molality}\times M}{1000}$$

$$\therefore \quad \text{molality} = \frac{0.39\times1000}{17\times18} = 1.275$$

For dilute solution molarity = molality

$$\therefore \quad \pi = CST = 1.275\times 0.0821\times 293 = 30.66 \textbf{ atm}$$

Also, for water vapours $PV = nRT$

$$P = \frac{w}{V}\cdot\frac{RT}{m}$$

$$\frac{w}{V} = \frac{Pm}{RT} = \frac{17.0\times18}{760\times0.0821\times293}$$

density of $H_2O_V = 1.673\times10^{-2}$ g / litre

$= 1.673\times10^{-5}$ g / mL

111. $$\Delta T_b = \frac{1000\times w\times K_b}{m\times W}\times(1+\alpha)$$

$\because$ $w = 10$ g; $W = 100-10 = 90$ g

$$0.27 = \frac{1000\times10\times0.512}{342\times90}\times(1+\alpha) \quad \therefore \alpha = \mathbf{0.623}$$

Also, $$\frac{m_N}{m_{exp}} = 1+\alpha$$

$$\therefore \quad m_{exp} = \frac{342}{1.623} = \mathbf{210.7 \text{ g mol}^{-1}}$$

112. $$\log_{10} P = 3.54595+\frac{313.7}{T}+1.40655\log_{10} T$$

$$\ln P = (3.54595\times2.303)-\frac{313.7\times2.303}{T}+1.40655\ln T$$

$$\therefore \quad \frac{d}{dT}\ln P = \frac{313.7\times2.303}{T^2}+\frac{1.40655}{T} \quad \left[\frac{d}{dT}\ln P = \frac{\Delta H}{RT^2}\right]$$

$$\therefore \quad \Delta H = [313.7\times2.303+1.40655T]R$$

at 80K $\Delta H = \mathbf{1670 \text{ cal}}$

113. According to Henry's law,

$$\frac{a}{P} = K$$

$$\therefore \quad a = 3.1\times10^{-2}\times4 = \mathbf{0.124 \text{ mol / litre}}$$

114. $$x_{N_2} = \frac{P_{N_2}}{K_H} = \frac{0.987}{76480} = 1.29\times10^{-5}$$

If n represents number of mole of N_2 in 1 litre H_2O or $\left(\frac{1000}{18}\text{ mole}\right)$ 55.6 mole H_2O, then

$$x_{N_2} = \frac{n}{n+55.6} = \frac{n}{55.6} = 1.29\times10^{-5}$$

Thus, $n = 1.29\times10^{-5}\times55.6$ mol

$= 7.18\times10^{-4}$ mol

$= \mathbf{0.718 \text{ milli mol.}}$

SINGLE INTEGER ANSWER PROBLEMS

1. The vapour pressure of a mixture of two volatile liquids is expressed as $P_m = 6.0 + 1.5\,X_B$, where X_B is mole fraction of B in mixture. The vapour pressure of 'A' at the same temperature is :
2. van't Hoff factor of a mixture of two mole of KI with 1 mole HgI_2, in a solution of water is .....
3. The freezing point depression of 10^{-3} molal aqueous solution of a compound $K_x[Fe(CN)_6]$ is 7.44×10^{-3} K. Given K_f of $H_2O = 1.86$ k $mol^{-1}kg$, the value of X is .....
4. The boiling point of a solution of 5 g sulphur in 100 g CS_2 is 0.5°C above pure solvent. If the K_b of CS_2 is 2.56 K molality^{-1} then the atomicity of sulphur in this solvent is .....
5. A solution of 6.2 g ethylene glycol in 55 g H_2O is cooled to −3.72°C. The ice separated from solution is : ($K_f H_2O = 1.86$ K molality^{-1})
6. A complex is represented as $CoCl_3 \cdot XNH_3$. Its 0.1 molal solution in water shows $\Delta T_F = 0.558$°C. K_f of H_2O is 1.86 K molality^{-1}. Assuming 100% ionisation, calculate the no. of NH_3 molecules associated with Co.
7. A 0.4 molal aqueous solution of $M_X A$ has freezing point 3.72°C. The K_f of H_2O is 1.86 K molality^{-1}. The value of X is .....
8. 3 mole of liquid A (V.P. = 60 mm) and a mole of B (V.P. = 40 mm) results in a solution having V.P. of 50 mm. The value of a is .....
9. An aqueous solution of a substance molar mass 240 has osmotic pressure 0.2 atm at 300 K. The density of solution in g / dm^3 is : ($R = 0.08$ litre atm K^{-1} mol^{-1}).
10. The osmotic pressure of a solution in atm obtained on mixing each 50 mL of 1.2% mass/vol. urea solution and 2.4% mass/vol. glucose solution at 300 K ($R = 0.08$ litre atm K^{-1} mol^{-1}).
11. How many g of glucose must be present in 0.5 litre of a solution for its osmotic pressure be same as that of 8 g glucose in 1 litre?
12. The osmotic pressure of a solute is 600 mm at 300 K. The solution is diluted and the temperature is raised to 400 K and the solution shows an osmotic pressure of 200 mm. The solution was diluted to ..... times.
13. 'n' mole of a non electrolyte are added to 'N' mole of solvent. The addition causes a lowering in vapour pressure of solvent by 20%. The ratio of mole of solvent and its solute is .....
14. A solution of liquids A and B having vapour pressure in pure state P_A^0 and P_B^0. The solution contains 30% mole of A which is in equilibrium with 60% mole of A in vapour phase. If P_B^0 is 2 cm, the P_A^0 is ..... cm.
15. A mixture of two immiscible liquids nitrobenzene and water boiling at 99°C has a partial pressure of water 733 mm and of nitrobenzene 27 mm. The ratio of masss of water and nitrobenzene in mixture is .....
16. How much of the following will not show abnormal colligative properties in aqueous medium. Urea, $NaNO_3$, Thiourea, Glucose, Benzoic acid, Acetic acid.
17. Solute A is binary electrolyte and solute B is non electrolyte. If 0.2M solution of solute B produces an osmotic pressure of 2 atm then 0.1M solution of A at the same temperature will produce an osmotic pressure equal to.....
18. A 0.1m aqueous solution of complex represented as $CoCl_3 \cdot XNH_3$ shows a freezing point of 0.558°C. If K_f of water is 1.86 K molality^{-1}, how much Cl atoms are outside the co-ordination sphere, assuming co-ordination number of Co as six and 100% ionisation of complex ?
19. 9 g of a metal fluoride MF_x (molar mass 180) is dissolved in 100 g water to register an increase in b.pt by 1.00 K. Assuming complete dissociation of MF_x and 100% ionisation and K_b for water 0.50 K mol^{-1} kg calculate the value of x.
20. 20 g of solute A present in 500 mL solution exerts same osmotic pressure as 2500 mL of 40 g of solute A and 60g of solute B solution at same temperature. Assuming A and B non electrolytes, calculate the ratio of molar masses of B and A.
21. The vapour pressure of two liquids A and B are 50 and 100 mm respectively. The ratio of mole fractions of B and A in vapour phase over the liquid if they are mixed in 1 : 1 ratio is.....
22. 4 g of solutes A and B each are dissolved separately in 100 g H_2O to produce depression in freezing pt 0.1° and 0.2° respectively. If both A and B are nonelectrolyte, then what is the ratio of molar masses of A and B?
23. How many of the following are natural semipermeable membrane.
    Gall bladder, Plant cell, Phenol layer, $Cu_2Fe(CN)_6$, Root hair
24. 100 g solution of 10% (mass/mass) urea solution is placed together with 200 g of 10% mass/mass glucose solution in closed jar to attain equilibrium. The number of mole of water transferred from one solution to other in order to attain equilibrium is ..... .
25. Osmotic pressure of an aqueous solution of a non-volatile solute which neither associates nor dissociates at 300 K is 4.737 atm. If K_f of water 0.52,

$\therefore \quad 31.2 + 4.8n = 151.2 - 25.2a$

$\therefore \quad 30a = 120 \quad (\because n = a)$

or $a = +4$

Thus oxide is $\mathbf{CrO_2}$.

81. $10e + (Mn^{7+})_2 \longrightarrow 2Mn^{2+}] \times 61$

$(Fe^{2+}) \longrightarrow Fe^{3+} + e$

$(C^{2+})_6 \longrightarrow 6C^{4+} + 12e$

$(N^{3-})_6 \longrightarrow 6N^{5+} + 48e$

$Fe^{2+} + C^{2+} + N^{3-} \longrightarrow Fe^{3+} + C^{4+} + N^{5+} + 61e] \times 10$

$61Ba(MnO_4)_2 + 10K_4[Fe(CN)_6] \longrightarrow 122Mn^{2+} + Fe^{3+} + 6C^{4+} + 6N^{5+}$

$\because$ 10 mole $K_4Fe(CN)_6 \equiv 61$ mole $Ba(MnO_4)_2$

$\therefore$ 1 mole $K_4Fe(CN)_6 \equiv$ **6.1 mole $Ba(MnO_4)_2$**

● SINGLE INTEGER ANSWER PROBLEMS ●

1. 'n' factor of FeC_2O_4 during its oxidation by acidified $KMnO_4$ is .....
2. An element A in a compound has oxidation state A^{n-}. If 1.68×10^{-3} mole of $K_2Cr_2O_7$ are required for complete oxidation of 3.26×10^{-3} mole of ABD for oxidation to A^{n-} to elemental state. The value of n is .....
3. 1.6 g pyrolusite ore was titrated with $50\,cm^3$ of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left was raised to 250 mL in a flask 25 mL of this solution when treated with 0.1 N $KMnO_4$ required 32 mL of the solution. The percentage of available oxygen in pyrolusite is :
4. 1 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with Zn dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution requires 17 mL of 0.0167M solution of an oxidant for titration. The number of electrons taken up by oxidant in the above titration is .....
5. 0.31 g of an alloy of Fe + Cu was dissolved in excess dilute H_2SO_4 and the solution was made upto 100 mL. 20 mL of this solution required 3 mL of $\frac{N}{30}K_2Cr_2O_7$ solution for exact oxidation. The % purity (in closest value) of Fe in wire is :
6. The reaction $Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^-$ to be carried out in basic medium. 1.5 mole of Cl_2 are allowed to react can with 0.1 mole of $S_2O_3^{2-}$ in presence of 3.0 mole of OH^-. Mole of OH^- left after the reaction is .....
7. Equivalent mass of O_3 in the reaction : $2O_3 \longrightarrow 3O_2$ is .....
8. 'n' factor for H_2S during its oxidation to SO_2 is .....
9. 'n' factor for Cu_2S in the reaction

   $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + SO_2 + Mn^{2+}$ is:
10. A 5.6 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed with water and dissolved in dil. H_2SO_4. The solution required 40 mL of 0.25 N $KMnO_4$ solution for titration. The % of CaO in limestone is .....
11. 80 mL of $M/24$ $K_2Cr_2O_7$ solution oxidises 22.4 mL H_2O_2 solution. The volume strength of H_2O_2 solution is .....
12. 10 mL of 0.2 M solution of $K_xH(C_2O_4)_y$ requires 8 mL of 0.2 M acidified $KMnO_4$ solution. The value of x is .....
13. 'n' factor for SO_2 in $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$ is .....
14. 30 mL of 0.3 M $MnSO_4$ is completely oxidised by 3 mL of $KMnO_4$ of unknown normality, each forming Mn^{4+} oxidation state. The normality of $KMnO_4$ is .....
15. 2 M solution of HNO_3 is reduced to NO by suitable reductant. The normality of HNO_3, if HNO_3 is used like this is .....
16. 'n' factor for S in SO_2 is 4 and in SO_3 is 6. The 'n' factor of S in $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$ is .....
17. 'n' factor of C_2H_5OH in the reactions is....

    $C_2H_5OH \longrightarrow CH_3CHO$
18. 4 mole each of Hg^{2+} and I^- will form how much mole of $[HgI_4]^{2-}$.
19. 2.5 mole of $Fe_2(C_2O_4)_3$ requires how much mole of $KMnO_4$ for its complete oxidation in acidic medium?
20. C_3H_8 is completely oxidised to CO_2 and H_2O, the ratio of equivalent mass of CO_2 formed and C_3H_8 taken is.....
21. The number of mole of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ oxidised by 4 mole of acidified $KMnO_4$ is.....
22. CrO_5 reacts with H_2SO_4 to give $Cr_2(SO_4)_3$, H_2O and O_2. The mole of O_2 released during the reaction of 4 mole of CrO_5 with excess of H_2SO_4.
23. 2 mole of FeC_2O_4 are oxidised by 'X' mole of $KMnO_4$ whereas 2 mole of $FeSO_4$ are oxidised by 'Y' mole of $KMnO_4$. The ratio of $X : Y$ is.....

24. Number of H_2O_2 mole needed to convert two mole of $Cr(OH)_3$ in alkaline medium to sodium chromate is.....

25. 6×10^{-3} mole $K_2Cr_2O_7$ reacts completely with 9×10^{-3} mole X^{n+} to give XO_3^- and Cr^{3+}. The value of n is .....

26. Mole of $KMnO_4$ required to oxidise a mixture of 2 mole each of $FeSO_4$, FeC_2O_4 and $Fe_2(C_2O_4)_3$ in acid medium.

27. Mole of $K_2Cr_2O_7$ required to oxidise one mole of $Fe_2(C_2O_4)_3$ in acid medium.

28. Equivalent mass of nitrogen in the reaction :
$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$ is $\frac{M}{X}$. The value of X is .....

29. A 1.10 g sample of copper ore is dissolved and Cu^{2+} formed are titrated with excess of KI. The liberated iodine requires 12.12 mL of 0.10 N $Na_2S_2O_3$ solution for titration. The % of copper by mass in sample is .....

30. 9.824 g of $FeSO_4.(NH_4)_2SO_4.X\,H_2O$ were dissolved in 250 mL of solution. 20 mL of this solution required 20 mL of $KMnO_4$ containing 3.52 g of 90% by mass $KMnO_4$ dissolved per litre. The value of 'X' is .....

31. A 0.56 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed and dried and then dissolved in H_2SO_4. The solution required 4mL of 0.25 N $KMnO_4$ for oxidation of oxalate. The % of CaO in limestone is .....

32. Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

under conditions where 1 mole of gas occupies 50 dm^3, 100 cm^3, of XM solution of H_2O_2 produces 5 dm^3 of O_2. Thus X is .....

33. 15g sample of an alloy containing Cu (at mass 63.6) and Zn reacts completely with 3M HNO_3 as :

$$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2(g) + H_2O$$

$$Zn + HNO_3 \longrightarrow Zn^{2+} + NH_4^+ + H_2O$$

The liberated $NO_2(g)$ was found to occupy 4.647 litre at 1 atm and 300 K. The mass of Zn (to the closest value) in alloy is .....

34. n-factor of Mn_2O_7 in the change :
$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$ is .....

35. n-factor for Fe_3O_4 in its reaction during its oxidation to Fe_2O_3 is .....

36. Number of mole of As_2S_3 required to reduce 56 mole of HNO_3 according to equation :
$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

37. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is :
[IIT 2011]

38. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product, the magnitude of X is:
[JEE (Advanced) I 2016]

ANSWERS

1. Three	2. Three	3. Nine	4. Six	5. Nine	6. Two	7. Eight	8. Six	9. Eight	10. Five	11. Five	12. Three
13. Five	14. Two	15. Six	16. Two	17. Two	18. One	19. Three	20. Three	21. Five	22. Seven	23. Three	24. Three
25. One	26. Four	27. One	28. Six	29. Seven	30. Six	31. Five	32. Two	33. Nine	34. Six	35. One	36. Six
37. Five	38. Six										

OBJECTIVE PROBLEMS (One Answer Correct)

1. Which of the following is not colligative property?
   (a) Molarity (b) Vapour pressure
   (c) Osmotic pressure (d) Elevation in b.pt.
2. Pick up the wrong statement :
   (a) Hygroscopic and deliquescent salts are highly soluble in water.
   (b) Vapour pressure of water in hygroscopic substances in their solution state is lower than humidity of air.
   (c) Efflorescent crystals have higher vapour pressure of water than humidity of air.
   (d) For isotonic solution concentrations of two solutions must be always same.
3. A 20 mL urea solution of 2% (mass by vol.) is mixed with 80 mL of glucose solution of 4% (mass by vol.) at 300 K. Calculate the osmotic pressure of solution :
   (a) 6.02 atm (b) 1.642 atm
   (c) 4.378 atm (d) 3.01 atm
4. In two solutions of same solute-solvent system exerts osmotic pressures of 6 atm and 2 atm at 300 K respectively. If these are separated by a semipermeable membrane, which would be observed :
   (a) solvent will move from 6 atm solution to 2 atm solution
   (b) solute will move from 6 atm solution to 2 atm solution
   (c) solvent will move from 2 atm solution to 6 atm solution
   (d) no movement of solute or solvent
5. Two liquids A and B are mixed. The partial vapour pressures of A and B in pure state are 100 and 200 mm respectively. If they are mixed in 1 : 4 mole ratio, then at equilibrium pressure of the mixture, assuming that mixture obeys Raoult's law, the mole fractions of A and B present in gaseous state are :
   (a) $\frac{1}{5}, \frac{4}{5}$ (b) $\frac{1}{3}, \frac{2}{3}$
   (c) $\frac{1}{7}, \frac{6}{7}$ (d) $\frac{1}{9}, \frac{8}{9}$
6. A solution of an organic compound develops an osmotic pressure of 2.07×10^{-2} Nm^{-2}. If the density of solution is 0.88 g dm^{-3}, the height which it will develop on separating with its solvent through semipermeable membrane is :
   (a) 2.40×10^{-5} m (b) 2.40×10^{-3} m
   (c) 2.4 m (d) 2.40×10^{-4} m
7. Two solutions each in 100 mL having 4 g glucose and 10 g sucrose respectively. Which one is correct to develop isotonic character in them (Assume T constant)?
   (a) 0.42 g urea in glucose solution
   (b) 0.42 g glucose in glucose solution
   (c) 0.42 g sucrose in glucose solution
   (d) 0.42 g urea in sucrose solution
8. The vapour pressure of two volatile liquid mixtures is $P_T = 5.3 + 2X_B$ (in cm of Hg), where X_B is mole fraction of B is mixture. What is the ratio of X_A and X_B in vapour phase?
   (a) $\frac{73}{53}$ (b) $\frac{73}{53} \times \frac{P'_A}{P'_B}$
   (c) $\frac{53}{73}$ (d) $\frac{53}{73} \times \frac{P'_B}{P'_A}$
9. 25 g ethylene glycol is present in 100 g of water. The solution is cooled to $-10°C$. K_f for H_2O is 1.86 K kg mol^{-1}. The amount of ice separated on cooling is :
   (a) 25 g (b) 50 g
   (c) 75 g (d) 20 g
10. The solution having highest vapour pressure is : (Assume 100% ionisation of electrolytes)
   (a) 1 N KNO_3 (b) 1 N $Ba(NO_3)_2$
   (c) 1 N $Al_2(SO_4)_3$ (d) 1 N $Th(NO_3)_4$
11. Elevation in b.pt. of an aqueous glucose solution is $0.6K_b$ for water is 0.52 K molality^{-1}. The mole fraction of glucose in the solution is :
   (a) 0.02 (b) 0.03
   (c) 0.01 (d) 0.04
12. Normal boiling point (T_N) is defined as the temperature when V.P. of liquid becomes equal to 1 atm and standard boiling point (T_S) is defined as the temperature when V.P. of liquid becomes equal to 1 bar. Which one is not correct if water is considered?
   (a) $T_N = 100°C$ (b) $T_S > 100°C$
   (c) $T_S < 100°C$ (d) $T_S < T_N$
13. The vapour pressure of a solution at 373 K is 700 mm of Hg. The molality and mole fraction of solute in solution is :
   (a) 0.0789, 4.76 (b) 0.789, 2.38
   (c) 0.0789, 4.76×10^{-3} (d) 0.789, 4.76×10^{-1}
14. The ratio of vapour pressures of two liquids A and B in pure state are 1 : 2. If the two liquids are mixed and the ratio of their mole fraction in vapour phase are 2 : 1, the liquids A and B were mixed in the ratio of their mole :
   (a) 1 : 2 (b) 2 : 1
   (c) 4 : 1 (d) 1 : 4
15. During the freezing of a solution at its f.pt., which of the equilibrium exists?
   (a) $\text{Solution}_{(l)} \rightleftharpoons \text{Solid solution}_{(s)}$
   (b) $\text{Solvent}_{(l)} \rightleftharpoons \text{Solvent}_{(s)}$
   (c) $\text{Solution}_{(l)} \rightleftharpoons \text{Solute}_{(s)} + \text{Solvent}_{(s)}$
   (d) $\text{Solution}_{(l)} \rightleftharpoons \text{Solute}_{(s)} + \text{Solvent}_{(l)}$

16. A solution of 6% (mass/vol.) urea is isotonic with $NaCl_{aq}$. What is the mass/vol. % of NaCl in solution?
(a) 5.85% (b) 2.925%
(c) 11.7% (d) 1.463%

17. Which of the aqueous equimolal solution will have its vapour pressure near to solvent?
(a) Urea (b) $Ba(NO_3)_2$
(c) $NaNO_3$ (d) $Al(NO_3)_3$

18. Which of the following semipermeable membrane does not at all allow the solute particles to pass through it?
(a) Gelatinous $Cu_2Fe(CN)_6$
(b) Hair root of plants
(c) Bladder of pig
(d) All of these

19. A saturated aqueous solution of sparingly soluble salt AB_3 has the vapour pressure 0.08 mm lesser than the vapour pressure 17.33 mm of solvent at 25°C. The solubility product of AB_3 is :
(a) 1.087×10^{-2} (b) 1.48×10^{-4}
(c) 5.35×10^{-5} (d) 4.56×10^{-4}

20. 30 mL of 0.1 M KI_{aq} and 10 mL of 0.2 M $AgNO_3$ are mixed. The solution is then filtered out. Assuming no change in total volume, the resulting solution will freeze at : (Given, K_f for $H_2O = 1.86$ K kg mol^{-1} assume molarity = molality)
(a) 0.28 (b) 0.22
(c) 0.0744 (d) 0.149

21. Select the incorrect statement :
(a) If ΔT is depression in freezing point and m is molality, then $\left(\text{limit}\ \frac{\Delta T}{m}\right)_{T\to0}$ = molal depression constant
(b) On dissolution of Fe in aqueous HCl, work is done by the system
(c) Osmosis is bilateral process
(d) For isotonic solutions C_1 must be equal to C_2.

22. 38.2 g of $Na_2B_4O_7\cdot nH_2O$ dissolved in 250 g water shows an elevation in b.pt by 0.582°C. If K_f of water is 0.52 kg molality^{-1}, then n is :
(a) 6 (b) 5
(c) 8 (d) 10

23. 100 g of 10% by mass/mass urea solution is placed together with 200g of 10% (mass/mass) glucose solution in closed jar and allowed to attain equilibrium, the new (mass/mass)% of urea in its solution at equilibrium is :
(a) 4.26 (b) 6.17
(c) 5.43 (d) 7.68

24. A 0.2 mole fraction of non-electrolyte in water shows vapour pressure of solution equal to 10 mm of Hg. The mole fraction of solute of same electrolyte when it shows a vapour pressure of 5 mm of Hg is :
(a) 0.4 (b) 0.52
(c) 0.8 (d) 0.48

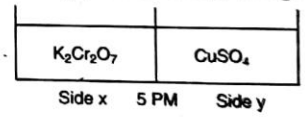
25. Benzoic acid undergoes dimerisation to 60% in benzene. The observed mass of benzoic acid will be :
(a) = 61 (b) > 122
(c) < 122 (d) = 244

26. A non-ideal solution obtained by mixing 30 mL chloroform and 50 mL acetone will show :
(a) ΔH = –ve and total volume < 80 mL
(b) ΔH = –ve and total volume = 80 mL
(c) ΔH = +ve and total volume > 80 mL
(d) ΔH = +ve and total volume = 80 mL

27. A commercial sample of cyclohexane freezes at 6.0°C. If freezing point of cyclohexane is 6.5° and K_f = 20.0 K molality^{-1}, then purity of sample is :
(a) 99.8% (b) 98%
(c) 90.9% (d) 99.5%

28. The slope of π *vs* C was made against insulin concentration (C) in g mL^{-1} and temperature 27°C. If C is in g litre^{-1} and the slope of line obtained is 4.65×10^{-3} g/mL, the molar mass (in g mol^{-1}) of insulin is :
(a) 9×10^5 (b) 3×10^5
(c) 4.5×10^5 (d) 5.30×10^6

29. 0.05 M $CuSO_4$ when treated with 0.01 M $K_2Cr_2O_7$ gives green colour solution of $Cu_2Cr_2O_7$. The two solutions are separated as shown in figure. Due to



osmosis :
(a) Green colour formation inside Y
(b) Green colour formation inside X
(c) Molarity of $K_2Cr_2O_2$ is lowered
(d) Molarity of $CuSO_4$ solution is lowered

30. When an immiscible liquid with water was steam distilled at 95°C at a total pressure of 748 mm, the distillate obtained contain 1.25g of liquid per g of water. The vapour pressure of water is 648 mm at 95°C. The molar mass in g mol^{-1} of liquid is :
(a) 145.8 (b) 166
(c) 176 (d) 8

31. An ideal solution has two components A and B. If A is more volatile than B and also $P_A^\circ > P_T$, then the correct relation between mole fractions of A in liquid (X) and vapour (Y) phase is :
(a) $X_A = Y_A$ (b) $X_A > Y_A$
(c) $X_A < Y_A$ (d) nothing can be said

32. The incorrect relationship according to Raoult's law for two miscible liquid mixture is :
(a) $P_T = P_A^0 + (P_B^0 - P_A^0)\,X_B$

(b) $P_A' + P_B' = P_T$

(c) $P_T = P_B^0 + (P_A^0 - P_B^0) X_A$

(d) $P_T = P_A^0 + (P_A^0 - P_B^0) X_A$

33. The ratio of vapour pressure of two miscible liquids A and B in pure state are in the ratio 1 : 3 respectively at a temperature. n_A mole of A and n_B mole of B are mixed to form an ideal solution. If the ratio of mole of A and B in vapour phase was found to be 4 : 3, the ratio of mole of A and B in which they are mixed was :

(a) $\frac{4}{5}$ (b) 4

(c) $\frac{2}{3}$ (d) $\frac{1}{3}$

34. The boiling point of water and HCl are 100°C and 86°C respectively. An azeotropic mixture boils at about 120°C. Fractional distillation of this solution will give :

(a) Pure HCl first at 86°C

(b) Pure H_2O then at 100°C

(c) A mixture of HCl and H_2O in the ratio $\frac{373}{359}$

(d) A mixture of HCl in the ratio in which they are present in mixture

35. How many mole of $Th(NO_3)_4$ should be dissolved in 15 mole of water so that vapour pressure of water is reduced by 40% :

(a) 1 (b) 2

(c) 3 (d) 4

36. The boiling point elevation constant for toluene (b.pt = 110.7°C) is 3.32 K molality^{-1}. The entropy of vaporisation of toluene in J K^{-1}ml^{-1} is :

(a) 33.02×10^3 (b) 88.5

(c) 0.885 (d) 33.02

37. A solution of complex salt, $CrCl_3 \cdot 6H_2O$ having co-ordination no. 6 shows an osmotic pressure 73.89 atm at 300 K, when 1.0 molar solution of complex is used. One litre of this solution on treatment with excess of $AgNO_3$ solution ($\alpha_{AgNO_3} = 1$) leads to the formation of AgCl :

(a) 1 (b) 2

(c) 3 (d) 1.5

38. An ideal solution contains two volalite liquid A ($P° = 100$ torr) and B ($P° = 200$ torr). If liquid mixture contains 1 mole of A and 4 mole of B then total vapour pressure of the mixture obtained by condensing the vapour above this solution in a beaker is :

(a) 180 (b) 188.8

(c) 178.8 (d) 198.8

39. 0.2 M $AgNO_3$ and 0.1 M KI are mixed in the 1 : 3 volume ratio. The osmotic pressure of resultant solution at 300 K is :

(a) 4.93 atm (b) 3.69 atm

(c) 2.93 atm (d) 3.93 atm

40. The relationship which describes the variation of vapour pressure of a liquid with temperature is called :

(a) Hess's law

(b) Clausius Clapeyron equation

(c) Kirchhoff equation

(d) Arrhenius equation

41. An azeotropic solution of two liquids has boiling point lower than either of them when it :

(a) shows negative deviation from Raoult's law

(b) shows no deviation from Raoult's law

(c) shows positive deviation from Raoult's law

(d) is saturated

42. For a dilute solution, Raoult's law states that :

(a) the lowering of vapour pressure is equal to the mole fraction of solute

(b) the relative lowering of vapour pressure is equal to mole fraction of solute

(c) the relative lowering of vapour pressure is proportional to the mass of solute in solution

(d) the vapour pressure of the solution is equal to the mole fraction of solvent.

43. When mercuric iodide is added to the aqueous solution of potassium iodide then :

(a) freezing point is raised

(b) freezing point is lowered

(c) freezing point does not change

(d) boiling point does not change

44. Which of the following 0.1M aqueous solution will have the lowest freezing point?

(a) Potassium sulphate (b) Sodium chloride

(c) Urea (d) Glucose

45. The freezing point of equimolal aqueous solution will be highest for :

(a) $C_6H_5\overset{+}{N}H_3Cl^-$ (aniline hydrochloride)

(b) $Ca(NO_3)_2$

(c) $La(NO_3)_3$

(d) $C_6H_{12}O_{16}$ (glucose)

46. 0.2 molal acid HX is 20% ionised in solution. $K_f = 1.86$ K molality^{-1}. The freezing point of the solution is :

(a) − 0.45°C (b) − 0.90°C

(c) − 0.31°C (d) − 0.53°C

47. The molar mass of benzoic acid in benzene as determined by depression if freezing point method corresponds to :

(a) ionization of benzoic acid

(b) dimerization of benzoic acid

(c) trimerization of benzoic acid

(d) solvation of benzoic acid

48. A liquid mixture containing two immiscible liquids water and an alkyl bromide (molar mass 137 g mol^{-1}) is distilled at 90°C. The ratio of the vapour pressure of

water and alkyl bromide in the distillate is 5 : 1, the mass ratio of distillate is :

(a) 1.52 : 1 (b) 0.657 : 1
(c) 1 : 5 (d) 5 : 1

49. The plots of osmotic pressure π (in atm) *vs.* concentration (in g/cm^3) of a polymer at 300 K gives a straight line having slope 2×10^{-3}. The molar mass of polymer is :

(a) 1.23×10^6 (b) 1.23×10^7
(c) 4×10^7 (d) 4×10^6

50. Assuming 100% ionisation of each complex osmotic pressures of equimolar solutions of $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $Fe_4[Fe(CN)_6]_3$ and $Fe_3[Fe(CN)_6]_2$ at 300 K are in the order :

(a) 5 : 4 : 7 : 5 (b) 4 : 5 : 7 : 5
(c) 7 : 5 : 5 : 4 (d) 4 : 5 : 5 : 7

51. What mass of solute (molar mass = 60 g mol^{-1}) should be dissolved in 180 g water to reduce the vapor pressure to $\frac{4}{5}$ th of pure water :

(a) 120 g (b) 175 g
(c) 150 g (d) 100 g

52. The degree of association for a solute undergoing a change $4P \longrightarrow P_4$ can be given by

(a) $\frac{4[m\times K_f-\Delta T_f]}{3K_f\times m}$ (b) $\frac{2[m\times K_f-\Delta T_f]}{K_f\times m}$
(c) $\frac{[m\times K_f-\Delta T_f]}{K_f\times m}$ (d) $\frac{[K_f-\Delta T_f]}{\Delta T_f}$

53. During depression of freezing point in a solution, the following are in equilibrium : **(IIT 2003)**

(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

54. A 0.004 *M* solution of Na_2SO_4 is isotonic with a 0.01 *M* solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is : **(IIT 2004)**

(a) 25% (b) 50%
(c) 75% (d) 85%

55. The elevation in boiling point of a solution of 13.44g of $CuCl_2$ assuming 100% ionisation in 1 kg of water using the following information will be (formula mass of $CuCl_2 = 134.4$ and $K_b = 0.52$ K molal^{-1}) **(IIT 2005)**

(a) 0.16 (b) 0.05
(c) 0.1 (d) 0.2

56. 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72$ K mol^{-1} kg), a freezing point depression of 2 K is observed. The van't Hoff factor is : **(IIT 2007)**

(a) 0.5 (b) 1
(c) 2 (d) 3

57. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of mole of N_2 from air dissolved in 10 mole of water at 298 K and 5 atm pressure is : **(IIT 2009)**

(a) 4.0×10^{-4} (b) 4.0×10^{-5}
(c) 5.0×10^{-4} (d) 4.0×10^{-6}

58. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (molar mass 329 g mol^{-1}) in 100 g of water ($K_f = 1.86$ K kg mol^{-1}) is : **(IIT 2011)**

(a) -2.3×10^{-2} (b) -5.7×10^{-2}
(c) -5.7×10^{-3} (d) -1.2×10^{-2}

59. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76$ K kg mol^{-1}) : **(IIT 2012)**

(a) 724 (b) 740
(c) 736 (d) 718

SOLUTIONS (One Answer Correct)

1. (b) Vapour pressure lowering is colligative property and not vapourpressure.

2. (d) $c_1 = c_2$ or $c_1 > c_2$ or $c_1 < c_2$ for isotonic solution depending on the nature of solute.

3. (a) $\because \pi_T = \frac{w}{mV}ST = \pi_T = \left[\left(\frac{w}{m}\right)_{\text{urea}} + \left(\frac{w}{m}\right)_{\text{glucose}}\right] \times \frac{ST}{V}$

Now, w_{urea} in 20 mL $= \frac{2\times 20}{100} = 0.4$ g,

w_{glucose} in 80 mL $= \frac{4\times 80}{100} = 3.2$ g,

$\therefore \pi_T = \left[\frac{0.4}{60} + \frac{3.2}{180}\right] \times \frac{0.0821\times 300\times 1000}{100}$

$\left(V = 20+80 = 100\text{ mL} = \frac{100}{1000}l\right)$

$= 6.02$ atm

4. (c) Osmosis movement of solvent occurs from dil. (low O.P.) to conc. (higher O.P.) solution.

5. (d) $P_M = 100\times\frac{1}{5} + 200\times\frac{4}{5}$

$\because \frac{n_A}{n_A+n_B} = \frac{1}{5}$ and

$\frac{n_B}{n_A+n_B} = \frac{4}{5} = 20+160 = 180$ mm

Also, $P'_A = P_M \cdot (X_A)_{\text{V.P.}} = P^\circ \cdot (X_A)_{\text{L.P.}}$

$180\cdot(X_A)_{\text{V.P.}} = 100\times\frac{1}{5}$

$\therefore (X_A)_{\text{V.P.}} = \frac{1}{9}$

$\therefore \frac{n'_A}{n'_A+n'_B} = \frac{1}{9}$ and $\frac{n'_B}{n'_A+n'_B} = \frac{8}{9}$

6. (b) $d = 0.88\text{ g/mL} = 0.88\text{ g/cm}^3 = \frac{0.88\times 10^{-3}}{10^{-3}\text{ m}^3}$

$= 0.88\text{ kg/m}^3$

$\therefore \pi = h\cdot d\cdot g,$

$2.07\times 10^{-2} = h\times 0.88\times 9.8$

$\therefore h = 2.40\times 10^{-3}$

7. (a) $\pi_G = \frac{4}{180}\times 0.1\times 0.0821\times T = 1.82\times 10^{-4}\ T$

$\pi_S = \frac{10}{342}\times 0.1\times 0.0821\times T = 2.40\times 10^{-4}\ T,$

$(2.40-1.82)\times 10^{-4}\ T = \frac{w_{\text{urea}}}{60}\times 0.1\times 0.0821\times T$

$w = 0.42$ g

8. (b) $P_T = P'_A\cdot X_A + P'_B\cdot X_B,\quad P_T = 5.3+2X_B$

if $X_B = 0$ $P^\circ_A = P_T = 5.3$ cm and if $X_B = 1$

$P^\circ_B = P_T = 7.3$

Now mole fraction in mixture : $P'_A = P^\circ_A\cdot X_A$

$P'_B = P^\circ_B\cdot X_B$

$\therefore \frac{X_A}{X_B} = \frac{73\,P'_A}{53\,P'_B}$

9. (a) $\Delta T = \frac{1000\times K_f\times w}{m\times W}$

$10 = \frac{100\times 1.86\times 25.}{62\times W}$

(W_{glycol} remains constant on cooling; only water freezes.)

$\therefore W = 75$ g

$\therefore$ Ice separated $= 100-75 = 25$ g

10. (c)

	No. of particles
$1N\ KNO_3 = 1M\ KNO_3$	$= 1\times 2 = 2$
$1N\ Ba(NO_3)_2 = \frac{1}{2}M\ Ba(NO_3)_2$	$= \frac{1}{2}\times 3 = 1.5$
$1N\ Al_2(SO_4)_3 = \frac{1}{6}M\ Al_2(SO_4)_3$	$= \frac{1}{6}\times 5 = 0.83$
$1N\ Th(NO_3)_4 = \frac{1}{4}M\ Th(NO_3)_4$	$= \frac{1}{4}\times 5 = 1.25$

Thus, more is the No. of particles furnished more will be lowering or minimum will be V.P.

11. (a) $\Delta T = \frac{1000\times K_b\times n\times M}{W\times M} = \frac{1000\times K_b\times n}{N\times M}$

or $\frac{n}{N} = \frac{\Delta T\times M}{1000\times K_b} = \frac{0.6\times 18}{1000\times 0.52} = 0.02$

$\therefore \frac{N}{n} = 50$ or $1+\frac{N}{n} = 51$

$\therefore \frac{n+N}{n} = 51\ \therefore \frac{n}{n+N} = 0.02$

12. (b) $T_S = 372.6$ K for water since 1 bar < 1 atm

(1 bar = 0.998 atm)

13. (a) $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N}$

$\frac{760-700}{760}$ = m.f. of solute = 0.0789 (b.pt. of water is 373 K, thus $P_{H_2O} = 760$ mm)

Also, $\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{n\times M\times 1000}{W\times 1000}$

$\therefore$ Molality $= \frac{760-700}{700}\times\frac{1000}{18} = 4.76$

14. (c) $P'_A = P^\circ_A\cdot X_{A(l)} = P_M\cdot X_{B(G)},$

$P'_B = P^\circ_B\cdot X_{B(l)} = P_M\cdot X_{B(G)},$

$\therefore \frac{P^\circ_A}{P^\circ_B}\cdot\left[\frac{X_A}{X_B}\right]_l = \left[\frac{X_A}{X_B}\right]_G$

$\therefore \left[\frac{X_A}{X_B}\right]_l = \frac{2}{1}\times\frac{2}{1} = 4:1$

15. (b) At f.pt. only solvent freezes out.

16. (b) $\pi_{\text{urea}} = \pi_{\text{NaCl}}$

$\frac{w}{m}\times\frac{ST}{V} = \frac{w}{m}\times\frac{ST}{V}\times(1+\alpha)$

$\frac{6}{60}\times\frac{1000}{100}\times ST = \frac{w\times 1000\times ST}{58.5\times 100}\times 2$

($\because \alpha = 1$ for NaCl)

$\therefore w = 2.925$ g $\quad\therefore$ % by mass/vol. = 2.925%

17. (a) $\frac{P°-P_s}{P°}=\frac{n}{n+N}(1+\alpha)$ ΔP is minimum since $\alpha=0$ for urea. Thus, urea solution will have its V.P. closer to solvent.

18. (a) Only artificially prepared semipermeable membranes are perfectly semipermeable.

19. (d) For dilute solution :

$$\frac{P°-P_s}{P°}=\frac{n}{N}(1+\alpha)=\frac{n\times M\times 1000}{W\times 1000}\times(1+\alpha)$$

$$=\text{molality}\times\frac{M}{1000}\times(1+3\alpha)\qquad(\alpha=1)$$

$$\text{molality}=\frac{0.08}{17.33}\times\frac{1000}{18\times 4}=0.0641\,\text{m}$$

$\therefore$ Molarity = 0.0641 M

(since molarity = molality for dilute solution)

$$AB\rightarrow A^{3+}+3B^-$$

$\therefore K_{sp}$ of $AB_3=27\times S^4=27\times(0.0641)^4=4.56\times10^{-4}$

20. (a)

	KI	+ $AgNO_3$	$\longrightarrow KNO_3$	+ AgI
millimole	30×0.1	10×0.2		
	3	2	0	0
mm left	1	0	2	2

$\therefore$ [KI] in solution $=\frac{1}{40}$ and $[KNO_3]=\frac{2}{40}$

(molarity = molality)

$\therefore$ $\Delta T_f=\Delta T_f$ (by KI) + ΔT_f by (KNO_3)

$=$ molality $\times 1.86\times(1+\alpha_1)+$ molality $\times 1.86\times(1+\alpha_2)$

$$=\frac{1}{40}\times1.86\times2+\frac{2}{40}\times1.86\times2$$

$$=0.093+0.186=0.279$$

21. (d) $C_1=C_2$ is valid only when solute neither dissociates nor associates.

22. (d) $Na_2B_4O_7\longrightarrow 2Na^+ + B_4O_7^{2-}$

$i=3$; $\qquad w=\frac{38.2}{202+18n}$

$$\therefore\ \Delta T_b=\frac{1000\times K_f\times w}{m\times w}\cdot i$$

w = mass of water from borax + mass of water

$$w=\frac{38.2\times18n}{202+18n}+250$$

$$0.582=\frac{1000\times0.52\times38.2\times3}{(250+18n)\times\left[\frac{38.2\times18n}{202+18n}+250\right]}$$

$\therefore\quad n=10$

23. (b) Initial mole fraction of water in urea $=\frac{\frac{90}{18}}{\frac{10}{60}+\frac{90}{18}}=0.96$

(mass of water = mass of solution − mass of solute)

Initial mole fraction of water in glucose

$$=\frac{\frac{180}{18}}{\frac{20}{180}+\frac{180}{18}}=0.98$$

$\therefore$ $P_s\propto$ mole fraction of solvent

$\therefore$ V.P. of glucose > V.P. of urea;

Thus to attain equilibrium some mole of water will flow from glucose solution to urea solution. At eq. both solution have same mole fraction of solvent.

For urea	For glucose

$$\frac{\frac{90}{18}+X}{\frac{10}{60}+\frac{90}{18}+X}=\frac{\frac{180}{18}-X}{\frac{20}{180}+\frac{180}{18}-X}$$

$\therefore$ $X=4$ mole $=72\,\text{g}\ H_2O$

$\therefore$ New mass of water in urea = 90 + 72 = 162 g

$\therefore$ % of urea $=\frac{10}{162}\times100=6.17$

24. (b) $P_s\propto$ mole fraction of solvent

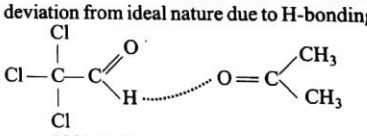
$$10\propto 0.8$$

$$6\propto a\quad\therefore\quad a=0.48$$

$\therefore$ mole fraction of solute = 0.52

25. (b) Due to 60% dimerisation the molar mass of benzoic acid > molar mass 122 g mol^{-1} and < 244 g mol^{-1}.

26. (a) Chloroform and acetone mixture show negative deviation from ideal nature due to H-bonding



27. (a) $0.5=\frac{1000\times20\times w}{m\times W}$

$$\therefore\ \frac{w}{m}=\frac{0.5\,W}{20\times1000}=2.5\times10^{-5}W$$

Let 1000g of cyclohexane contains $\frac{w}{m}$ mole of impurity

Mole of W g of cyclohexane $=\frac{W}{84}=1190\times10^{-5}W$

Mole of pure cyclohexane

$$=(1190\times10^{-5}-2.5\times10^{-5})W$$

$$=1187\times10^{-5}W$$

$\therefore$ % purity $=\frac{1187\times10^{-5}}{1190\times10^{-5}}\times100=99.8$

28. (d) $\pi=CRT=\frac{w}{V}\frac{RT}{m}$

$\pi=C$ (in g / mL) $\frac{RT}{m}$

$\therefore$ slope $=\frac{RT}{m}=4.65\times10^{-3}\times10^{-3}$ (in g / L)

$\therefore$ $m=\frac{0.0821\times300}{4.65\times10^{-6}}=5.3\times10^6$ g mol^{-1}

29. (d) During osmosis only solvent particles migrate from $K_2Cr_2O_7$ (dil.) to $CuSO_4$ (conc.) side.

30. (a) At boiling point $P_M = 748\text{ mm} = P'_{H_2O} + P'_l$

$\because\ P'_{H_2O} = 648\text{ mm} \quad \therefore\ P'_l = 100\text{ mm}$

Now $P'_{H_2O} = P_m \times \text{m.f. of } H_2O_V$

$$P'_l = P_m \times \text{m.f. of liq}_V$$

$$\therefore \frac{P'_{H_2O}}{P'_l} = \frac{\text{mole of } H_2O_V}{\text{mole of liq.v}} = \frac{w \times M}{m \times W} = \frac{1 \times M}{1.25 \times 18} = \frac{648}{100}$$

$\therefore\ M = 145.8\text{ g mol}^{-1}$

31. (c) $P^0_A X_A = P_T \cdot Y_A$

$$\therefore \frac{X_A}{Y_A} = \frac{P_T}{P^o_A} < 1 \qquad (\because P_T < P^0_A)$$

$X_A < Y_A$

32. (d) $P_M = P'_A + P'_B$

$P_M = P^0_A \cdot X_A + P^0_B \cdot X_B$

$= P^0_A \cdot X_A + P^0_B(1 - X_A) = (P^0_A - P^0_B) \cdot X_A + P^0_B$

$= P^0_A\ (1 - X_B) + P^0_B \cdot X_B = (P^0_B - P^0_A) X_B + P^0_A$

33. (b) $P_M = P^0_A \cdot X_A + P^0_B \cdot X_B$

Also, $P'_A = P^0_A \cdot X_A = P_M \cdot X'_A$

$P'_B = P^0_B \cdot X_B = P_M \cdot X'_B$

where X'_A and X'_B are mole fraction of A and B in vapour phase.

$$\therefore \frac{P'_A}{P'_B} = \frac{P^0_A \cdot X_A}{P^0_B \cdot X_B} = \frac{X'_A}{X'_B}$$

or $\frac{1}{3} \times \frac{X_A}{X_B} = \frac{4}{3}$

$$\therefore \frac{X_A}{X_B} = 4$$

34. (d) Azeotropic mixture remains unchanged in their composition at their b.pt.

35. (b) $\frac{P^0 - P_s}{P_s} = \frac{n}{N} \times i = \frac{5n}{15}$

(1 mole of Th $(NO_3)_4$ gives 5 mole)

$$\frac{100 - 60}{60} = \frac{5n}{15}$$

$$\therefore \quad n = 2$$

36. (b) $\Delta H_V = \frac{M_{C_7H_8} \times R \times T^0_{C_7H_8}}{1000 \times K}$

$$= \frac{92 \times 8.314 \times (383.7)^2}{1000 \times 3.32} = 33.92\text{ kJ ml}^{-1}$$

Now, $\Delta s = \frac{\Delta H_V}{T_b} = \frac{33.92 \times 11^3}{383.2} = 88.5\text{ JK}^{-1}\text{mol}^{-1}$

37. (b) $\pi = CRT \times i$

$$i = \frac{73.89}{1 \times 0.0821 \times 300} = 3$$

Thus, $[Cr(H_2O)_5Cl]Cl_2.H_2O \longrightarrow [Cr(H_2O)_5.Cl]_{aq.} + 2Cl^-_{aq.}$

or, 1 mole (mole $= M \times V_{\text{in L}}$) of complex will give 2 mol of Cl^-

2 mole of Cl^- will give 2 mole of AgCl

38. (b) $P_T = P^0_A \cdot X_A + P^0_A \cdot X_B$

$$= 100 \times \frac{1}{5} + 200 \times \frac{4}{5} = 180$$

Now, $X'_{A\,(V.P)} = \frac{P^0_A \cdot X_A}{P_T} = \frac{100 \times 1}{180 \times 5} = \frac{1}{9}$

$$\therefore \quad X'_B = \frac{8}{9}$$

$$\therefore P_T = 100 \times \frac{1}{9} + 200 \times \frac{8}{9} = \frac{1700}{9} = 188.8\text{ torr}$$

39. (b)

	$AgNO_3$	+ KI	$\longrightarrow$ AgI↓	+ KNO_3
mm	$0.2 \times V$	$0.1 \times 3V$	0	0
	0	$0.1V$	$0.2V$	$0.2V$

Two solution contains $0.1V$ milli mole of KI and $0.2V$ m mole of KNO_3

$$[KI] = \frac{0.1V}{4V} = \frac{0.1}{3};\quad [KNO_3] = \frac{0.2V}{4} = \frac{0.2}{4}$$

$\pi = (C_1 + C_2)\,RT \times i$ (i = for KNO_3 and KI both)

$$= \left(\frac{0.1}{4} + \frac{0.2}{4}\right) \times 0.0821 \times 300 \times 2$$

$= 3.69$ atm

40. (b) $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$ is Clausius – Clapeyron equation

41. (c) Lower b. pt means higher vapour pressure of mixture *i.e.*, positive deviation from Raoult's law.

42. (b) $\frac{P^0 - P_S}{P^0} = \frac{n}{n + N}$

43. (a) $2KI_{aq} \rightarrow 2K^+ + 2I^-$ (four particles)

$2KI + HgI_2 \rightarrow K_2HgI_4 \rightarrow 2K^+ + [HgI_4]^{2-}$

(insoluble in water) (three particles)

44. (a) 1 molecule of K_2SO_4 furnishes three ions and thus ΔT_f will be more or T_f will be low.

45. (d) Lower is the number of particles furnished in solution lower will be ΔT_f or higher will be T_f. Glucose does not ionise.

46. (a) $\Delta T_f = K_f \times \text{molality} \times (1 + \alpha)$

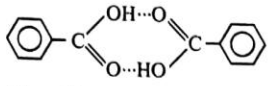
$$\underset{1-\alpha}{HA} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{A^-}$$

$\Delta T_f = 1.86 \times 0.2 \times 1.2$ ($\alpha = 0.2$)

$\Delta T_f = 0.45$

$\therefore\ T_f = -0.45°\text{ C}$

47. (b) Benzoic acid forms dimer in benzene.



48. (b) $P'_{H_2O} = P_M \times X_{H_2O}$

$P'_{AB} = P_M \times X_{AB}$

$$\therefore \quad \frac{P'_{H_2O}}{P'_{AB}} = \frac{n_{H_2O}}{n_{AB}} = \frac{w_{H_2O} \times m_{AB}}{m_{H_2O} \times w_{AB}}$$

$$\frac{5}{1} = \frac{w_{H_2O} \times 137}{w_{AB} \times 18}$$

$$\text{or } \frac{w_{H_2O}}{w_{AB}} = \frac{5 \times 18}{1 \times 137} = \frac{90}{137} = 0.657 : 1$$

49. (b) $\pi = \frac{CRT}{V} = \frac{wRT}{mV_{\text{in L}}}$

$$= \frac{w \times RT \times 1000}{m \times V_{\text{in mL}}}$$

$$\pi = \frac{1000RT}{m} \times C_{g/cm^3}$$

$$\therefore \text{ slope} = \frac{1000RT}{m} = 2 \times 10^{-3}$$

$$\therefore \quad m = \frac{1000 \times 0.0821 \times 300}{2 \times 10^{-3}} = 1.23 \times 10^7 \text{ g mol}^{-1}$$

50. (a) $\pi \propto i$ *i.e.*, van't Hoff factor.

51. (c) $\frac{P^\circ - P_S}{P_S} = \frac{w \times M}{m \times W}$

$$\frac{P^\circ - \frac{4P^\circ}{5}}{\frac{4P^\circ}{5}} = \frac{w \times 18}{60 \times 180}$$

$$\therefore w = 150 \text{ g}$$

52. (a) $\underset{1-\alpha}{4P} \longrightarrow \underset{\frac{\alpha}{4}}{P_4}$

$$\therefore i = 1 - \alpha + \frac{\alpha}{4} = \frac{4 - 3\alpha}{4}$$

Now $\Delta T_f = K_f \times \text{molality} \times i$

$$= K_f \times m \times \frac{(4 - 3\alpha)}{4}$$

$$\therefore \quad \frac{4 - 3\alpha}{4} = \frac{\Delta T_f}{K_f \times m}$$

$$4 - 3\alpha = \frac{4\Delta T_f}{K_f \times m}$$

$$\therefore \quad \alpha = \frac{4 - \frac{4\Delta T_f}{K_f \times m}}{3} = \frac{4K_f \times m - 4\Delta T_f}{3K_f \times m}$$

$$= \frac{4[m \times K_f - \Delta T_f]}{3K_f \times m}$$

53. (a) Only liquid freezes at freezing point. Thus equilibrium between solid and liquid forms of solvent exist at freezing point.

54. (c) $\pi_{Na_2SO_4} = \pi_{\text{Glucose}}$

$$CRT\,(1 + 2\alpha) = CRT$$

$$0.004\,(1 + 2\alpha) = 0.01$$

$$\therefore \quad \alpha = 0.75 \text{ or } = 75\%$$

55. (a) $\Delta T_b = K_b \times \text{molality}\,(1 + 2\alpha)$

$$\underset{1-\alpha}{CuCl_2} \rightleftharpoons \underset{\alpha}{Cu^{2+}} + \underset{2\alpha}{2Cl^-} \qquad (\because \alpha = 1)$$

$$= 0.52 \times \frac{13.44}{134.4 \times 1} \times (1 + 2)$$

$$\Delta T_b = 0.156 \simeq 0.16$$

56. (a) $\Delta T_f = K_f \times \text{molality} \times i$

$$\therefore \quad i = \frac{2 \times 172 \times 50}{1.72 \times 20 \times 1000} = 0.5$$

57. (a) $P' = P_T\, X_{N_2}$ (From Dalton's law)

$$\therefore \quad P'_{N_2} = 5 \times 0.8 = 4.0 \text{ atm}$$

From Henry's law $P_{N_2} = K_H \cdot X_{N_2}$ dissolved

$$\therefore \quad X_{N_2} = \frac{4}{1 \times 10^5} = 4 \times 10^{-5}$$

$$\text{or } \frac{n_{N_2}}{n_{N_2} + N_{H_2O}} = \frac{n_{N_2}}{n_{N_2} + 10} = 4 \times 10^{-5}$$

$$\therefore \quad n_{N_2} = 4 \times 10^{-5} \times 10 = 4 \times 10^{-4}$$

58. (a) $K_3[Fe(CN)_6] \longrightarrow 3K^+ + Fe(CN)_6^{3-}$

Before dissociation	1	0	0
After dissociation	0	3	1

Total no. of particles furnished by

$K_3[Fe(CN)_6] = n = 4$

$\therefore$ van't Hoff factor, $i = 4$

Now $\Delta T_f = \frac{1000 \times K_f \times w}{m \times W} \times i$

$$= \frac{1000 \times 1.86 \times 0.1 \times 4}{329 \times 100}$$

$$= 2.3 \times 10^{-2} {}^\circ\text{C}$$

$$\therefore \quad T'_f = 0 - 2.3 \times 10^{-2}$$

$$= -2.3 \times 10^{-2} {}^\circ\text{C}$$

59. (a) $w_{\text{solute}} = 2.5\text{g}, W_{\text{solvent}} = 100\text{g}$

$\Delta T_b = 2^\circ$

$$\therefore \quad \Delta T_b = \frac{1000 \times K_b \times w}{W \times m}$$

$$\text{or } 2 = \frac{1000 \times 0.76 \times 2.5}{100 \times m}$$

$$\therefore \quad m = 9.5$$

Now, $\frac{P^0 - P_s}{P^0} = \frac{w \times m}{m \times W}$ (Given dilute solution)

$$\frac{760 - P_s}{760} = \frac{2.5 \times 18}{9.5 \times 100} = 0.047$$

$$\therefore \quad P_s = 724 \text{ mm}$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Two miscible liquids A and B having vapour pressure in pure state P_A° and P_B° are mixed in mole fraction X_A and X_B to get a mixture having total vapour pressure of mixture P_M. Which of the following relations are correct?
   (a) $X_A = \dfrac{P_M - P_B^\circ}{P_A^\circ - P_B^\circ}$ (b) $\dfrac{X_{A(l)}}{X'_{A(V)}} = \dfrac{P_M}{P_A^\circ}$
   (c) $\dfrac{X_{A(l)}}{X'_{A(V)}} = \dfrac{P_M}{P_B^\circ}$ (d) all of these
2. A mixture of two immiscible liquids A and B, having vapour pressure in pure state obey's the following relationships if X_A and X_B are mole fractions of A and B in vapour phase over the solution :
   (a) $P'_A = P_M \cdot X'_A$
   (b) $\dfrac{P'_A}{P'_B} = \dfrac{w_A \times m_B}{m_A \times w_B}$
   (c) if $P'_A > P'_B$ then $X'_A < X'_B$
   (d) if $P'_A > P'_B$ then $n_A > n_B$
3. Which relations are correct for an aqueous dilute solution of K_3PO_4 if its degree of dissociation is α?
   (a) $\dfrac{\Delta P}{P^\circ} = \dfrac{\text{molality} \times 18 \times (1+3\alpha)}{1000}$
   (b) $\dfrac{\Delta P}{P^\circ} = \dfrac{\pi_{obs.} \times 18 \times (1+3\alpha)}{ST \times 1000}$
   (c) $\dfrac{\Delta P}{P^\circ} = \dfrac{\Delta T_{f\,obs.} \times 18}{K_f \times 1000}$
   (d) Molar mass of K_3PO_4 = Molar mass$_{obs.} \times (1+3\alpha)$
4. 1.2575 g sample of $[Cr(NH_3)SO_4 \cdot Cl]$ (molar mass 251.5 g mol^{-1}) is dissolved to prepare 250 mL solution showing an osmotic pressure of 1.478 atm of Hg at 27°C. Which are correct about this solution ?
   (a) Each molecule furnishes three ions in solution
   (b) The van't Hoff factor is = 3
   (c) Equilibrium molarity of $[Cr(NH_3)_6SO_4Cl] = 0$
   (d) Equilibrium molarity of $[Cr(NH_3)_6^+]^{3+} = 0.02\ M$
5. 2 litre of 1 molar solution of a complex salt $CrCl_3 \cdot 6H_2O$ (molar mass 266.5 g mol^{-1}) shows an osmotic pressure of 98.52 atm. The solution is now treated with 1 litre of 6 M $AgNO_3$, which of the following are correct?
   (a) Mass of AgCl precipitated is 861 g
   (b) The clear solution will show an osmotic pressure = 98.52 atm
   (c) The clear solution will show an osmotic pressure = 65.68 atm
   (d) 2 mole of $[Cr(H_2O)_6](NO_3)_3$ will be present in solution
6. In the depression of freezing point experiment, it is found that the :
   (a) vapour pressure of the solution is less than that of pure solvent
   (b) vapour pressure of the solution is more than that of pure solvent
   (c) only solute molecules solidify at the freezing point
   (d) only solvent molecules solidify at the freezing point
7. To 10 mL of 0.5 M $BaCl_2$ solution, 5mL of 0.5M K_2SO_4 is added. $BaSO_4$ precipitates with. What will happen with respect to original solution of $BaCl_2$?
   (a) f.pt will decrease (b) f.pt will increase
   (c) b.pt will increase (d) b.pt will decrease
8. Salinity of water can be removed by :
   (a) Desalination (b) Boiling
   (c) Osmosis (d) Reverse osmosis
9. The vapour pressure of a solution depends upon :
   (a) Surface area
   (b) Temperature
   (c) Mole fraction of solvent
   (d) Degree of dissociation of solute
10. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are): **[JEE (Advanced) II 2013]**
    (a) ΔG is positive (b) ΔS_{system} is positive
    (c) $\Delta S_{surroundings} = 0$ (d) $\Delta H = 0$

SOLUTIONS (More Than One Answer Correct)

1. (a,b) $P_M = P_A^\circ \cdot X_A + P_B^\circ \cdot X_B$;

Also, $P' = P_M \cdot X_{A(V)} = P_A^\circ \cdot X_{A(l)}$

$= P_A^\circ \cdot X_A + P_B^\circ (1 - X_A)$

$\therefore \quad X_A = \dfrac{P_M - P_B^\circ}{P_A^\circ - P_B^\circ}$

2. (a,b,d) For immiscible liquids

$P_A' = P_M \cdot X_A'$

$P_B' = P_M \cdot X_B'$

$\therefore \quad \dfrac{P_A'}{P_B'} = \dfrac{X_A'}{X_B'} = \dfrac{n_A}{n_B} = \dfrac{w_A \times m_B}{m_A \times w_B}$,

if $P_A' > P_B'$ then $n_A > n_B$

3. (a,c,d) $\dfrac{\Delta P}{P^\circ} = \dfrac{n}{N} = \dfrac{n \times M \times 1000}{W \times 1000} = \dfrac{\text{molality} \times M}{1000}$

For electrolyte $\dfrac{\Delta P}{P^\circ} = \dfrac{\text{molality} \times M}{1000} \times (1 + 3\alpha)$

($M = 18$ for H_2O)

Also, $\pi_{\text{obse.}} = C \times S \times T\,(1 + 3\alpha)$

$\therefore \quad \dfrac{\Delta P}{P^\circ} = \dfrac{\pi_{\text{obse.}}}{ST} \times \dfrac{18}{1000}$

$\Delta T_{f\,\text{obse.}} = K_f \times \text{molality} \times (1 + 3\alpha)$

$\dfrac{\Delta P}{P^\circ} = \dfrac{\Delta T_{f\,\text{obse.}} \times 18}{K_f \times 100}$

$i = (1 + 3\alpha) = \dfrac{\text{Cal. Molar mass}}{\text{Obser. Molar mass}}$

$\therefore$ Molar mass of $K_3PO_4 = M_{\text{obse.}} \times (1 + 3\alpha)$

4. (a,b,c,d) Molarity $= \dfrac{1.2575 \times 1000}{251.5 \times 250} = 0.02M$, $\pi = CST$

$\therefore \quad \pi_{\text{obse.}} = 0.02 \times 0.0821 \times 300 = 0.4926\,\text{atm}$

$= 374.38\,\text{mm}.$

$\dfrac{\pi_{\text{obse.}}}{\pi_{\text{cal.}}} = i = \dfrac{1478 \times 760}{374.38} = 3$

$\because \quad \alpha = \dfrac{i-1}{n-1}$ and $\alpha = 1, \quad \therefore \quad n = 3$

Also,

$$\underset{\text{Eq. conc.}}{\underset{0}{[Cr(NH_3)_6]}\underset{0.02}{SO_4} \cdot Cl} \rightleftharpoons \underset{0.02}{[Cr(NH_3)_6^{3+}]} + \underset{0.02}{SO_4^{-2}} + \underset{0.02}{Cl^-}$$

5. (a,c,d) $CrCl_3 \cdot 6H_2O$

$\pi = CST\,(1 - \alpha + x\alpha + y\alpha)$

$98.52 = 1 \times 0.0821 \times 300 \times (x + y)\,(\alpha = 1)$

$\therefore (x + y) = 4$

$\therefore$ $CrCl_3 \cdot 6H_2O$ can be written as :

$$\underset{1-\alpha}{[Cr(H_2O)_6]Cl_3} \rightleftharpoons \underset{\alpha}{[Cr(H_2O)_6]^{3+}} + \underset{3\alpha}{3Cl^{-1}}$$

3 mole of $AgNO_3$ will react 1 mole of $Cr(H_2O)_6Cl_3$

$$\underset{\text{mole}}{\underset{2\times1=2}{\underset{0}{Cr(H_2O)_6Cl_3}}} + \underset{1\times6=6}{\underset{0}{3AgNO_3}} \longrightarrow \underset{2}{\underset{0}{[Cr(H_2O)_6](NO_3)_3}} + \underset{6}{\underset{0}{3AgCl}}$$

$\therefore$ Mole of AgCl formed = 6;

Mass of AgCl formed = $6 \times 143.5 = 861\,\text{g}$

$[Cr(H_2O)_6](NO_3)_3 = \dfrac{2}{3}$

$\therefore \quad \pi = CST \times (1 + 3\alpha) = \dfrac{2}{3} \times 0.0821 \times 300 \times 4 = 65.68\,\text{atm}$

6. (a,d) Addition of solute to a solvent lowers the f.pt.

7. (b, d) $\underset{2.5}{\underset{5}{BaCl_2}} + \underset{0}{\underset{2.5}{K_2SO_4}} \longrightarrow \underset{2.5}{\underset{0}{BaSO_4}} + \underset{5.0}{\underset{0}{2KCl}}$

$\Delta T = \dfrac{1000K \times n \times i}{W}$

initially for $BaCl_2$: $\dfrac{n \times i}{W} = \dfrac{0.5 \times 3}{1000} = 1.5 \times 10^{-3}$

Finally for mixture : $\dfrac{n \times i}{W} = \underset{(\text{For } BaCl_2)}{\dfrac{2.5 \times 10^{-3} \times 3}{15}} + \underset{(\text{For KCl})}{\dfrac{5 \times 10^{-3} \times 2}{15}}$

$= \dfrac{17.5 \times 10^{-3}}{15} = 1.16 \times 10^{-3}$

Thus $\dfrac{n \times i}{W}$ decreases on mixing, therefore ΔT_b and ΔT_f of mixture are lowered. Thus T_b decreases and T_f increases.

8. (a, d) Follow text.

9. (b, c, d) $P_S \propto \dfrac{N}{n+N}$

and $\dfrac{P^\circ - P_S}{P_S} = \dfrac{n}{(n+N)} \times i$

10. (b,c,d)

For ideal solution

$\Delta H_{\text{mixing}} = 0$

$\Delta S_{\text{mixing}} = +\text{ve}$

$\therefore \Delta G_{\text{mixing}} = -\text{ve}$

$\Delta S_{\text{surrounding}} = 0$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Mixing of two liquids may or may not bring in ideal solution nature, (*i.e.*, $\Delta H_{mixing} = 0$; $\Delta V_{mixing} = 0$) and the solution obeys Raoult's law or not. If either of the liquid disturbs the forces of attractions among the molecules, ideal nature disappeares, Benzene and toluene mixture however provides ideal solution. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C are given by $P = 179X_B + 92$, where X_B is mole fraction of C_6H_6.

[1] Vapour pressure of pure liquids in mm are :
(a) $P_{C_6H_6} = 271$, $P_{C_7H_8} = 92$
(b) $P_{C_6H_6} = 92$, $P_{C_7H_8} = 271$
(c) $P_{C_6H_6} = 179$, $P_{C_7H_8} = 92$
(d) $P_{C_6H_6} = 92$, $P_{C_7H_8} = 179$

[2] Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 and 736 g toluene.
(a) 200 (b) 201.4
(c) 199.4 (d) 198.4

[3] If the vapours are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in vapour state?
(a) 0.072 (b) 0.064
(c) 0.928 (d) 0.936

Comprehension 2 : A solution containing 0.1 mole of naphthalene and 0.9 mole of benzene is cooled out until some benzene freezes out. The solution is then decanted off from the solid and warmed upto 353 K where its vapour pressure was found to be 670 torr. The freezing point and boiling point of benzene are 278.5 K and 353 K respectively and its enthalpy of fusion is 10.67 kJ mol^{-1}.

[1] The temperature to which the solution was cooled originally:
(a) 279.39°C (b) 278.39°C
(c) 8.11°C (d) 270.39 K

[2] The amount of benzene that must have frozen out. Assume ideal behaviour:
(a) 70.2 (b) 58.06
(c) 12.14 (d) 48.06

[3] The mass of benzene present after cooling the original solution at –2.61°C is:
(a) 58.06 (b) 12.14
(c) 70.2 (d) 48.06

Comprehension 3 : Addition of non-volatile solute to a solvent always increases the colligative properties such as osmotic pressure, ΔP, ΔT_b and ΔT_f. All these colligative properties are directly proportional to molality if solutions are dilute. The decrease in colligative properties on addition of non-volatile solute is due to increase in number of particles.

[1] For different aqueous solutions of 0.1 *N* urea, 0.1 *N* NaCl, 0.1 *N* Na_2SO_4 and 0.1 *N* Na_3PO_4 solution at 27°C the correct statements are :
1. The order of osmotic pressure is NaCl > Na_2SO_4 > Na_3PO_4 > urea
2. $\pi = \frac{\Delta T_b}{K_b} \times ST$ for urea solution
3. Addition of salt on ice increases its melting point
4. Addition of salt on ice brings in melting of ice earlier

(a) 2, 3, 4 (b) 1, 2, 4
(c) 1, 2, 3 (d) 3, 4

[2] 1 g mixture of glucose and urea present in 250 mL aqueous solution shows the osmotic pressure of 0.74 atm at 27°C. Assuming solution to be dilute, which are correct?
1. Percentage of urea in mixture is 17.6
2. Relative lowering in vapour pressure of this solution is 5.41×10^{-4}
3. The solution will boil at 100.015, if K_b of water is 0.5 K molality^{-1}
4. If glucose is replaced by same mass of sucrose, the solution will show higher osmotic pressure at 27°C
5. If glucose is replaced by same mass of NaCl, the solution will show lower osmotic pressure at 27°C

(a) 1, 2, 3 (b) 1, 2, 3, 5
(c) 2, 4, 5 (d) 1, 4, 5

Comprehension 4 : Addition of a non-volatile solute to a solvent lowers its vapour pressure. Therefore, the vapour pressure of a solution (*i.e.*, V.P. of solvent in a solution) is lower than that of pure solvent, at the same temperature. A higher temperature is needed to raise the vapour pressure upto one atmosphere pressure, when boiling point is attained. However increase in b.p. is small. For example 0.1 molal aqueous sucrose solution boils at 100.05°C.

Sea water, an aqueous solution, which is rich in Na^+ and Cl^- ions, freezes about 1°C lower than frozen water. At the freezing point of a pure solvent, the rates at which two molecules stick together to form the solid and leave it to return to liquid state are equal when solute is present. Fewer solvent molecules are in contact with surface of solid. However, the rate at which the solvent molecules leave the surface of solid remains unchanged. That is why temperature is lowered to restore the equilibrium. The freezing point depression in a dilute solution is proportional to molality of the solute.

[1] An aqueous solution of 0.1 molal concentration of sucrose should have freezing point of ($K_f = 1.86$ K molality^{-1}) :
(a) + 0.186°C (b) 1.86°C
(c) – 1.86°C (d) – 0.186°C

[2] When 250 mg of eugenol is added to 100 g of camphor ($K_f = 39.7$ K molality^{-1}), it lowered the freezing point by 0.62°C. The molar mass of equenol is :

(a) 1.6×10^2 g/mol (b) 1.6×10^4 g/mol
(c) 1.6×10^3 g/mol (d) 200 g/mol

[3] The freezing point of a 5% by mass $CH_3COOH(aq)$ solution is –1.576°C. The van't Hoff factor is:
(K_f of water = 1.86 Km^{-1})
(a) 0.996 (b) 2
(c) 0.5 (d) 1.016

[4] The freezing point of benzene solution was 5.4°C. The osmotic pressure of same solution at 10°C is (boiling point of benzene = 5.5°C). Assume solution to be dilute. [K_f for C_6H_6 is 4.9 K molality^{-1}]
(a) 0.274 atm (b) 0.474 atm
(c) 0.674 atm (d) 0.874 atm

[5] The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g water is found to be –34°C. Assuming dilute solution, the density of solution is :
[K_f for H_2O = 1.86 K molality^{-1}]
(a) 1.133 g/cm^3 (b) 2.133 g/cm^3
(c) 0.133 g/cm^3 (d) 1.62 g/cm^3

[6] The amount of ice separated out on cooling a solution containing 50 g ethylene glycol in 200 g water to –9.3°C is : [K_f for H_2O = 1.86 K molality^{-1}]
(a) 38.71 g (b) 61.29 g
(c) 138.71 g (d) 161.29 g

[7] 2 g of benzoic acid dissolved in 25 g of C_6H_6 shows a depression in f.pt. equal to 1.62 K. K_f for C_6H_6 is 4.9 K molality^{-1}. The percentage association of acid, if it forms double molecules in solution is :
(a) 0.8% (b) 99.2%
(c) 90.2% (d) 9.8%

Comprehension 5 : Colligative properties of a solution depends upon number of ions furnished by the solute in solution measured in terms of van't Hoff factor *i*.

$$i=\frac{\text{Exp. colligative property}}{\text{Cal. colligative property}}$$

The van't Hoff factor '*i*' is $1-\alpha+x\alpha+y\alpha$ for solutes showing dissociation where $(x+y)$ is the number of particles furnished by 1 mole of solute on 100% ionisation. Also van't Hoff coefficient $(g)=\frac{i}{(x+y)}$ ...(i)

For associated solute $i=1-\alpha+\frac{\alpha}{n}$; where '*n*' is association number ...(ii)

The term osmomolarity is expressed as :
osmomolarity = g × no. of particle furnished by 1 molecule on complete dissociation ×molarity ...(iii)
or osmomolality = g × no. of particle furnished by 1 molecule on complete dissociation ×molality ...(iv)

[1] Osmomolarity of 0.2 *M* K_2SO_4 is :
(a) 0.3 (b) 0.4
(c) 0.5 (d) 0.6

[2] Osmomolality of 0.2 *m* benzoic acid in benzene, assuming 100% association is :
(a) 0.4 m (b) 0.1 m
(c) 0.05 m (d) 0.3 m

[3] Osmomolarity of KCl solution in water is 0.2 *M*. What will be its osmotic pressure at 300 K.
(a) 60 *R* (b) 30 *R*
(c) 40 *R* (d) 50 *R*

Comprehension 6 : A solution *M* is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9. Given :

Freezing point depression constant of water (K_f^{water}) = 1.86 K kg mol^{-1}	Standard boiling point of water = 373 K
Freezing point depression constant of ethanol ($K_f^{ethanol}$) = 2.0 K kg mol^{-1}	Standard boiling point of ethanol = 351.5 K
Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol^{-1}	Vapour pressure of pure water = 32.8 mm Hg
Boiling point elevation constant of ethanol ($K_b^{ethanol}$) = 1.2 K Kg mol^{-1}	Vapour pressure of pure ethanol = 40 mm Hg
Standard freezing point of water = 273 K	Molar mass of water = 18 g mol^{-1}
Standard freezing point of ethanol = 155.7 K	Molar mass of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(IIT 2008)**

[1] The freezing point of the solution *M* is :
(a) 268.7 K (b) 268.5 K
(c) 234.2 K (d) 150.9 K

[2] The vapour pressure of the solution *M* is :
(a) 39.3 mmHg (b) 36.0 mmHg
(c) 29.5 mmHg (d) 28.8 mmHg

[3] Water is added to the solution *M* such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is :
(a) 380.4 K (b) 376.2 K
(c) 375.5 K (d) 354.7 K

SOLUTIONS

Comprehension 1

[1] (a) Given, $P = 179X_B + 92$

For pure C_6H_6, $X_B = 1$

$\therefore$ $P_B^\circ = 179 + 92 = \mathbf{271\ mm}$

For pure C_7H_8, $X_B = 0$

$\therefore$ $P_T^\circ = 179 \times 0 + 92 = \mathbf{92\ mm}$

[2] (c) Now,

$$P_M = P_B^\circ \cdot X_B + P_T^\circ \cdot X_T$$

$$= 271 \times \frac{12}{12+8} + 92 \times \frac{8}{12+8}$$

$$= 162.6 + 36.8$$

$$= \mathbf{199.4\ mm}$$

Mole of C_6H_6 $= \frac{936}{78} = 12$

Mole of C_7H_8 $= \frac{736}{92} = 8$

[3] (c) Now mole fraction of C_6H_6 in vapour phase of initial mixture (X_B')

$$X_B' = \frac{P_B'}{P_M} = \frac{162.6}{199.4} = \mathbf{0.815}$$

Mole fraction of C_7H_8 in vapour phase of initial mixture (X_T')

$$X_T' = \frac{P_T'}{P_M} = \frac{36.8}{199.4} = \mathbf{0.185}$$

These fractions are taken out and condensed into liquid. The liquid is again brought to 50° C to get again vapour-liquid equilibrium.

Thus, mole fraction of C_6H_6 in vapour phase of initial mixture

= Mole fraction of C_6H_6 in liquid phase of II mixture X_B'

Similarly, mole fraction of C_7H_8 in vapour phase of initial mixture

= Mole fraction of C_7H_8 in liquid phase of II mixture X_T'

New $P_M = P_B' + P_T'$

Therefore, new $P_M = P_B^\circ \cdot X_B' + P_T^\circ \cdot X_T'$

$= 271 \times 0.815 + 92 \times 0.185$

$= 220.865 + 17.02 = 237.885$ mm

$\therefore$ New mole fraction of C_6H_6 in vapour phase

$$= \frac{\text{New } P_B'}{\text{New } P_M} = \frac{220.865}{237.885} = \mathbf{0.928}$$

Comprehension 2

$P^\circ = 760$ mm at boiling point of benzene (353 K)

$$\therefore \quad \frac{760-670}{670} = \frac{W_N \times M_B}{M_N \times W_B} = \frac{0.1 \times 78}{W_B}$$

$$\left(\text{or } N = \frac{W_N}{M_N} = 0.1\right)$$

$\therefore$ $W_B = \mathbf{58.06\ g}$

Also in original solution $W_B = 0.9 \times 78 = 70.2$ g

$\therefore$ C_6H_6 frozen out $= 70.2 - 58.06 = \mathbf{12.14\ g}$

Now ΔT (for original solution)

$$= K_f \times \text{molality} = \frac{RT_0^2}{1000l} \times \text{molality}$$

$$= \frac{8.314 \times 278.5 \times 278.5}{1000 \times \frac{10.67 \times 10^3}{78}} \times \frac{1000 \times 0.1}{58.06}$$

$$= 8.11\ \text{K}$$

Thus, original solution must have been cooled to

$= 278.5 - 8.11 = \mathbf{270.39\ K} = -2.61°\ \text{C}$

[1] (d)

[2] (c)

[3] (a)

Comprehension 3

[1] (b) **1.** Molar concentrations are 0.1 M urea, 0.1 M NaCl, $\frac{0.1}{2} M$ Na_2SO_4 and $\frac{0.1}{3} M$ Na_3PO_4

$\therefore$ $\pi \propto CX(1-\alpha+X\alpha+Y\alpha) \propto C(X+Y)$, if $\alpha = 1$

$\therefore$ $\pi_{\text{urea}} \propto 0.1 \times 1$; $\pi_{\text{NaCl}} \propto 0.1 \times 2$;

$\pi_{Na_2SO_4} \propto \frac{0.1}{2} \times 3$; $\pi_{Na_3PO_4} \propto \frac{0.1}{3} \times 4$

2. Also $\pi = C_M \times S \times T$ and ΔT_b = Molality $\times K_b$

if Molarity = Molality (for dilute solution)

$$\pi = \frac{\Delta T_b}{K_b} \times S \times T$$

3. Addition of salt on ice lowers the freezing point.

4. Also addition of salt on ice lowers its melting point and thus, ice melts earlier.

[2] (a) **1.** Let a g glucose, b g urea be present in 1 g

$\therefore$ $a + b = 1$ ...(i)

Thus, $0.74 \times \frac{250}{1000} = \left[\frac{a}{180} + \frac{b}{60}\right] \times 0.0821 \times 300$ ...(ii)

By eqs. (i) and (ii), $b = 0.176$, $a = 0.824$

2. $$\frac{P^0 - P_S}{P^0} = \frac{w \times M \times 1000}{m + W \times 1000}$$

$\therefore$ $$\text{Molality} = \frac{P^0 - P_S}{P^0} \times \frac{1000}{M}$$

or $$\frac{\pi}{ST} = \frac{P^0 - P_S}{P^0} \times \frac{1000}{M}; \qquad (\because M = m)$$

$\therefore$ $$\frac{P^0 - P_S}{P^0} = \frac{0.74 \times 18}{0.0821 \times 300 \times 1000} = 5.41 \times 10^{-4}$$

3. $$\Delta T = \text{molality} \times K_b = \frac{\pi}{ST} \times K_b$$

$$= \frac{0.74}{0.0821 \times 300} \times 0.5 = 0.015$$

$\therefore$ b.pt. $= 100.015°$

4. On replacing glucose (Molar mass 180 g mol^{-1}) by sucrose (Molar mass 342 g mol^{-1}), π will decrease as

$$\pi \propto \frac{1}{\text{Molar mass}}$$

5. On replacing glucose (Molar mass 180 g mol^{-1}) by NaCl (Molar mass 58.5 g mol^{-1}), π will increase as

$$\pi \propto \frac{1}{\text{Molar mass}} \times 2 \text{ for NaCl}$$

Comprehension 4

[1] (d) $\Delta T_f = \dfrac{1000 \times K_f \times w}{m \times W} = K_f \times \text{molality}$

$= 1.86 \times 0.1 = 0.186$;

Thus, f.pt. $= 0 - 0.186°\,C = -0.186°\,C$

[2] (a) $m = \dfrac{1000 \times K_f \times w}{W \times \Delta T}$

$= \dfrac{1000 \times 39.7 \times 250 \times 10^{-3}}{100 \times 0.62} = 160\,\text{g/mol}$

[3] (d) $\Delta T_f = \dfrac{1000 \times K_f \times w}{m \times W} = \dfrac{1000 \times 1.86 \times 5}{60 \times 100} = 1.55$

$i = \dfrac{\Delta T_{f_{exp}}}{\Delta T_{f_{cal}}} = \dfrac{1.576}{1.55} = 1.016$

Acetic acid ionises in water and thus, $i > 1$

[4] (b) $\Delta T_f = 5.5 - 5.4 = 0.1°\,C$

$\pi = C_M ST$ (C_M = molarity)

$\Delta T_f = C_m \times K_f$ (C_m = molality)

For dilute solutions $C_M = C_m$

$\therefore \quad \pi = \dfrac{\Delta T_f}{K_f} \times ST = \dfrac{0.1}{4.9} \times 0.0821 \times 283 = 0.474$ atm

[5] (a) $\Delta T_f = \dfrac{1000 \times K_f \times w}{m \times W}$

$\therefore \quad 34 = \dfrac{1000 \times 1.86 \times 50 \times d}{62 \times 50}$

$\therefore \quad d = 1.133\ \text{g/cm}^3$

[6] (a) $\Delta T = \dfrac{1000 \times K_f \times w}{m \times W}$

$9.3 = \dfrac{1000 \times 1.86 \times 50}{62 \times W}$

$\therefore \quad W_{\text{water}} = 161.29$ g

$\therefore$ Ice separated $= 200 - 161.29 = 38.71$ g

[7] (b) $\Delta T = \dfrac{1000 \times K_f \times w}{m \times W} = \dfrac{1000 \times 4.9 \times 2}{122 \times 25} = 3.213$

$i = \dfrac{\Delta T_{exp}}{\Delta T_{cal}} = 1 - \alpha + \dfrac{\alpha}{n}$

$\therefore \quad \dfrac{1.62}{3.213} = 1 - \alpha + \dfrac{\alpha}{2}$

$\therefore \quad \alpha = 0.992$ or 99.2%

Comprehension 5

$$\text{Osmomolarity} = \frac{i}{(x+y)} \times (x+y) \times \text{molarity}$$

$$= i \times \text{molarity}$$

[1] (d) osmomolarity $= 3 \times 0.2 = 0.6M$

[2] (b) osmomolality $= i \times$ molality $= \dfrac{1}{2} \times 0.2 = 0.1\,m$

$$i = 1 - \alpha + \frac{\alpha}{2} = 1 - 1 + \frac{1}{2}$$

[3] (a) $\pi = c \times R \times T \times i$

$= c \times i \times RT$

$= 0.2 \times RT$

$= 0.2 \times 300 \times R = 60R$

Comprehension 6

[1] (d) $\Delta T_f = K_f \times \text{molality} = K_f \times \dfrac{n \times 1000}{W}$

$= \dfrac{K_f \times n \times 1000 \times M_{\text{ethanol}}}{W \times M_{\text{ethanol}}}$

$= \dfrac{K_f \times n_w \times 1000}{N_{\text{ethanol}} \times M_{\text{ethanol}}} = \dfrac{2.0 \times 0.1 \times 1000}{0.9 \times 46} = 4.83$

$\therefore \quad T_f = 155.7 - 4.83 = 150.86°\,C$

[2] (a) $P_m = P^{\circ}_{H_2O} \cdot X_{H_2O} + P^{\circ}_{\text{ethanol}} \cdot X_{\text{ethanol}}$

$= 32.8 \times 0.1 + 40 \times 0.9 = 39.28$ mm

[3] (b) $\Delta T_b = K_f \times \dfrac{n_{\text{ethanol}} \times 1000}{N_{\text{ethanol}} \times M_{H_2O}} = \dfrac{0.52 \times 0.1 \times 1000}{0.9 \times 18}$

$= 3.20$

$\therefore \quad T_b = 373 + 3.20 = 376.20°\,C$

Note : Non-volatile nature of solute should be assumed only for 1 and 3 otherwise the formula cannot be used. For problem 2, see that V.P. of ethanol is given.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanations **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) **S** is correct but **E** is wrong
(b) **S** is wrong but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. **S** : Evaporation and vapour pressure depends upon available surface area of solvent.
E : Larger is surface area of solvent for evaporation more is evaporation.

2. **S** : Formation of semipermeable membrane between the walls of porous pot on hanging pot filled with $CuSO_4(aq.)$ partially dipped in $K_4Fe(CN)_6$ is due to osmosis.
E : The ions moves through the walls of porous pot and between the walls Cu^{2+} and $Fe(CN)_6^{4-}$ gives insoluble gelatinous mass of $Ca_2[Fe(CN)_6]_4$.

3. **S** : Addition of HgI_2 to $KI(aq.)$ shows an increase in freezing point.
E : HgI_2 (insoluble) reacts with $KI(aq.)$ to form complex K_2HgI_4 and thus, number of particles present in solution decreases.

4. **S** : Osmosis is one sided movement of solvent particles.
E : In osmosis, the net movement of solvent particles from dil. to conc. solution and from conc. to dil. solution takes place through semipermeable membrane, showing finally the direction of dil. to conc.

5. **S** : van't Hoff factor for solute showing dissociation is always greater than for solute showing association.
E : Dissociation leads to increase in number of particles whereas, association leads to a decrease in number of particles.

6. **S** : At equilibrium of Liquid $\rightleftharpoons$ Vapour, kinetic energy of liquid phase and vapour phase is same.
E : Kinetic energy of liquid or vapour is given by $\frac{3}{2}RT$ for 1 mole.

7. **S** : Osmotic pressure of 1 M glucose is lesser than 1 M NaCl$(aq.)$ but vapour pressure of 1 M glucose is higher than 1 M NaCl.
E : Osmotic pressure is colligative property but vapour pressure is not colligative property however, lowering in V.P. is colligative property.

8. **S** : For rubber and water, $V(l) > V(s)$.
E : The density of both rubber and water is more in liquid state.

9. **S** : Hoar frost is reverse of sublimation.
E : Formation of snow by freezing of clouds or vapours is called Hoar frost, *i.e.*, to reduce pressure over ice so that its external pressure becomes equal to vapour pressure.

10. **S** : Hot water extinguishes fire more quickly than cold water.
E : Hot water being at higher temperature is converted to steam in lesser time which by stopping combustion extinguishes the fire.

11. **S** : Water in a beaker cannot be made to boil by placing it in a bath of boiling water.
E : Water in the beaker will be heated to 100°C but will not boil as for boiling it requires latent heat of steam which is not provided by water bath as both attains 100°C.

12. **S** : Water can be made boiling without heating.
E : A decrease in external pressure to the vapour pressure of water at room temperature causes boiling of water.

13. **S** : Addition of a non-volatile solute causes a depression in vapour pressure.
E : Vapour pressure of a solution is directly proportional to mole fraction of solvent.

14. **S** : Osmosis is a bilateral process.
E : In osmosis net flow from dilute to concentrated solution is noticed.

15. **S** : Raoult's law for solute-solvent systems can be written as $\frac{P^o - P_s}{P_s} = \frac{n}{N}$
E : For dilute solutions Raoult's law may be written as $\frac{P^o - P_s}{P_s} = \frac{n}{N}$.

16. **S** : Boiling point of water is 100°C although water boils below 100°C on mountains.
E : Boiling point of a liquid is the temperature at which V.P. of liquid becomes equal to 1 atm.

17. **S** : An ideal solution is one which obey Raoult's law.
E : $KCl_{(aq)}$ is an ideal solution.

18. **S** : Ebullioscopy or cryoscopy cannot be used for the determination of molar mass of polymers.
E : High molar mass solute leads to very low value of ΔT_b or ΔT_f.

19. **S** : For isotonic solutions $C_1 = C_2$
E : For isotonic solutions $\pi_1 = \pi_2$

20. **S :** Osmotic pressure of non aqueous solutions can be determined by Berkeley-Hartley method.
E : The semipermeable membrane used in Berkeley-Hartley method is $Cu_2[Fe(CN)_6]$.

21. **S :** Near the freezing point of an aqueous solution of a nonvolatile solute only ice separates out.
E : The remaining solution shows equilibrium between solid solvent-liquid solvent.

22. **S :** van't Hoff factor for electrolytes is always greater than unity.
E : The number of particles increases in solution due to electrolytic dissociation.

23. **S :** Addition of solvent to a solution always lowers the V.P.
E : The increase in relative surface area give rise to an increase in V.P. for a given solution.

24. **S :** A cook cries more in cutting onion rather than cutting an onion taken out from refrigerator.
E : The cold onion has lower vapour pressure of its volatile content.

25. **S :** At low concentration, benzene and toluene forms ideal solution.
E : Components with structural similarity forms ideal solution.

26. **S :** Addition of HgI_2 to aqueous solution of KI shows an increase in vapour pressure.
E : The number of particles present in solution decreases due to formation of complex K_2HgI_4.

27. **S :** Great care is taken in intra-venous injections to have comparable concentration of solutions to be injected to patient.
E : By not controlling the concentration the red blood cells may shrink or swell.

28. **S :** Ice melts earlier if NaCl is poured on it.
E : The freezing point of water is lowered on addition of NaCl.

29. **S :** A mixture of cyclohexane and ethanol shows -ve deviation from Raoult's law.
E : Cyclohexane reduces the intermolecular attraction between ethanol molecules.

ANSWERS (Statement Explanation Problems)

1. (b) Vapour pressure is independent of surface area.
2. (b) Diffusion occurs and not osmosis.
3. (c) Explanation is correct reason for statement.
4. (b) Osmosis is net movement of solvent particles from dil. to conc. and conc. to dil., *i.e.*, a bilateral process; The more movement is from dil. to conc. thus net flow from dil. to conc. is noticed.
5. (c) Explanation is correct reason for statement.
6. (c) —do—
7. (c) —do—
8. (c) —do—
9. (c) —do—
10. (c) —do—
11. (c) —do—
12. (c) —do—
13. (c) $P_s \propto \frac{N}{n+N}$ or $P_s = P^o \frac{N}{n+N}$ or $\frac{P_s}{P^o} = \frac{N}{n+N}$

or $1-\frac{P_s}{P^o} = 1-\frac{N}{n+N}$ or $\frac{P^o - P_s}{P^o} = \frac{n}{n+N}$

14. (c) Explanation is correct reason for statement.
15. (d) $\frac{P^o - P_s}{P^o} = \frac{n}{n+N}$ or $\frac{P^o}{P^o - P_s} = \frac{n+N}{n} = 1+\frac{N}{n}$

or $\frac{P^o - P^o + P_s}{P^o - P_s} = \frac{N}{n}$ or $\frac{P^o - P_s}{P_s} = \frac{n}{N}$

[For dilute solution $n+N \approx N$ $\therefore \frac{P^o - P_s}{P^o} = \frac{n}{N}$]

16. (c) Water boils at low temperature at mountains where atmospheric pressure is low, *i.e.*, when P^o = atmospheric pressure.
17. (a) KCl is ionic salt and it dissociates in solution.
18. (c) If molar mass is low, ΔT_b or ΔT_f being low cannot be read out accurately. A little error in measurement of ΔT_b will cause abnormal values of molar mass.
19. (b) For isotonic solutions osmotic pressures are same. Concentrations are same only when solute neither dissociates nor associates.
20. (b) $Cu_2[Fe(CN)_6]$ is soluble in non-aqueous solutions.
21. (c) Explanation is correct reason for statement.
22. (c) Explanation is correct reason for statement.
23. (b) Note that addition of solute to solvent (and not solvent to solute which will show reverse effect) shows a lowering in V.P. due to decrease in relative surface area.
24. (c) Vapour pressure decreases with decrease in temperature.
25. (c) Explanation is correct reason for statement.
26. (c) Explanation is correct reason for statement.
27. (c) Explanation is correct reason for statement.
28. (c) Explanation is correct reason for statement.
29. (b) The given explanation is correct and a reduction in molecular attraction will increase vaporisation nature and lead for higher vapour pressure than that calculated by Raoult's law. Thus, mixture will show positive deviation.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List A	List B
(a) 0.1 N NaCl	(i) OP = 0.125 ST
(b) 0.2 N Na_2SO_4	(ii) OP = 0.133 ST
(c) 0.1 N $Ca(NO_3)_2$	(iii) OP = 0.15 ST
(d) 0.1 N $Al(NO_3)_3$	(iv) OP = 0.30 ST
(e) 0.1 N $Th(NO_3)_4$	(v) OP = 0.20 ST

2.

List A	List B
(a) Additive property	(i) Molarity
(b) Constitutive property	(ii) Dipole moment
(c) Additive and constitutive property	(iii) Optical activity
(d) Colligative property	(iv) Molar mass

3.

List A	List B
(a) Hygroscopic	(i) RBC neither contracts nor swells
(b) Efflorescent	(ii) RBC swells up
(c) Hypertonic	(iii) RBC shrinks
(d) Hypotonic	(iv) Loosing water
(e) Isotonic	(v) Gaining water

4.

List A	List B
(a) Plasmolysis	(i) Swelling of RBC
(b) Haemolysis	(ii) Shrinking of RBC
(c) Reverse osmosis	(iii) Osmosis from plant cell sap to soil
(d) Wilting up of plants	(iv) Desalination of water
(e) Growth of plants	(v) Osmosis from soil to plant cell sap.

5.

List A	List B
(a) Vapour pressure of solution	(i) Mole fraction of solute
(b) Lowering in vapour pressure of solution	(ii) Mole fraction of solvent
(c) Acetone-$CHCl_3$ solution	(iii) ΔH_{mixing} = +ve
(d) Hexane-ethanol solution	(iv) ΔH_{mixing} = −ve
(e) van't Hoff factor	(v) Greater than unity
(f) van't Hoff factor for glucose–H_2O	(vi) Equal to unity
(g) van't Hoff factor for NaCl–H_2O	(vii) Lesser than unity

Type II : More Than One Match Are Possible

6.

List A	List B
1. Gases	a. Victor Meyer's method
2. Volatile liquids	b. Hoffmann's method
3. Non volatile solids	c. Duma's method
4. Solids of low molar mass	d. Ebullioscopy or cryoscopy
5. Solids of high molar mass such as polymers	e. Osmotic pressure
	f. Raoult's law

ANSWERS

1. a–v; b–iv; c–iii; d–ii; e–i
2. a–iv; b–iii; c–ii; d–i
3. a–v; b–iv; c–iii; d–ii; e–i
4. a–ii; b–i; c–iv; d–iii; e–v
5. a–ii; b–i; c–iv; d–iii; e–vii; f–vi; g–v
6. 1–a, b, c; 2–a, b, c, f; 3–d, e, f; 4–d, f; 5–e

10 Surface Chemistry

• NUMERICAL PROBLEMS •

1. What would be the total surface area of a cube of edge length 1 cm? Also what would be the total surface area of the same material if it were subdivided into colloidal size cubes, each having an edge length of 10^{-7} cm ?
2. Calculate the surface area of a catalyst that adsorbs 10^3 cm^3 of nitrogen reduced to STP per gram in order to form the monolayer. The effective area occupied by N_2 molecule on the surface is 1.62×10^{-15} cm^2.
3. Calculate the volume at 300 K and 1 atm and the amount adsorbed of O_2 per g by 2g solid surface, if 4g O_2 is allowed to be adsorbed at 300 K and 0.8 atm.
4. 1.30 litre N_2 gas at 2 atm and 300 K in 1.30 litre container is exposed to 4g of solid surface. After complete adsorption the pressure of N_2 is reduced by 30%. Calculate the value of x / m.
5. 1g of activated charcoal has a surface area 10^3 m^2. If complete monolayer coverage is assumed and effective surface area of NH_3 molecule is 0.129 nm^2, how much NH_3 in cm^3 at STP could be adsorbed on 25 g of charcoal?
6. H_2 gas was adsorbed on 1 g powdered copper surface forming monolayer of molecules. On desorption total H_2 collected measured 1.36 cm^3 at STP. Assuming volume of 1 molecule of H_2 4.742×10^{-23} cm^3, calculate specific area of copper powder.
7. A solution of palmitic acid (molar mass = 256 g mol^{-1}) in benzene contains 4.24 g of acid per litre. This solution on pouring on water surface forms a monomolecular level of palmitic acid as benzene gets evaporated. If 500 cm^2 area of water surface is to be covered by a monolayer, what volume of solution in benzene is needed? Area covered by one molecule of palmitic acid is 0.21 nm^2.
8. One gram of activated charcoal has a surface area of 10^3 m^2. If complete coverage by monolayer is assumed, how much NH_3 in cm^3 at STP would be adsorbed on the surface of 25 g of the charcoal? Given diameter of NH_3 molecule = 0.3 nm.
9. 20% surface sites have adsorbed N_2. On heating N_2 gas is evolved from sites and were collected at 0.001 atm and 298 K in a container of volume 2.46 cm^3. Density of surface sites is 6.023×10^{14} cm^{-2} and surface area is 1000 cm^2. Find out the number of surface sites occupied per molecule of N_2. **(IIT 2005)**
10. 1 g of charcoal adsorbs 100 mL of 0.5 *M* CH_3COOH to form a monolayer and thereby the molarity of CH_3COOH reduces to 0.49. Calculate the surface area of charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.01×10^2 m^2/g. **(IIT 2003)**
11. It is observed that five hours are needed to dissolve a 1 cm cube of NaCl in large amount of water. Calculate the time required for dissolution, if the cube is ground to a powder containing 10^{16} equal sized spheres. Assume that the rate of dissolution is directly proportional to initial area of contact between NaCl and water.
12. The chemisorption of H_2 on an activated surface becomes 40% faster if temperature is raised from 500 K to 1000 K. Calculate energy of activation.
13. An aqueous solution having different concentration is placed with charcoal which adsorbs a part of solute from solution as reported below at equilibrium. Calculate the value of k and n.

$C_{sol.} \times 10^2$	2.0	4.0
x / m	0.185	0.290

SOLUTIONS (Numerical Problems)

1. Surface area of cube of edge length 1 cm = $\mathbf{6 \times 1\ cm^2}$

Surface area of cube of edge length 1×10^{-7} cm

$= 6\times10^{-14}\ cm^2$

Let n cubes of $6\times10^{-14}\ cm^2$ are present on breaking the cube of $6\,cm^2$

$\therefore$ $n\times$ volume of cube of edge length 10^{-7} cm = volume of cube of edge length 1 cm.

$$n\times\frac{4}{3}\times\pi\times[10^{-7}]^3 = \frac{4}{3}\times\pi\times(1)^3$$

$\therefore$ $\quad n = \mathbf{10^{21}}$

$\therefore$ New total surface area

$= 10^{21}\times6\times10^{-14} = \mathbf{6\times10^7}$

2. No. of N_2 molecules $= \dfrac{10^3\times6.023\times10^{23}}{22400} = 2.69\times10^{22}$

Total area covered by $N_2 = 2.69\times10^{22}\times1.62\times10^{-15}$

$= 435\times10^5\ cm^2$

$= \mathbf{4350\ m^2}$

3. Mass of solid $(m) = 2$ g

Amount of O_2 adsorbed = 4g

$\therefore$ $\quad \dfrac{x}{m} = \dfrac{4}{2} = \mathbf{2\ g}$

Also V_{O_2} adsorbed at 1 atm and 300 K $= \dfrac{wRT}{Pm}$

$= \dfrac{4\times0.0821\times300}{1\times32} = 3.078$ litre

$\therefore$ $\quad V_{O_2}$ adsorbed per g $= \dfrac{3.078}{2} = \mathbf{1.539\ litre}$

4. $P_{N_2} = 2$ atm, P_{N_2} left $= \dfrac{2\times70}{100} = 1.4$ atm

$\therefore$ w_{N_2} adsorbed $= \dfrac{PV\times m}{RT} = \dfrac{(2-1.4)\times1.3\times28}{0.0821\times300} = 0.89$ g

$\therefore$ $\quad \dfrac{x}{m} = \dfrac{0.89}{4} = \mathbf{0.22\ g}$

5. Total surface area available for adsorption $= 25\times10^3\ m^2$

Effective surface area of one NH_3 molecule

$= 0.129\times10^{-18}\ m^2$

$\therefore$ No. of molecules of NH_3 adsorbed $= \dfrac{25\times10^3}{0.129\times10^{-18}}$

$= 1.94\times10^{23}$

$\therefore$ $\quad$ Moles of $NH_3 = \dfrac{1.94\times10^{23}}{6\times10^{23}} = 0.323$

$\therefore$ $V_{NH_3} = \dfrac{nRT}{P} = \dfrac{0.323\times0.0821\times273}{1} = 7.2395$ litre

$= \mathbf{7239.5\ cm^3}$

6. No. of molecules of H_2 in $1.36\,cm^3 = \dfrac{6.023\times10^{23}\times1.36}{22400}$

$= 3.66\times10^{19}$

$\therefore$ $\quad$ Volume of H_2 molecule $= 4.742\times10^{-23}$

$\therefore$ $\quad \dfrac{4}{3}\pi r^3 = 4.742\times10^{-23}$

$\therefore$ $\quad r = 2.246\times10^{-8}$ cm

$\therefore$ Area of cross-section of H_2 molecule $= \pi r^2$

$= 3.14\times(2.246\times10^{-8})^2$

$= 1.583\times10^{-15}\ cm^2$

Area of molecules adsorbed

$= (3.66\times10^{19})\times1.583\times10^{-15}\ cm^2$

= Area of adsorption of Cu powder

= specific area of Cu powder, *i.e.*, area /g.

$\therefore$ Specific area of adsorption of Cu

$= 1.583\times10^{-15}\times3.66\times10^{19}$

$= \mathbf{5.79\times10^4\ cm^2}$

7. Let V litre of solution be needed to do so

Mass of palmitic acid $= V\times d = V\times4.24$ g

Moles of palmitic acid $= \dfrac{V\times4.24}{256}$

$\therefore$ No. of molecules of palmitic acid

$= \dfrac{4.24\times V\times6.023\times10^{23}}{256}$

$\therefore$ Total area covered $= \dfrac{4.24\times V\times6.023\times10^{23}}{256}\times0.21\times10^{-18}\times10^4\ cm^2$

or $\quad 500 = \dfrac{4.24\times V\times6.023\times10^{23}\times0.21\times10^{-18}\times10^4\ cm^2}{256}$

$\therefore$ $\quad V = \mathbf{2.386\times10^{-5}\ litre}$

8. Total surface area to be covered $= 25\times10^3$ m

$2r$ for $NH_3 = 0.3\times10^{-9}$ nm $= 0.3\times10^{-9}\times10^2$ cm

$= 0.3\times10^{-7}$ cm

$\therefore$ $\quad r = 1.5\times10^{-8}$ cm

$\therefore$ Surface area of 1 molecule $= \pi r^2 = 3.14\times(1.5\times10^{-8})^2$

$= 7.065\times10^{-16}\ cm^2$

No. of NH_3 molecules adsorbed

$= \dfrac{25\times10^3}{7.065\times10^{-20}} = 3.539\times10^{23}$

$\therefore$ Mole of NH_3 adsorbed $= \dfrac{3.539\times10^{23}}{6.023\times10^{23}} = 0.5875$

Now using $PV = nRT$

$$V = \frac{0.05875\times0.0821\times273}{1}$$

$\therefore$ $\quad V = \mathbf{13.168\ litre}$

9. For adsorbed N_2 on surface sites

$P_{N_2} = 0.001$ atm, $V = 2.46\,cm^3 = 2.46\times10^{-3}$ litre,

$T = 298$ K

$\therefore$ $\quad n_{N_2} = \dfrac{PV}{RT} = \dfrac{0.001\times2.46\times10^{-3}}{0.0821\times298} = 1.0\times10^{-7}$ mol

$\therefore$ Molecules of adsorbed $N_2 = 1.0\times10^{-7}\times6.023\times10^{23}$
$= 6.023\times10^{16}$

Total surface sites available
= Number of sites per cm^2 × Area
$= 6.023\times10^{14}\times1000 = 6.023\times10^{17}$

Surface sites on which N_2 is adsorbed
= 20% × Available sites
$= \frac{20}{100}\times6.023\times10^{17} = 12.046\times10^{16}$

$\therefore$ Number of sites adsorbed per molecule of N_2
$= \frac{12.046\times10^{16}}{6.023\times10^{16}} = \mathbf{2}$

10. Millimole of acetic acid taken $= 100\times0.5 = 50$
Millimole of acetic acid left $= 100\times0.49 = 49$
Millimole of acetic acid adsorbed $= 50-49 = 1$
Molecules of acetic acid adsorbed
$= 1\times10^{-3}\times6.023\times10^{23} = 6.023\times10^{20}$
Total area of 1 g charcoal covered by these molecules
$= 3.01\times10^{2}\ m^2$

$\therefore$ Area covered by 1 molecule $= \frac{3.01\times10^{2}}{6.023\times10^{20}}$
($\because$ unilayer adsorption)
$= \mathbf{5\times10^{-19}\ m^2}$

11. Volume of 1 cm cube $= 1cm^3$

Volume of powder in spherical shape $= 10^{16}\times\frac{4}{3}\pi r^3$

(Volume of one sphere $= \frac{4}{3}\pi r^3$)

$\therefore$ $\frac{4}{3}\pi r^3\times10^{16} = 1cm^3$

$\therefore$ $r = 2.88\times10^{-6}$

$\therefore$ Total surface area $= \pi r^2$
$= \frac{22}{7}\times(2.88\times10^{-6})^2\times10^{16} = 2.61\times10^{5}$

Initial surface area of cube $= 6\times1^2 = 6cm^2$

Rate of dissolution $\propto$ surface area or $\frac{ds}{dt} \propto$ surface area

Thus, time required for dissolution of same amount is

$$t \propto \frac{1}{\text{surface area}} \quad \therefore \quad 5 \propto \frac{1}{6}$$

$$t \propto \frac{1}{2.61\times10^{5}}$$

$\therefore$ $t = 1.15\times10^{-4}$ hr $= 1.15\times10^{-4}\times3600$ sec $= \mathbf{0.41\ sec}$

12. Rate of chemisorption at 500 K $= a$

Rate of chemisorption at 1000 K $= \frac{a\times40}{100} + a = 1.4\,a$

Since, rate $\propto \theta$ (where θ is surface covered) $= K\theta$

$\therefore$ $2.303\log\frac{K_2}{K_1} = \frac{E_a}{R}\frac{(T_2-T_1)}{T_1T_2}$

$$2.303\log\frac{1.4\,a}{a} = \frac{E_a}{8.314}\left[\frac{1000-500}{1000\times500}\right]$$

$E_a = 2798\ J = \mathbf{2.8\ kJ}$

13. $\log\frac{x}{m} = \frac{1}{n}\log C + \log k$

$\therefore$ $\log0.185 = \frac{1}{n}\log2\times10^{-2} + \log k$

$\log0.290 = \frac{1}{n}\log4\times10^{-2} + \log k$

Thus, $n = \mathbf{1.5312}$, $k = \mathbf{2.380}$, and $\log k = \mathbf{0.376}$

• SINGLE INTEGER ANSWER PROBLEMS •

1. How many of the following represents surface phenomenon?
   Adsorption, Surface tension, Surface energy, Viscosity, Absorption, Dissolution of soap in water, Silica gel in presence of moisture
2. 11.42 g O_2 gas is adsorbed on 2 g of metal powder. The volume of O_2 adsorbed in litre/g of metal powder at STP is .....
3. What is the surface area in cm^2 of a cube having an edge length of 1 cm ?
4. 10^a cubes of edge length 10^{-4} cm should be fused to get a cube of edge length 1 cm. What is the value of a.
5. For chemical adsorption obeying Langmuir adsorption isotherm for a given gaseous adsorbate-adsorbent system, $a = 0.6\ bar^{-1}$ and $b = 0.3\ bar^{-1}$. At what pressure 75% of the surface be covered.
6. A cationic surfactant solution shows micellization at $1.2 \times 10^{-3}\ M$. Assuming that 1 mm^3 of solution contains on an average of 2.4×10^{12} micelle particles, the number of ions present in one micelle is 3×10^a (Av. no. is 6×10^{23}). What to the value of a.

ANSWERS

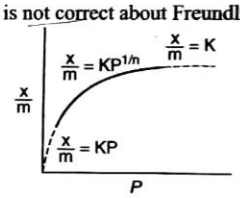
1. Five 2. Four 3. Six 4. Eight 5. Two 6. Two

OBJECTIVE PROBLEMS (One Answer Correct)

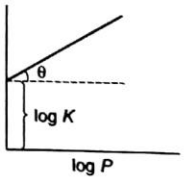
1. The gas which is more adsorbed on activated charcoal is :
   (a) SO_2 (b) N_2
   (c) O_2 (d) H_2
2. About positive catalyst or negative catalyst, which one is incorrect :
   (a) positive catalyst lowers the energy of activation
   (b) negative catalyst increases the energy of activation
   (c) positive catalyst increases the rate of reaction
   (d) negative catalyst functions to remove active intermediates
3. Which is wrong about a positive catalyst?
   (a) Lowers the energy of activation of forward reaction
   (b) Lowers the threshold energy level
   (c) Lowers the energy of activation of backward reaction
   (d) Makes the reaction more exothermic or endothermic
4. Catalytic poisoning is due to :
   (a) increasing activation energy
   (b) adsorption of poisoner on the reactants surface
   (c) adsorption of poisoners on the catalyst surface
   (d) increase in heat of reaction
5. Which is not correct about the reaction?

$$RCOCl + H_2 \xrightarrow[Pd\text{-}BaSO_4]{} RCHO + HCl$$

   (a) Pd acts as positive catalyst
   (b) It is Rosenmunds reaction
   (c) $BaSO_4$ acts as poison for Pd
   (d) $BaSO_4$ acts as promoter for Pd
6. Which of the following is not correct?
   (a) Acid hydrolysis of ester is reversible
   (b) Hydrolysis of ester becomes faster after sometime due to the formation of CH_3COOH
   (c) H^+ formed during hydrolysis acts as autocatalyst
   (d) Alkaline hydrolysis of ester is reversible
7. Select the incorrect statement :
   (a) Enzyme catalysed reactions are usually hydrolytic in nature.
   (b) Enzyme catalysed reactions takes place with evolution of gases.
   (c) The rate of reaction does not depend upon enzyme concentration.
   (d) Enzymes are colloidal in nature.
8. Which one is not correct about zeolites?
   (a) These are water softners
   (b) These do not act as molecular sieves
   (c) Zeolites are complex oxide catalyst commonly used in petrochemical industries
   (d) The activity of zeolites is increased by heating them in vacuum
9. Select the incorrect statement :
   (a) Physical adsorption is multilayer, non-directional, non-specific and decreases with temperature.
   (b) Chemical adsorption is unilayer, directional, specific and increases with temperature initially.
   (c) Rate of fruit fermentation increases with time.
   (d) Langmuir adsorption is not valid for chemisorption.
10. The lowering of activation energy by catalyst is due to :
   (a) formation of adsorbed activated complex and to provide new pathway to reaction
   (b) adsorption is always exothermic
   (c) the adsorbed activated complex possesses lower energy level than simple activated complex
   (d) all of the above
11. Which one is not correct about Freundlich isotherm if?



   (a) $n = \frac{1}{\tan\theta}$ at average pressure
   (b) $\theta = 45°$ at low pressure
   (c) $\theta = 45°$ at high pressure
   (d) $\log\left(\frac{x}{m}\right)$



12. Which statement is not correct?
   (a) Colloidal state is a particular state and not a class of compounds.
   (b) The dispersed phase may consists of a single macro molecule or an aggregate of atoms or ions.
   (c) The sol particles can be seen under microscope.
   (d) Colloidal state is an intermediate (but heterogeneous) state between true solution and suspension state.
13. Which of the following cannot be used to prepare an emulsion of benzene in water?
   (a) 
   (b) 
   (c) 
   (d) $(CH_3)_4\overset{+}{N}\,Br^-$

14. Addition of KI drop by drop to $AgNO_3$ aqueous solution gives an impure sol of AgI. The impurities needed not to be removed by dialysis is :
(a) suspended state of AgI (b) excess of $AgNO_{3(aq.)}$
(c) excess of $KI_{(aq.)}$ (d) excess of $KNO_{3(aq.)}$

15. Cementation process involves formation of :
(a) gel (b) emulsion
(c) sol (d) solid aerosol

16. Which of the following will show more intensity of scattering?
(a) Protein sol (b) Starch sol
(c) Gold sol (d) Milk

17. Alum is used in purifying water by :
(a) forming silicon complex with clay particles
(b) sulphate part combines with dirt and removes it
(c) coagulating the mud particles
(d) making mud water soluble

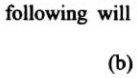
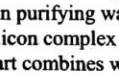
18. Which is not correct for physical adsorption?
(a) Adsorption is spontaneous
(b) Both enthalpy and entropy of adsorption are negative
(c) Adsorption on solid is reversible
(d) Adsorption increases with increase in temperature

19. Identify the correct statement regarding enzymes :
(a) Enzymes are specific biological catalysts and their action is independent of pH
(b) Enzymes are normally heterogeneous catalyst that are very specific in their action
(c) Enzymes are specific biological catalyst that cannot be poisoned
(d) Enzymes are specific biological catalysts that can normally function at very high temperature ($T = 1000$ K)

20. The volume of colloidal particles, V_c as compared to the volume of solute particles in true solution, V_s could be :
(a) ~ 1 (b) $\sim 10^{23}$
(c) $\sim 10^{-3}$ (d) $\sim 10^{3}$

21. The dispersed phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged respectively which of the following statement is not correct?
(a) Magnesium chloride solution coagulates gold sol readily thin iron (III) hydroxide sol
(b) Sodium sulphate solution causes coagulation in both sol
(c) Mixing of the two sols has no effect
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22. In Langmuir's model of adsorption of a gas on a solid surface:
(a) the rate of desorption of adsorbed molecules from the surface does not depend on the surface covered
(b) the adsorption at a single site on the surface may involve multiple molecules at the same time
(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

23. Non-electrolytic colloidal surfactant is :
(a) $C_{17}H_{35}COONa$
(b) 
(c) $C_nH_{2n+1}(OCH_2CH_2)_x.OH$
(d) 

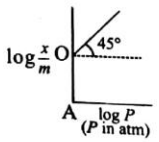
24. Gaseous adsorption on solid surface is exothermic because, adsorption brings in:
(a) increase in enthalpy
(b) increase in entropy
(c) increase in free energy
(d) interaction forces developed between gaseous molecule and solid surface

25. Adsorption of gases on solid surface depends upon:
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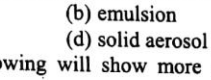
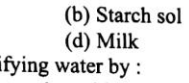
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(a) dispersion
(b) condensation
(c) peptization
(d) dispersion and condensation both

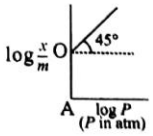
27. Which is not correct for an oil-water emulsion?
(a) Imparts dye colour with water soluble dye
(b) Can be diluted with water
(c) Has higher viscosity in comparison to water-oil emulsion
(d) Consists of vanishing cream

28. A graph plotted between $\log \frac{x}{m}$ *vs.* $\log P$ is shown in figure given below



If intercept is equal to log 3, then value of $\frac{x}{m}$ at a pressure of 3 atm :
(a) 2 (b) 9
(c) 6 (d) 8

14. Addition of KI drop by drop to $AgNO_3$ aqueous solution gives an impure sol of AgI. The impurities needed not to be removed by dialysis is :
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28. A graph plotted between $\log \frac{x}{m}$ *vs.* $\log P$ is shown in figure given below :



If intercept is equal to log 3, then value of $\frac{x}{m}$ at a pressure of 3 atm :
(a) 2 (b) 9
(c) 6 (d) 8
29. 50 mL of 0.3 *M* acetic acid is shaken with 5 g activated charcoal. The concentration of acetic acid is reduced to 1/3 of original molarity. The mass of acetic acid adsorbed per g of charcoal is:

(a) 2×10^{-4} g (b) 1.2×10^{-2} g
(c) 2×10^{-2} g (d) 3×10^{-2} g

30. One g of activated charcoal has total surface area equal to 10^3 m^2. If radius of a gaseous molecule is 10^{-8} cm and the gas shows only monolayer adsorption on the surface of charcoal, then volume of gas at STP adsorbed on total surface of $\frac{22}{7}$ g charcoal is:
(a) 3.73 litre (b) 7.46 litre
(c) 22.4 litre (d) 24.5 litre

31. A catalyst has total surface area of 10^3 cm^2 and adsorption sites available on it are 6×10^{15} sites/cm^2. H_2 gas is adsorbed on this surface occupying only 5% of the available sites of total surface area. On heating catalyst releases H_2 back and whole of the H_2 adsorbed is measured to occupy 2.46 mL at 0.03 atm and 300 K. The no. of H_2 molecules adsorbed on each site is equal to:
(a) 6 (b) 2
(c) 3 (d) 4

32. A cationic colloidal electrolyte forms micelle at 10^{-4} *M* concentration in water. If 1 mm^3 solution contains 10^{12} micelle structure, then the no. of cations involved in one micelle are :
(a) 20 (b) 40
(c) 60 (d) 80

33. One litre vessel having 20 g charcoal (density 2.0 g/cm^3) was filled with a gas at 300 K. The pressure of a gas was 760 torr. Due to adsorption the pressure of gas falls to 608 torr. What is the no. of gas molecule adsorbed per g of charcoal?
(a) 2.4×10^{21} (b) 2.4×10^{20}
(c) 2.4×10^{22} (d) 2.4×10^{23}

34. A negatively charged sol of $[AgI]^{I^-}$ will not be coagulated by :
(a) $[AgI]^{Ag^+}$ (sol) (b) $FeCl_3$ (aq)
(c) $[As_2S_3]^{S^{2-}}$ (sol) (d) $MgCl_2$

35. A negatively charged sol will require minimum amount of which electrolyte for its coagulation:
(a) $NaNO_3$ (b) $Mg(NO_3)_2$
(c) $Al(NO_3)_3$ (d) $Th(NO_3)_4$

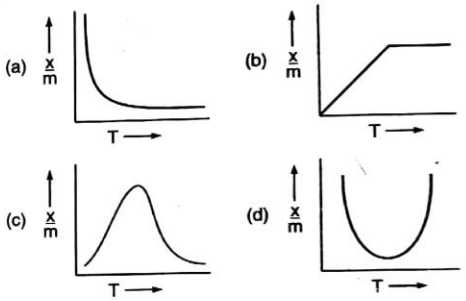
36. Gel on standing excludes small amount of liquid. The phenomenon is called :
(a) Synerisis (b) Efflorescence
(c) Adsorption (d) Thixotropy

37. The density of gold is 19 g / cm^3. If 1.9×10^{-4} g of gold is dispersed in one litre of water to give a sol having spherical gold particles of radius 10 nm, then the number of gold particles per mm^3 of the sol will be :
(a) 1.9×10^{12} (b) 6.3×10^{14}
(c) 6.3×10^{10} (d) 2.4×10^{6}

38. The heat of adsorption are ..... kJ mol^{-1} for physisorption and chemisorption respectively :
(a) 20–40, 40–400 (b) 20–40, 80–100
(c) 60–80, 80–100 (d) 80–100, 20–40

39. Number of layers formed during chemisroption is :
(a) 1 (b) 2
(c) 3 (d) 4

40. Which plot represents for chemisorption at constant pressure ?



41. 1 g charcoal show chemical adsorption of some acetic acid on coming in contact with 100 mL of 0.50 *M* acetic acid and the molarity of acetic acid is reduced to 0.49 *M*. If surface area of charcoal is 3.015×10^2 m^2/g, the surface area of each chemically adsorbed molecule of acetic acid is :
(a) 3.015×10^2 m^2 (b) 5×10^{-19} m^2
(c) 2.5×10^{-19} m^2 (d) 1.25×10^{-19} m^2

42. A plot for $\log\frac{x}{m}$ *vs* $\log P$ shows a straight line with an angle 60° and intercept of 0.3010 on *y*-axis. The amount of gas adsorbed per g of adsorbent if initial pressure is 1 atm is :
(a) 1 (b) 2
(c) 3 (d) 4

43. Efficiency of a catalyst does not depends upon :
(a) molar mass (b) free valencies
(c) physical state (d) amount used

44. Which one is correct match for catalyst used in given process ?

1. Haber's process for NH_3	A. V_2O_5 or Pt
2. Ostwald's process for HNO_3	B. NO
3. Bosch process for H_2	C. Fe + Mo
4. Chamber process for H_2SO_4	D. $Fe_2O_3 + Cr_2O_3$

(a) 1—C, 2—B, 3—A, 4—D
(b) 1—C, 2—D, 3—B, 4—A
(c) 1—C, 2—A, 3—D, 4—B
(d) 1—D, 2—A, 3—D, 4—B

45. Tetra ethyl lead minimises the knocking effect when mixed with petrol. It acts as :
(a) positive catalyst (b) negative catalyst
(c) poison (d) auto catalyst

46. Which one is correct for catalyst and poisoners used in given process?

Process		Poison
1. Hydrogenation of ethylene	A	CO
2. Hydrogenation of oils	B	Br_2 (vapours)
3. Rosenmund's reaction	C	$BaSO_4$
4. Decomposition of H_2O_2	D	HCN

(a) 1—A, 2—D, 3—B, 4—C
(b) 1—A, 2—B, 3—C, 4—D
(c) 1—A, 2—B, 3—C, 4—D
(d) 1—A, 2—D, 3—B, 4—C

47. Select the correct statements :
(i) greater is the valency of effective in electrolyte more will be coagulation power of electrolyte for a given sol.
(ii) greater is the valency of effective ion in electrolyte lesser will be its coagulation value for a given sol.
(iii) peptisation is a characteristic property of colloidal solution.
(iv) micelle formation occurs only above Kraft's temperature as well as above critical micelle concentration.
(v) lower is the gold number more is protecting power of colloid.
(a) (i), (ii), (iii) and (iv) only
(b) all of these
(c) (i), (ii), (iv) and (v) only
(d) (ii), (iii), (iv) only

48. Select the correct statements about colloids :
(i) soaps are anionic class of detergents.
(ii) butter is water dispersed in fat and milk is fat dispersed in water
(iii) floculation value is reported in milli mol/litre
(iv) during electro osmosis, dispersion medium moves in presence of electric field
(v) special methods are required for preparation of hydrophilic colloidal solution
(a) (ii), (iii) and (iv) only
(b) all of these
(c) (i), (ii), (iii) and (iv) only
(d) (ii), (iii), (iv) and (v) only

49. Select the correct statements :
(i) gold and As_2S_3 solution are multimolecular colloids and hydrophobic sols.
(ii) cleansing action of soap is due to adsorption of oily, dirt and greasy material at hydrophobic centres of soap
(iii) hydrophobic part of soap penetrates in oil and hydrophilic part in water to impart stability to emulsion
(iv) hydrophobic solution show more brighter tyndall light than hydrophilic solution
(v) conductance of soap solution changes sharply at CMC
(a) (ii), (iii), (iv) and (v) only
(b) (i), (ii), (iii) and (iv) only
(c) (i), (ii), (iii) and (v) only
(d) all of these

50. A soap of sodium stearate in solution starts micellisation at 1.2×10^{-3} *M*. A colloidal (micelle) particle, on an average contains 2.4×10^{13} molecules of soap in 1 mm^3. The average number of anions (stearate ions) is :
(a) 120 (b) 90
(c) 60 (d) 30

51. Addition of KI drop by drop to $AgNO_3$ aqueous solution gives an impure sol of AgI. The impurities needed not to be removed by dialysis is :
(a) suspended state of AgI (b) excess of $AgNO_3$ (*aq.*)
(c) excess of KI(*aq.*) (d) excess of KNO_3 (*aq.*)

52. Cementation process involves formation of :
(a) gel (b) emulsion
(c) sol (d) solid aerosol

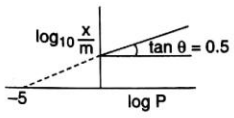
53. Which of the following will show more intensity of scattering ?
(a) Protein sol (b) Starch sol
(c) Gold sol (d) Milk

54. Alum is used in purifying water by :
(a) forming silicon complex with clay particles
(b) sulphate part combines with dirt and removes it
(c) coagulating the mud particles
(d) making mud water soluble

55. Which of the following cannot be used to prepare an emulsion of benzene in water?
(a) 
(b) 
(c) 
(d) $(CH_3)_4\overset{+}{N}Br^-$

56. Gold number of casein, haemoglobin and gelatin are 0.01, 0.03 and 0.005 respectively. Which is most powerful protecting agent?
(a) Casein
(b) Haemoglobin
(c) Gelatin
(d) All are equally having same power

57. The adsorption of a gas on metal surface obeys Freundlich adsorption isotherm : $\frac{x}{m} = KP^{1/n}$,



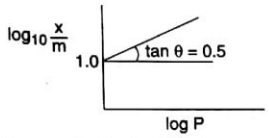
where K and n are constant and P is pressure of gas. If $\log_{10}\frac{x}{m}$ *vs* $\log P$ graph is :

The correct values of intercept and n are :

(a) 0.25, 2 (b) 0.5, 0.5

(c) 0.25, 4 (d) 0.5, 1

58. A gas showing Freundlich adsorption isotherm leads a graph between $\log_{10}\frac{x}{m}$ *vs* $\log P$ as :



The mass of N_2 gas adsorbed at 0.1 atm per g on charcoal surface is equal to :

(a) 0.0316 g (b) 0.316 g

(c) 3.16 g (d) 33.16 g

59. Which of the following gas can displace all the remaining gases from adsorbent surface :

(a) H_2 (b) N_2

(c) O_2 (d) NH_3

60. A monolayer of N_2 molecules is adsorbed on the surface of 1g of $Fe \mid Al_2O_3$ catalyst at 77 K. Upon warming the desorbed N_2 molecules occupied 2.86 cm^3 at 0°C and 760 torr. If effective area of N_2 molecules is 0.167 nm^2, what is surface area (in nm^2) of catalyst.

(a) 0.167 (b) 1.284×10^{19}

(c) 1.67×10^{19} (d) 1.40×10^{19}

61. Which one of the following statements is not correct?

(a) Catalyst does not initiate any reaction.

(b) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.

(c) Enzymes catalyse mainly bio-chemical reactions

(d) Coenzymes increase the catalytic activity of enzyme.

SOLUTIONS (One Answer Correct)

1. (a) Lower is the critical temperature of gas, more are van der Waals' forces of attractions among gaseous molecules, more is adsorption.

2. (b) Working of negative catalyst is their nature to terminate the chain reaction.

3. (d) Catalyst cannot make the reaction more exothermic or endothermic; $\Delta H = E_{a(f)} - E_{a(b)}$.

4. (c) Negative catalyst is adsorbed on the surface of catalyst to make it inert.

5. (d) $BaSO_4$ deactivates the activity of Pd so that —CHO formed is not oxidised to —COOH.

6. (d) Alkaline hydrolysis of ester also called saponification is irreversible.

7. (c) The rate of enzyme catalysed reaction depends upon enzyme concentration.

8. (b) Zeolites are shape selective catalyst. The ions or molecules of the right size can be adsorbed by them and thus they act as molecular sieves.

9. (d) Langmuir adsorption is valid for chemisorption.

10. (d) All these leads to lower energy of activation.

$$R \longrightarrow \underset{\text{activated complex}}{\text{Intermediate}} \longrightarrow \text{Product}$$

$$R + C \longrightarrow \underset{\text{adsorbed - activated complex; } \Delta H = -\text{ve}}{\text{Intermediate}} \longrightarrow \text{Product}$$

11. (c) At high pressure $\frac{x}{m} = K$

12. (c) Sol particles are not detected even in microscope.

13. (d) Surface active agents are used as emulsifiers. The surface active agents must have hydrophobic chain $(R) \geq 5$.

14. (a) Dialysis is used to remove soluble impurities present in sol.

15. (a) Water is dispersed in silica and other components of cement.

16. (c) Gold sol is lyophobic and it will show more scattering due to larger size of gold particles and more $\Delta\mu(\mu_G \sim \mu_{\text{water}})$.

17. (c) Alum contains trivalent Al^{3+} which coagulates negative sol of clay and dirt in water.

18. (d) Adsorption decreases with increase in temperature because increase in temperature leads to increase in kinetic energy of molecules.

19. (b) It is a fact.

20. (d) $\frac{V_c}{V_s} = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi r_s^3} = \frac{r_c^3}{r_s^3} = \left(\frac{10}{1}\right)^3 = 10^3$

Diameter of sol particles $\simeq$ 10 Å.

Diameter of true solution particle $\simeq$ 1 Å.

21. (c) Mixing of +ve and −ve sols causes mutual coagulation.

22. (c) According to Langmuir, $\frac{x}{m} \propto P$

(specifically for chemisorption)

23. (c) It does not possess ionisable species.

24. (d) Attraction always leads to decrease in heat enthalpy and thus ΔH = –ve.

25. (d) Higher is the value of a, T_c, P, more will be adsorption.

26. (d) First of all on passing electric arc, metal vapours are formed (dispersion) which are than condensed in water to form sol particles.

27. (c) Water in oil emulsions (butter) are more viscous than oil in water (milk) emulsion.

28. (b) $OA = \log \frac{x}{m}$ at $\log P = 0$, *i.e.*, at $P = 1$, $\log \frac{x}{m} = \log 3$

$\therefore \frac{x}{m} = K = 3$; $\because \frac{x}{m} = KP^{1/n}$ and $n = 1$ ($\tan\theta = 1$)

if $P = 3$ atm then $\frac{x}{m} = 3 \times 3 = 9$

29. (b) Initial milli mole = $50 \times 0.3 = 1.5$

milli mole left after adsorption = $50 \times 0.3 \times \frac{1}{3} = 0.5$

$\therefore$ milli mole of acid adsorbed = $1.5 - 0.5 = 1.0$

$\therefore$ mole of acid adsorbed = 1.0×10^{-3}

mole adsorbed per g = $\frac{1.0 \times 10^{-3}}{5} = 2 \times 10^{-4}$

mass adsorbed per g = $2 \times 10^{-4} \times 60 = 0.012$ g

30. (a) Total surface area of $\frac{22}{7}$ g charcoal

$$= \frac{22}{7} \times 10^3 \text{ m}^2 = \frac{22}{7} \times 10^7 \text{ cm}^2$$

Total surface area of one molecule of gas

$$= \pi r^2 = \frac{22}{7} \times 10^{-16} \text{ cm}^2$$

$\therefore$ No. of gaseous molecules adsorbed on charcoal surface = $\frac{\frac{22}{7} \times 10^7}{\frac{22}{7} \times 10^{-16}} = 10^{23}$

$\therefore$ mole of gas adsorbed = $\frac{10^{23}}{6 \times 10^{23}} = \frac{1}{6}$

$\therefore$ $V = \frac{22.4}{6} = 3.73$ litre

31. (a) Total mole of H_2 adsorbed

$$= \frac{PV}{RT} = \frac{0.03 \times 2.46 \times 10^{-3}}{0.0821 \times 300} = 3 \times 10^{-6}$$

$\therefore$ No. of H_2 molecules adsorbed

$$= 3 \times 10^{-6} \times 6 \times 10^{23} = 18 \times 10^{17}$$

Total no. of sites available

$$= 6 \times 10^{15} \times 10^3 = 6 \times 10^{18}$$

18×10^{17} molecules were adsorbed on

$$\frac{6 \times 10^{18} \times 5}{100} \text{ sites} = 3 \times 10^{17} \text{ sites}$$

$\therefore$ No. of H_2 molecules/site = 6

32. (c) No. of particles of cationic colloidal electrolyte/litre before micelle formation = $10^{-4} \times 6 \times 10^{23} = 6 \times 10^{19}$

$\therefore$ No. of particles of cationic colloidal electrolyte/mm^3 = $6 \times 10^{19} \times 10^{-6} = 6 \times 10^{13}$

Number of micelles formed = 10^{12}/mm^3

$\therefore$ Number of cations in one micelle = $\frac{6 \times 10^{13}}{10^{12}} = 60$

33. (b) Volume occupied by charcoal = $\frac{20}{2.0} = 10 \text{ cm}^3$

Volume of container left for gas = $1000 - 10 = 990 \text{ cm}^3$

Moles of gas adsorbed

$$= \frac{(760 - 608) \times 990}{760 \times 1000 \times 0.0821 \times 300} = 8.04 \times 10^{-3} \text{ mole}$$

$\therefore$ Molecules of gas adsorbed

$$= 8.04 \times 10^{-3} \times 6 \times 10^{23} = 4.8 \times 10^{21}$$

$\therefore$ Molecules of gas adsorbed per g

$$= \frac{4.8 \times 10^{21}}{20} = 2.4 \times 10^{20}$$

34. (c) Negative sols are either coagulated by +ve sol or by electrolyte.

35. (d) Higher is the valency of effective ion (carrying charge opposite to sol particles) more is coagulating power, lesser is coagulating value.

36. (a) Spontaneous outcome of internal liquid (Dispersed phase) from a gel a called synerisis, whereas outcome of internal liquid from a gel on shear is called thixotropy.

37. (d) Volume of gold used = $\frac{m}{d} = \frac{1.9 \times 10^{-4}}{19} = 1 \times 10^{-5} \text{ cm}^3$

Volume of one gold particle = $\frac{4}{3}\pi r^3$

$$= \frac{4}{3} \times \frac{22}{7} \times (10 \times 10^{-7})^3$$

$$= 4.19 \times 10^{-18} \text{ cm}^3$$

$\therefore$ Total no. of particles = $\frac{1 \times 10^{-5}}{4.19 \times 10^{-18}} = 2.4 \times 10^{12}$

Thus 2.4×10^{12} particles of gold are present in 1 litre or 10^{-3} m^3.

$\therefore$ Number of particles per mm^3 = $\frac{2.4 \times 10^{12}}{10^{-3} \times 10^9}$

$$= 2.4 \times 10^6$$

38. (b) This is a fact, chemisorption is stronger than physisorption.

39. (a) Chemisorption is unilayer.

40. (c) Chemisorption first increases and then decreases with temperature.

41. (b) milli mole of acetic acid used = $100 \times 0.5 = 50$

milli mole of acetic acid left = $100 \times 0.49 = 49$

Thus milli mole of acetic acid adsorbed = $50 - 49 = 1$

$\therefore$ Molecules of acetic acid adsorbed

$$= 6.023 \times 10^{23} \times 1 \times 10^{-3}$$

$$= 6.023 \times 10^{20}$$

$\therefore$ Surface area of one molecule adsorbed = $\frac{3.015 \times 10^2}{6.023 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$

42. (b) $\tan 60° = 1.73 = \frac{1}{n}(\text{slope of } \log\frac{x}{m} = \frac{1}{n}\log P + \log K)$

$\log K = 0.3010$

$\therefore \quad \log\frac{x}{m} = 0.3010 + 1.73\log 1$

$\log\frac{x}{m} = 0.301$

$\therefore \quad \frac{x}{m} = 2$

43. (a) Molar mass has no role on efficiency of catalyst.

44. (c) These are facts.

45. (b) TEL acts as negative catalyst for combustion of petrol.

46. (b) This is fact.

47. (c) Peptisation is a method to prepare sol.

48. (c) Special methods are required for preparation of hydrophobic solutions.

49. (d) Gold and As_2S_3 are hydrophobic, less stable solutions.

50. (d) 1 litre soap solution contains 1.2×10^{-3} mole of soap or 10^6 mm^3 soap solution contains 1.2×10^{-3} mole $= 1.2 \times 10^{-3} \times 6 \times 10^{23}$ molecules of soap

or 1 mm^3 soap solution contains 7.2×10^{14} molecules of soap

$\because$ 1 mm^3 of colloidal particle contains 2.4×10^{13} molecules of soap

$\therefore$ No. of colloidal particles or micelle formed $= \frac{7.2\times10^{14}}{2.4\times10^{13}} = 30$

51. (a) Dialysis is used to remove soluble impurities present in sol.

52. (a) Water is dispersed in silica and other components of cement.

53. (c) Gold sol is hydrophobic and it will show more scattering due to larger size of gold particles and more $\Delta\mu(\mu_G \sim \mu_{water})$.

54. (c) Alum contains trivalent Al^{3+} which coagulates negative sol of clay and dirt in water.

55. (d) Surface active agents are used as emulsifiers. The surface active agents must have hydrophobic chain $(R) \geq 5$.

56. (c) Higher is gold no. lesser is protecting power.

57. (a) $\log_{10}\frac{x}{m} = \log K + \frac{1}{n}\log P$

$\frac{1}{n} = 0.5$

$\therefore \quad n = 2$

$\because \quad \log_{10}\frac{x}{m} = 0, \quad$ at $\log P = -5$

Also, $0 = \log K + \frac{1}{2}\times(-0.5)$

$\log K = 0.25 \quad$ (intercept)

58. (c) $\log\frac{x}{m} = \log K + \frac{1}{n}\log P$

$\because \quad \tan\theta = 0.5 \quad \therefore \quad n = 2$

$\log\frac{x}{m} = 1 + \frac{1}{2}\log 0.1$

$\log\frac{x}{m} = 1 + \frac{1}{2}\times(-1.0) = 0.5$

$\therefore \quad \frac{x}{m} = 3.16$

$m = 1 \quad \therefore \quad x = 3.16$

59. (d) NH_3 being polar possesses preferential adsorption. Preferential order of adsorption of some gases is $SO_2 > NH_3 > HCl > CO$

60. (b) $V_{N_2} = 2.86\,cm^3$ at NTP

Thus, $n_{N_2} = \frac{6.023\times10^{23}\times2.86}{22400} = 7.69\times10^{19}$

$\therefore$ Surface area of catalyst $= 7.69 \times 10^{19} \times 0.167\ nm^2$

$= 1.284 \times 10^{19}\ nm^2$

61. (b) Catalyst does not affect the value of equilibrium constant.

• PREVIOUS YEARS PROBLEMS •

1. In multimolecular colloidal sol, atoms or molecules are held together by :
   (a) H-bonding (b) van der Waals' forces
   (c) ionic bonding (d) covalent bonding
2. Rate of physisorption increases with : **(IIT 2003)**
   (a) decrease in temperature (b) increase in temperature
   (c) decrease in pressure (d) decrease in surface area
3. Adsorption of gases on solid surface is generally exothermic because : **(IIT 2004)**
   (a) enthalpy is positive (b) entropy decreases
   (c) entropy increases (d) free energy increases
4. Lyophilic sols are : **(IIT 2005)**
   (a) irreversible sols
   (b) they are prepared from inorganic compounds
   (c) not coagulated by adding electrolytes
   (d) self stabilizing
5. Pick out the wrong statement : **(IIT 2007)**
   (a) Micelles are formed by surfactant molecules above the cmc.
   (b) The conductivity of a solution having surfactant molecules decreases sharply at the cms.
   (c) Lower is the cmc of detergent, more is its detergency.
   (d) Cleansing action is not related to micelle.
6. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is : **(IIT 2008)**
   (a) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
   (b) $CH_3(CH_2)_{11}OSO_3^-Na^+$
   (c) $CH_3(CH_2)_6COO^-Na^+$
   (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$
7. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl the most effective coagulating agent for Sb_2S_3 sol is : **(IIT 2009)**
   (a) Na_2SO_4 (b) $CaCl_2$
   (c) $Al_2(SO_4)_3$ (d) NH_4Cl
8. The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide solution increases in the order : **[JEE (Main) 2013]**
   (a) $Ba^{2+} < Na^+ < Al^{3+}$ (b) $Al^{3+} < Na^+ < Ba^{2+}$
   (c) $Al^{3+} < Ba^{2+} < Na^+$ (d) $Na^+ < Ba^{2+} < Al^{3+}$
9. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is : **[JEE (Advanced) II 2013]**
   (a) The adsorption requires activation at 25°C
   (b) The adsorption is accompanied by a decrease in enthalpy
   (c) The adsorption increases with increase of temperature
   (d) The adsorption is irreversible
10. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is : **[JEE (Main) 2015]**
    (a) 18 mg (b) 36 mg
    (c) 42 mg (d) 54 mg
11. For a linear plot of $\log(x/m)$ *versus* $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants) **[JEE (Main) 2016]**
    (a) $1/n$ appears as the intercept
    (b) Only $1/n$ appears as the slope
    (c) $\log(1/n)$ appears as the intercept
    (d) Both k and $1/n$ appear in the slope term
12. Which of the following is an anionic detergent? **[JEE (Main) 2016]**
    (a) Sodium lauryl sulphate
    (b) Cetyltrimethyl ammonium bromide
    (c) Glyceryl oleate
    (d) Sodium stearate
13. The Tyndall effect is observed only when following conditions are satisfied : **[JEE (Main) 2017]**
    (1) The diameter of the dispersed particles is much smaller than the wavelength of the light used
    (2) The diameter of the dispersed particle is not much smaller than the wavelength of the light used
    (3) The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude
    (4) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude
    (a) (1) and (4) (b) (2) and (4)
    (c) (1) and (3) (d) (2) and (3)

SOLUTIONS (Previous Years Problems)

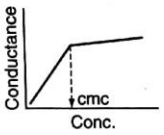
1. (b) It is a fact.

2. (a) Adsorption is exothermic.

3. (b) Randomness decreases during adsorption.

4. (d) Lyophilic sols usually organic, self stabilizing because there sols are reversible and are highly hydrated in solution.

5. (d) Cleansing action is due to micellisation and emulsifying action. Also point (b) is wrong because at cmc, conductivity of solution either becomes constant or show a little increase after cmc with increasing concentration of surfactant.



6. (a) Larger is the hydrophobic chain, lesser is cmc.

7. (c) As_2S_3 is negative sol. Higher is the valence of effective ion (*i.e.*, positive ion) more is coagulating power.

8. (d) Greater is the charge on effective ion (carrying +ve charge) opposite to charge on sol (As_2S_3 is –ve sol) more is coagulating power. This is Hardy-Schulze rule.

9. (b) Adsorption is physisorption and hence energy of activation is not required. Physisorption is exothermic and reversible and it decreases with increase in temperature.

10. (a) meq. of acetic acid present = $50 \times 0.06 = 3$

meq. of acetic acid left = $50 \times 0.042 = 2.1$

meq. of acetic acid adsorbed = $3 - 2.1 = 0.9$

Thus weight of acetic acid adsorbed

$$= \frac{0.9 \times 60}{1000} = 0.054$$

$\therefore$ Weight of acetic acid adsorbed per gram charcoal

$$= \frac{0.054}{3} = 0.018 = 18 \text{ mg}$$

11. (b) According to the Freundlich Adsorption Isotherm

$$\frac{x}{m} = kP^{1/n}$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P$$

$\log \frac{x}{m}$ *vs.* $\log p$ plots leads to straight line with slope $1/n$.

12. (a,d)

Sodium lauryl sulphate = detergent, anionic

(The anionic part undergoes aggregation)

Cetyltrimethyl ammonium bromide = detergent, cationic

(The cationic part undergoes aggregation)

Glyceryl oleate = detergent, non-ionic

(Whole undergoes aggregation)

Sodium stearate = soap, anionic

(The anionic part undergoes aggregation)

Note : Soaps are also anionic class of detergents and thus question has two answers (a) and (d).

13. (b) More is $\Delta\mu$ (*i.e.*, $\mu_{DP} \sim \mu_{DM}$) more is scattering. Also larger is size of dispersed phase, more is scattering.

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statements :
   (a) Lamp black in water is passed in colloid state on addition of gum.
   (b) White precipitate of $BaSO_4$ on washing continuously with water gives $BaSO_4$ sol.
   (c) Electrodialysis is used to remove ionic impurities faster.
   (d) Brownian motion was noticed in colloidal solution by Brown.
2. Which statements are correct about colloidal solution?
   (a) Coagulating value $\propto \frac{1}{\text{Coagulating power}}$
   (b) Coagulating value $\propto$ Charge on effective ion
   (c) Gold number $\propto \frac{1}{\text{Protective power}}$
   (d) Scattering $\propto \frac{1}{\lambda^4}$
3. Which statements are correct?
   (a) Addition of $Fe(OH)_3$ sol to As_2S_3 sol brings in mutual coagulation.
   (b) Addition of $[AgI]^{Ag^+}$ sol to $[AgI]^{I^-}$ sol brings in mutual coagulation.
   (c) Cloud Burst is due to mutual coagulation.
   (d) $Th(NO_3)_4$ cannot coagulate +ve sol.
4. Which are correct regarding stability of sol?
   (a) Lyophilic sols are stabilised due to a layer of solvent round sol particles
   (b) Lyophobic sols are stabilised due to presence of charge
   (c) Addition of lyophilic brings in more stability to lyophobic
   (d) Addition of lyophobic brings in more stability to lyophobic
5. Select the correct statements :
   (a) Blood is positively charged.
   (b) Haemoglobin particles in blood carry +ve charge.
   (c) $FeCl_3$ is very good coagulant for blood.
   (d) Blood is categorised in sol category.
6. Which are not examples of autocatalysis?
   (a) Breakdown of atomic fuel in reactor
   (b) Shock decomposition of glycerol trinitrate
   (c) ZSM-5 used to convert alcohol in petrol
   (d) Storage of chloroform along with little ethanol
7. Which are characteristic of adsorption?
   (a) Exothermic (b) Decreases entropy
   (c) Spontaneous (d) $\Delta H \gtrless T\Delta S$
8. Select the correct statements :
   (a) Gold sol prepared by different methods has altogether different colours due to size of gold particles in water.
   (b) The potential difference between fixed layer and movable layer is called zeeta potential.
   (c) At CMC, surfactant molecules undergo aggregation to form micelle.
   (d) Micelle formation is independent of temperature.
9. Select the correct statements :
   (a) Medicines are more effective in colloidal state due to smaller surface area.
   (b) The spontaneous outcome of internal liquid phase from gels is called weaping of gels or syneresis.
   (c) The outcome of internal liquid phase on shear from gels is called thixotropy.
   (d) The detergency action of detergents is due to their emulsifying nature and micellisation.
10. Select the correct statements :
    (a) Surface active agents possess surface activity to lower the surface area, *i.e.*, to reduce the surface energy.
    (b) Detergents possesses the property of surface activity and detergency.
    (c) All the surfactants are detergents.
    (d) Soaps are anionic class of surfactant.
11. A catalyst is a substance that :
    (a) helps in attaining equilibrium faster if any
    (b) increases the rate of forward and backward reaction (if any)
    (c) lowers the threshold energy level
    (d) provides new pathway to reaction
12. A catalyst :
    (a) lowers the energy of activation
    (b) makes the reaction more exothermic
    (c) makes the reaction less endothermic
    (d) has no effect on the magnitude of equilibrium constant
13. Which of the following are correct?
    (a) Silica gel adsorbs H_2O
    (b) $CaCl_2$ anhy. adsorbs H_2O
    (c) Gas masks works on the principle of selective adsorption
    (d) Zeolites are shape selective catalyst and water softners
14. Select the correct statements :
    (a) Physical adsorption is weak, multilayer, non-directional and non-specific.
    (b) Chemical adsorption is strong, unilayer, directional and strong.
    (c) Adsorption decreases with temperature.
    (d) Chemical adsorption is more stronger than physical adsorption.
15. Select the correct statements about adsorption :
    (a) $\Delta G = -$ ve (b) $\Delta H = -$ ve
    (c) $\Delta S = -$ ve (d) $\Delta G > T\Delta S$
16. Spontaneous adsorption of H_2 on glass surface also involves the change $H_2 \rightarrow 2H$ during adsorption. Which are correct for adsorption of H_2 on glass surface?
    (a) $\Delta H = +$ ve (b) $\Delta S = +$ ve
    (c) $T\Delta S > \Delta H$ (d) $\Delta G = -$ ve

17. Which one is not correct about Freundlisch adsorption isotherms if $\frac{x}{m}$ is amount adsorbed per unit mass of adsorbent?
(a) $\frac{x}{m} \propto (P)^{1/n}$
(b) $\log \frac{x}{m} = \log K + \frac{1}{n} \log P$
(c) $\frac{x}{m} \propto P$ (at V. low P)
(d) $\frac{x}{m} = K$ (at V. high P)

18. Which reactions represents heterogeneous catalysis?
(a) Decomposition of $KClO_3$ in presence of MnO_2
(b) Ostwald process for HNO_3
(c) Contact process for H_2SO_4
(d) Acidic hydrolysis of ester

19. Select the correct statements :
(a) Enzyme catalysed reactions are highly specific
(b) Enzyme catalysed reactions are highly susceptible to pH and temperature
(c) Decomposition of glycerol trinitrate is an example of autocatalysis
(d) The acid hydrolysis and alkaline hydrolysis of ester are reversible

20. Which of the following are correct about Langmuir adsorption isotherm at very high pressure?
(a) It is valid for chemisorption
(b) $\frac{x}{m} = \frac{a}{b}$
(c) $\ln \frac{x}{m} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$
(d) At very high pressure rate of adsorption > rate of desorption

21. What happens when detergent is added to water?
(a) Surface tension increase
(b) Surface tension decrease
(c) Viscosity increases
(d) Viscosity decreases

22. Which of the following are true for hydrophilic solution?
(a) They do not require electrolytes for stability
(b) Their coagulation is irreversible
(c) Their surface tension is usually lower than water
(d) Their viscosity is of the order of water

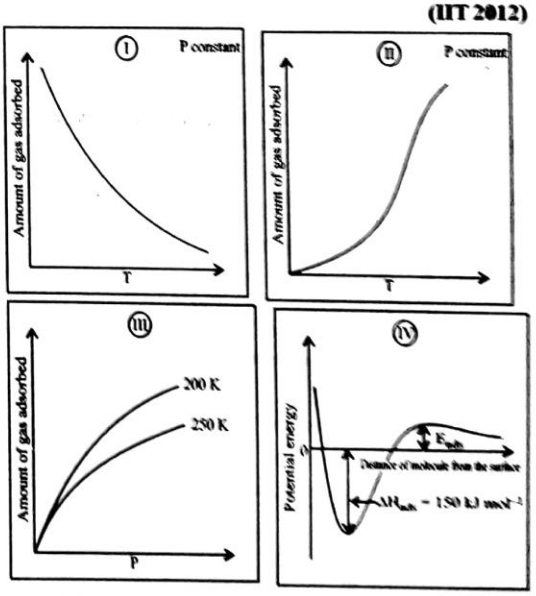
23. Which of the following statements is correct for the spontaneous adsorption of a gas ?
(a) ΔS is negative and therefore, ΔH should be highly positive
(b) ΔS is negative and therefore, ΔH should be highly negative
(c) ΔS is positive and therefore, ΔH should be negative
(d) ΔS is positive and therefore, ΔH should also be highly positive

24. Select the correct statement :
(a) Sols are destabilized by ageing and coagulation
(b) Spontaneous destabilization of sol is ageing
(c) Spontaneous destabilization is coagulation
(d) Electrolytes cause coagulation of sol

25. The correct statement (s) pertaining to the adsorption of a gas on solid surface is (are) : **(IIT 2011)**
(a) Adsorption is always exothermic
(b) Physisorption may transform into chemisorption at high temperature
(c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature
(d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation

26. Choose the correct reason(s) for the stability of the lyophobic colloidal particles. **(IIT 2012)**
(a) Preferential adsorption of ions on their surface from the solution
(b) Preferential adsorption of solvent on their surface from the solution
(c) Attraction between different particles having opposite charges on their surface
(d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles

27. The given graphs/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct? **(IIT 2012)**



(a) I is physisorption and II is chemisorption
(b) I is physisorption and III is chemisorption
(c) IV is chemisorption and II is chemisorption
(d) IV is chemisorption and III is chemisorption

28. The correct statement(s) about surface properties is (are):
(a) cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium
(b) adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system
(c) brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution
(d) the critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c) Brownian motion was no doubt given by *R.* Brown in pollen grains suspended in water. However the phenomenon was noticed in colloidal solution by Zsigmondy using ultramicroscope.

2. (a,c,d) More is the charge on effective ion (ion having charge opposite to sol), more is its coagulating power, lesser is coagulating value.

3. (a,b,c) Th^{4+} coagulates –ve sol whereas NO_3^- coagulates +ve sol.

4. (a,b,c) Protection is the property of lyophilic.

5. (a,b,c) Blood is emulsion.

6. (a,c,d) Due to the mixture of gases which acts as autocatalyst.

$$4C_3H_5(ONO_2)_3 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

7. (a,b,c,d) Adsorption is spontaneous only when $T\Delta S < \Delta H$. $\Delta G = \Delta H - T\Delta S$

8. (a,b,c) Micelle formation occurs below Kraft point. Each surfactant has its own Kraft temperature.

9. (a,b,c,d) No doubt medicines are more effective in colloidal solution. It is due to larger surface area available for adsorption.

10. (a,b,d) All the detergents are surfactants. The reverse is not true.

11. (a,b,c,d) All are facts.

12. (a,d) —do—

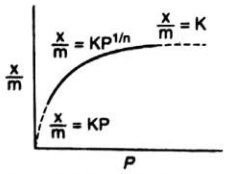
13. (a,c,d) $CaCl_2$ adsorbs H_2O.

14. (a,b,d) Chemisorption first increases with temperature as it requires energy of activation.

15. (a,b,c,d) $\Delta G = \Delta H - \Delta S \times T$ ΔH is always –ve and ΔS = – ve for adsorption.

16. (a,b,d) ΔG = – ve

17. (a,b,c,d) According to Freundlich : $\frac{x}{m} = KP^{1/n}$



18. (a,b,c) In acidic hydrolysis *R* and catalyst (H^+) both are miscible liquids.

19. (a,b,c) Alkaline hydrolysis of ester (saponification) is irreversible.

20. (a,b,c) At very high pressure rate of adsorption = rate of desorption. This $\frac{x}{m} = \frac{a}{b} = K_{eq.}$ or eq. is attained.

$$\Delta G^\circ = -2.303\,RT \log \frac{x}{m}$$

$$\Delta H^\circ - T\Delta S^\circ = -2.303\,RT \log \frac{x}{m}$$

21. (b,c) These are facts.

22. (a,c) These are facts.

23. (b) For spontaneous adsorption ΔS = –ve, ΔH = highly –ve. Thus ΔG = –ve.

24. (a,b,d) Destabilization of sol by artificial means is called coagulation.

25. (a,b,d) Chemisorption first increases than decreases with temperature. Physisorption decreases with temperature.

26. (a,d) Lyophobic sols are stable due to preferential adsorption of ions on their surface from solution and potential difference arised between the fixed layer and the diffused layer of opposite charges around the colloidal particles provides stability to lyophobic sol.

27. (a,c) Graph (I) and (III) represent physisorption because, in physisorption, the amount of adsorption decreases with the increase of temperature and increases with the increase of pressure.
Graph (II) represents chemisorption, because in chemisorption amount of adsorption increase with the increase of temperature. Graph (IV) represents the minima is potential energy at short distance and thus involves chemisorption. In physisorption, minima or potential energy is noticed at long distance.

28. (b,d) Adsorption is an exothermic process and is accompanied by decrease is entropy
ΔH_{sys} = –ve ; ΔS_{sys} = –ve
More is critical temperature (T_c), more are intermolecular forces of attraction and thus more will be adsorption clouds which are liquid dispersed in gas (aerosol) Brownian motion also depends on size of sol particles

COMPREHENSION BASED PROBLEMS

Comprehension 1 : The catalytic activity and colloidal nature of a substance area surface phenomenon. Both these properties depend upon the property of adsorption. Adsorption may be physisorption or chemisorption. Adsorption is spontaneous and always leads to decrease in entropy along with evolution of heat. Chemisorption is irreversible with temperature, unilayer, specific and directional. Adsorbate molecules adsorb on catalyst surface and thus, lower the energy of activation of reaction to provide a new pathway for reaction. In colloidal state dispersed phase particles possess the adsorption characteristics at the interface.

[A] Select the correct statements :

1. Adsorption is spontaneous at all the temperatures.
2. Gases having high critical temperature possess more tendency for adsorption.
3. An adsorbent possesses more tendency for adsorption if it is in colloidal state.
4. Chemical adsorption first decreases with increase in temperature and then increases.
5. Water molecules are adsorbed in $CaCl_2(s)$.

(a) 1, 2, 3, 4, 5 (b) 2, 3, 4
(c) 1, 2, 3, 4 (d) 2, 3

[B] Which statements are correct?

1. Addition of $AgNO_3$ drop by drop in excess of KI leads to the formation of +vely charged sol of AgI.
2. Adsorption characteristic of an adsorbent may be increased by passing it in finely divided form.
3. Catalyst helps in attaining the equilibrium earlier but does not influence equilibrium constant in reversible reactions.
4. Decolorisation of raw sugar is based on absorption.
5. Gas masks containing animal charcoal act on the basis of selective adsorption.
6. The micelle formation of soaps depends upon hydrophobic and hydrophilic entities present in soap.

(a) 2, 3, 5, 6 (b) 2, 3, 4, 5
(c) 1, 2, 5, 6 (d) 1, 2, 3, 4

SOLUTIONS

Comprehension 1

[A] (b)

1. Adsorption decreases with increase in temperature but $\Delta G = -$ve at high temperature,
   $\Delta H = -$ve and $\Delta S = -$ve, thus $T\Delta S = -$ve.
   $\therefore \Delta G = \Delta H - T\Delta S = -\text{ve} - (-\text{ve}) =$ less negative
2. Gases having high critical temperature are easily liquefiable due to higher forces of attractions among molecules and thus, also show more adsorption.
3. Adsorption extent of an adsorbent is more if its surface area is more.
4. Chemisorption requires energy of activation.
5. H_2O is absorbed in $CaCl_2$ and not adsorbed.

[B] (a)

1. Addition of $AgNO_3$ in KI_{excess} gives –ve sol due to adsorption of I^- on AgI, *i.e.*, preferential adsorption.
2. An increase in surface area of adsorbent increases the adsorption sites.
3. The forward reaction is catalysed and takes place fastly whereas the increase in products concentration makes reverse reaction fast and thus, equilibrium is attained earlier.
4. Animal charcoal adsorbs colouring matter of sugar.
5. CH_4 and CO are preferencially adsorbed on animal charcoal.
6. It is the reason why soaps form micelles.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanation **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) **S** is correct but **E** is wrong
(b) **S** is wrong but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. **S :** Now-a-days term catalyst means specifically for a substance that accelerates the reaction.
   E : The terms inhibitor is commonly used for substances which retards the rate of reaction.
2. **S :** The activity of catalyst is more or less specific.
   E : A catalyst for one reaction is not necessary to catalyse the other reaction.
3. **S :** The effectiveness of catalyst has found more applications in solid catalyst and gaseous reactant systems.
   E : A large number of industrial preparations are based on this type of reactions.
4. **S :** Thermal decomposition of $KClO_3(s)$ in presence of $MnO_2(s)$ is an example of homogeneous catalysis.
   E : A homogeneous catalysis involves phase $P = 1$.
5. **S :** A catalyst lowers the threshold energy level for reaction.
   E : Catalyst combines with reactant to form an exothermic intermediate and provide another pathway to reaction.
6. **S :** Lead tetraethyl acts as inhibitor for combustion of gasoline.
   E : It retards the precombustion of gasoline.
7. **S :** Enzymes are proteins and enzyme catalysed reactions are called biological catalysis.
   E : The activity of enzyme as catalyst is increased in presence of vitamins.
8. **S :** Zeolites are water softner as well as catalyst.
   E : The catalytic action of zeolites is based upon their shape selectivity.
9. **S :** Oxidation of Na_2SO_3 is not caused by air but in presence of Na_3AsO_3 both undergo oxidation simultaneously.
   E : Neither Na_2SO_3 nor Na_3AsO_3 is oxidised by air.
10. **S :** Physical adsorption is weaker than chemical adsorption.
    E : Activated complex formed during adsorption possess lower energy level in chemisorption as it is more exothermic.
11. **S :** A negative catalyst retards rate of chemical reaction.
    E : Presence of negative catalyst boosted up the energy of activation.
12. **S :** Presence of catalyst alters the individual energies of reactants and products.
    E : The numerical value of ΔH or ΔU for the given reaction does not change in presence of catalyst.
13. **S :** A colloidal state, a dispersion of a dispersed phase in a dispersion medium is a heterogeneous state.
    E : The particle size of dispersed phase ranges between true solution and suspension state.
14. **S :** The stability of lyophobic sols is lesser than lyophilic sols.
    E : Lyophilic sols possess loving nature for liquid.
15. **S :** The charge on lyophobic particles is responsible for their nature to exist as sol.
    E : It is the formation of thin layer around sol particles which is responsible for stability of lyophilic sols.
16. **S :** The separation of insoluble impurities from a colloidal solution requires dialysis.
    E : The ionic impurities present in colloidal solution are separated by electrodialysis.
17. **S :** The blue colour of sky is due to scattering of light by dirt or dust particles present in air.
    E : Larger size of dispersed phase particles show more scattering as well as higher is the wavelength of light longer is scattering.
18. **S :** A yellow coloured As_2S_3 sol on mixing with red coloured $Fe(OH)_3$ sol gives colourless solution.
    E : The –ve charge of As_2S_3 sol particles is neutralised by +ve charge of $Fe(OH)_3$ sol particles and thus, sols are destabilized and show mutual coagulation.
19. **S :** Gelatin is often used as protective colloid.
    E : Protection is a property of lyophilic colloids.
20. **S :** $C_{12}H_{25}NH_3Cl$ and $C_{12}H_{25}COONa$ are colloidal electrolyte.
    E : The substances which behave as electrolyte at lower concentration and above definite concentration forms sol are called colloidal electrolyte.
21. **S :** The micelle formation by a surfactant takes place at certain concentration at definite temperature.
    E : The temperature above which a surfactant forms micelle is called Kraft point.
22. **S :** The concentration of sulphide ores by froth floatation is based on emulsification.
    E : Pine oil in water forms emulsion.
23. **S :** The digestion of fat in intestine involves emulsification.
    E : Bile salts stabilize the emulsion so formed.

24. **S :** Addition of $AgNO_3$ (aq) to $KI(aq)$ gives –ve sol whereas addition of $KI(aq)$ to $AgNO_3$ gives +ve sol of AgI.
E : The sol particles adsorbs the common ions present in solution and acquire their charge.

25. **S :** Hard water consumes more soap.
E : The ion responsible for cleansing action is precipitated out by Ca^{2+} or Mg^{2+} ion.

26. **S :** Sol particles show Tyndall effect.
E : The scattering is directly proportional to size of sol particle.

27. **S :** Creaming from milk is known as phase inversion.
E : An agitation of milk brings in a change of D.P. into D.M. and *vice-versa.*

28. **S :** A needle can float on clear water but sinks when some detergent is added to it.
E : Detergent reduces the surface tension of water.

29. **S :** Medicines are more effective in colloidal form than in tablet form.
E : The colloidal state possess larger surface area than coarse form.

30. **S :** Micelles are formed by surfactants above CMC.
E : The conductivity of a solution having surfactant molecule decreases sharply at CMC. **(IIT 2007)**

ANSWERS (Statement Explanation Problems)

1. (d) Both are different facts but true.
2. (d) Both are different facts but true.
3. (c) Explanation is correct reason for statement.
4. (b) Heterogeneous system has $P \geq 2S + S$ has $P = 2$.
5. (c) Catalyst lowers energy of activation and threshold energy and provide another pathway to reaction.
6. (c) Explanation is correct reason for statement.
7. (d) Both are different facts but true.
8. (d) Both are different facts but true.
9. (a) It is called induced oxidation.
10. (c) Explanation is correct reason for statement.
11. (a) Working of negative catalyst is not related to energy of activation.
12. (b) The threshold energy level changes and not E_R or E_P.
13. (c) Explanation is correct reason for statement.
14. (c) Explanation is correct reason for statement.
15. (d) Both are different facts but true.
16. (b) Soluble impurities are removed by dialysis.
17. (c) Explanation is correct reason for statement.
18. (c) Explanation is correct reason for statement.
19. (d) Both are different facts but true.
20. (c) Explanation is correct reason for statement.
21. (d) Both are different facts but true.
22. (c) Explanation is correct reason for statement.
23. (c) Explanation is correct reason for statement.
24. (c) $AgNO_3 + \underset{\text{Excess}}{KI} \longrightarrow [AgI]^{I^-}$
$KI + \underset{\text{Excess}}{AgNO_3} \longrightarrow [AgI]^{Ag^+}$
The preferential adsorption of common ion on AgI particles provides –ve and +ve charge.
25. (c) $2RCOONa + Ca^{2+} \longrightarrow \underset{\text{Insoluble}}{(RCOO)_2\,Ca} + 2Na^+$
26. (c) Sol particles show Tyndall effect due to **scattering of light.**
Also the scattering is directly proportional to size of sol particles.
27. (c) Milk is o/w emulsion, cream is w/o emulsion. To convert a o/w emulsion into w/o emulsion is known as phase inversion which can be achieved by mechanical agitation.
28. (c) Explanation is correct reason for statement.
29. (c) Larger surface area provides more pronounced adsorption of medicine over tissues and thus effectiveness increases.
30. (d) Both are facts.

MATCHING TYPE PROBLEMS

Type I : Only One Match is Possible

1.

List A	List B
(A) CMC	1. Centrifuge
(B) Ge ; s	2. Phase inversion
(C) Demulsification	3. Syneresis
(D) Creaming of milk	4. van der Waals' bonding
(E) Detergency	5. Kraft temperature
(F) Multimolecular colloid	6. Lyophobic
(G) Macromolecular colloid	7. Lyophilic

Type II : More Than One Match are Possible

2. Match the following. More than one match are possible:

List A	List B
(A) $2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl + 3O_2(g)$	1. Homogeneous catalysis
(B) $2H_2O_2(l) \xrightarrow{Hg(l)} 2H_2O(g) + O_2(g)$	2. Heterogeneous catalysis
(C) $2H_2O_2(l) \xrightarrow{Pt} 2H_2O(g) + O_2(g)$	3. $\Delta n_{reaction} > 1$
(D) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$	4. $\Delta n_{reaction} < 1$

3.

List A	List B
(A) Homogeneous catalysis	1. Enzyme catalysis
(B) Heterogeneous catalysis	2. Manufacture of NH_3
	3. Hydrolysis of sugar
	4. Mutarotation of glucose
	5. Cracking of petroleum

Type III : Only One Match From Each List

4.

List A	List B	List C
A. Lyophilics	1. Froth floatation	a. Charge depends on pH
B. Lyophobics	2. Organic substances	b. Charge is independent of pH
C. Protection	3. Artificial rain	c. Digestion of food
D. Smoke	4. Inorganic substances	d. Spray of AgI
E. Coagulation	5. Blue tinge	e. Gelatin
F. Emulsification	6. Gold number	f. Tyndall effect

ANSWERS

1. A – 5; B – 3; C – 1; D – 2; E – 4; F – 6; G – 7
2. A – 2, 3; B – 2, 3; C – 2, 3; D – 1, 4
3. A – 1, 3, 4; B – 2, 5
4. A – 2 – a; B – 4 – b; C – 6 – e; D – 5 – f; E – 3 – d; F – 1 – c

11 Chemical Kinetics

The chapter deals with the rate and mechanism of chemical reactions. There are several reactions which take place instantaneously (*e.g.*, ionic reactions) for which rate cannot be determined. On the other hand, some reactions occur so slowly (*e.g.*, rusting of iron) for which rate determination is of no use. In between these two extremes, many molecular reactions occur with considerable rate for which rate determination is made. In a reaction of this type if, taking place in steps, the slow step reaction decides the rate of reaction.

$$R-Cl + KOH \longrightarrow ROH + KCl$$

$$R-Cl \xrightarrow[\text{Slow}]{} R^+ + Cl^- \xrightarrow[\text{Fast}]{OH^-} ROH$$

In chemical kinetics, reactions which occur in single step are simple or **elementary reactions** and those which take place in two or more steps are termed as complex reactions. For **elementary reactions,** order of reaction and molecularity are generally same.

The rate of reaction : Consider a reaction

$$A \longrightarrow \text{Product}$$

$t = 0$	a mole	0
$t = t$	$(a - X)$ mole	
$t = (t + dt)$	$(a - X - dX)$ mole	

Like other ways to define rate say change in position in unit time, the rate of reaction may also be given as,

$$\text{Rate} = \frac{\text{mole of reactant used}}{\text{time required for this change}} = \frac{X}{t} \quad \ldots(1)$$

However, as we know, rate of a reaction continuously decreases with time and thus, Eq. (1) simply reveals average rate of reaction and it is not advised to take this equation in account for instantaneous rate of reaction, *i.e.*, rate of reaction at any time.

To obtain instantaneous rate, one should consider the average rate when time interval is smallest say dt (*i.e.*, when dt approaches to zero). Therefore, consider an infinitesimally small time dt in which dX mole of reactant are used.

Then, Rate of formation of product $= \frac{dX}{dt}$

or Rate of decomposition of reactant $= -\frac{dC_A}{dt}$

when dC_A is concentration of reactant used in time dt; the negative sign indicates for decreasing trend of rate with time.

Furthermore, consider a reaction,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

It is clear from the reaction that rate of decomposition for N_2O_5 is twice as fast as the rate of formation of O_2 and therefore,

$$\text{Instantaneous rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\text{Average rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

If $\Delta t \to 0$, the average rate changes to instantaneous rate.

where, $-\frac{d}{dt}[N_2O_5]$ is rate of decomposition of N_2O_5

$\frac{+d[NO_2]}{dt}$ is rate of formation of NO_2

$\frac{d[O_2]}{dt}$ is rate of formation of O_2

In general, we can write for

$$n_1A + n_2B + \cdots \longrightarrow m_1Z + m_2Y + \cdots$$

$$\text{Rate of reaction} = -\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = \ldots$$

$$= \frac{1}{m_1}\frac{d[Z]}{dt} = \frac{1}{m_2}\frac{d[Y]}{dt} = \ldots\ldots$$

Factors influencing rate of reaction :

(1) Conc. of reactant, (2) Temperature, (3) Pressure, (4) Surface area of reactant, (5) Exposure to light, (6) Presence of catalyst, (7) Order of reaction.

Unit of rate : $\text{Rate} = \frac{dx}{dt}$

$$\therefore \text{ Unit of rate} = \frac{\text{unit of concentration}}{\text{unit of time}} = \text{mol litre}^{-1}\,\text{time}^{-1}$$

Rate constant and its variation with temperature : Rate constant is a characteristic constant for a given reaction and is defined as the rate of reaction when concentration of reactant is unity.

i.e., $\text{Rate} = K(a - x) \quad \because (a - x) = 1 \ \therefore \text{rate} = K$

The rate constant K varies only with temperature and is expressed as,

$$2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

for two temperature limits

or $K = Ae^{-E_a/RT}$ **for one temperature**

where E_a is energy of activation, T is temperature in Kelvin, A is frequency factor; R is molar gas constant.

NOTE : (1) Put R in the units in which E_a is given or desired.

(2) Temperature coefficient : The ratio of rate constant for each 10°C rise in temperature preferably 25°C and 35°C, *i.e.*, $K_{35}/K_{25} \approx 2 \sim 3$.

Unit of rate constant : Varies with order of reaction.

$$\text{Rate} = K\,[\text{Reactant}]^n$$

$$\therefore \quad K = \frac{\text{rate}}{[\text{Reactant}]^n} = \frac{\text{mol litre}^{-1}\text{time}^{-1}}{(\text{mol litre}^{-1})^n}$$

Unit of $K = \text{mol}^{1-n}\,\text{litre}^{n-1}\,\text{time}^{-1}$

where n is order of reaction.

Molecularity and order of reaction:

	Molecularity of reaction	Order of reaction
1.	It is defined as the no. of molecules of reactant taking part in a chemical reaction. *e.g.*, $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ $\therefore \quad m = 1$	It is defined as the no. of molecules of reactants whose concentration determines the rate of reaction. $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ and rate $= K[NH_4NO_2]$ $\therefore$ O.R. $= 1$
2.	It can neither be zero nor fractional.	It may be zero, fractional or integer.
3.	It is derived from mechanism of reaction.	It is derived from rate expression.
4.	It is theoretical value.	It is experimental value.
5.	Reactions with molecularity ≥ 4 are rare.	Reactions with O.R. ≥ 4 are also rare.
6.	Molecularity is independent of pressure and temperature.	O.R. depends upon pressure and temperature.

Salient features for determination of order of reaction:

(1) The rate expression is directly given, *i.e.*,

$$2NO + O_2 \longrightarrow 2NO_2$$

and $\text{Rate} = K[NO]^2[O_2]^1 \quad \therefore$ O.R. $= 2 + 1 = 3$

i.e., O.R. is also defined as sum of powers raised on concentration terms in order to write rate expression.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

and $\text{Rate} = K[CH_3COOC_2H_5]^1[H_2O]^0$

$\therefore$ O.R. $= 1 + 0 = 1$

(2) The problem is provided up in form of language, *i.e.*,

$2A + B \longrightarrow$ Product and Given

A shows first order kinetics and B shows zero order kinetics.

$\therefore$ O.R. $= 1 + 0 = 1$ and $\text{rate} = K[A]^1[B]^0$

(3) Either of reactant is mentioned as excess, *i.e.*,

(a) $2A + \underset{\text{excess}}{B} \longrightarrow$ Products

$\therefore$ O.R. $= 2 + 0 = 2$ and $\text{rate} = K[A]^2[B]^0$

(b) $\underset{\text{excess}}{2A} + B \longrightarrow$ Products

$\therefore$ O.R. $= 0 + 1 = 1$ and $\text{rate} = K[A]^0[B]^1$

(4) Experimental data is given :

(a) Case I : Rate is given using different conc. of A and B at same temperature.

Given that,	$[A]$	$[B]$	Rate
	a_1	b_1	r_1
	a_2	b_2	r_2
	a_3	b_3	r_3

$\therefore \quad r_1 = K[a_1]^m[b_1]^n$

$r_2 = K[a_2]^m[b_2]^n$

$r_3 = K[a_3]^m[b_3]^n$

where m and n are order for A and B respectively

Solve these to get m and n

$\therefore$ O.R. $= (m + n)$

(b) Case II : Half-life period ($t_{1/2}$) and initial concentration (a) are given.

Half-life period : Time to complete half of the reaction

$$t_{1/2} \propto (a)^{1-n}$$

when n is order of reaction;

(c) Case III : Characteristic study of experimental facts about a reaction.

(5) The given reaction is pseudo unimolecular or pseudo bimolecular.

Pseudo unimolecular reactions:

Reactions with O.R. $= 1$ but Molecularity ≥ 2

O.R. $= 1$, molecularity $= 2$ for reaction given below:

e.g., $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

$C_{12}H_{22}O_{11} + H_2O \rightleftharpoons C_6H_{12}O_6 + C_6H_{12}O_6$

Pseudo bimolecular reactions:

Reactions with O.R. $= 2$ but Molecularity ≥ 3

(6) Unit of rate constant is given :

Unit of $K = (\text{mol})^{1-n}\,(\text{litre})^{n-1}\,\text{time}^{-1}$

Types of order of reactions :

(I) Zero order reaction :

for $A \rightarrow$ Product

at $t = 0$ C_0

at $t = t$ C_A

$\text{Rate} = K[\text{Reactant}]^0$

i.e., $\frac{dx}{dt} = K$

On integrating, $\frac{x}{t} = K$

or $-\frac{dC_A}{dt} = K[C_A]^0$

on integrating $-C_A = Kt + C$

at $t = 0$, $C_A = C_0$

$\therefore \quad C = -C_0$

$\therefore \quad Kt = C_0 - C_A$

Characteristics : (1) Rate remains constant through out the course of reaction.

(2) Unit of rate constant = mol litre^{-1} time^{-1}.

(3) Half-life period : $t_{1/2} \propto (a)$, where a is initial concentration.

(II) I order reaction :

$$\text{Rate} = K[C]^1$$

$$i.e., \quad \frac{dx}{dt} = K[C]^1 = K[a-x]^1$$

for	A	$\rightarrow$	Product
	a		at $t = 0$
	$(a-x)$		at $t = t$

On integrating, we get $K \times t = 2.303 \log_{10} \frac{a}{a-x}$

Characteristics : (1) Rate continuously decreases with time.

(2) Unit of rate constant : Time^{-1}

(3) Half-life period : $t_{1/2} \propto (a)^0$

i.e., half-life for I order is independent of initial concentration.

(III) II order reaction :

Case I : If one reactant or two reactants with same initial concentration;

For

A	$\longrightarrow$	Products
a		at $t = 0$
$(a-x)$		at $t = t$

$$\text{Rate} = K[C]^2 \quad \text{or} \quad \frac{dx}{dt} = K(a-x)^2$$

On integrating, we get $K \times t = \frac{1}{a} \frac{x}{(a-x)}$

Case II : If reactants are two and initial concentrations are different;

For

	A	+	B	$\longrightarrow$	Products
at $t = t$	$(a-x)$		$(b-x)$		

$$\text{Rate} = K[A]^1[B]^1$$

$$\frac{dx}{dt} = K(a-x)(b-x)$$

On integrating, we get $K \times t = \frac{2.303}{(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

Characteristics : (1) Rate continuously decreases with time.

(2) Unit of rate constant : mol^{-1} litre^1 time^{-1}

(3) Half-life period : $t_{1/2} \propto (a)^{-1}$ or $t_{1/2} \propto 1/a$

Salient features of rate constant and half-life period :

Order of reaction	Half-life	Unit of rate constant
0	$t_{1/2} \propto a$	mol litre^{-1} time^{-1}
1	$t_{1/2} \propto (a)^0$	time^{-1}
2	$t_{1/2} \propto (a)^{-1}$	mol^{-1} litre^1 time^{-1}
3	$t_{1/2} \propto (a)^{-2}$	mol^{-2} litre^2 time^{-1}
n	$t_{1/2} \propto (a)^{1-n}$	mol^{1-n} litre^{n-1} time^{-1}

Experimental methods to determine order of reaction:

(1) By integration method : The experiments are carried out between the required amounts of reactants and products formed are analysed in terms of values as desired in various integrated forms of order of reactions. Using experimental values, rate constant is obtained by using different order rate equations. The one which gives most constant value for rate constant suggests the order of reaction. This is also known as **hit and trial method.** Most of the numericals are based on this method.

(2) Graphical method : Experiments are made to obtain the rates of reactions at different intervals using different amounts of reactants. Now the rates are plotted against $(a-x)^n$ values. The nature of graph suggests order of reaction. In I order reaction straight line is obtained when rate is plotted against $(a-x)$. In zero order reaction a straight line parallel to X-axis is formed.

(3) Time required to complete a definite fraction : As we have,

$$t_{1/m} \propto (a)^{1-n}$$

where n is order of reaction. Experiments are made to study the time required for a definite fraction to be completed using different amounts of reactants and then use of $t_{1/m} \propto (a)^{1-n}$ gives order.

(4) Isolation method : In this method, all the reactants except one are taken in very large excess and order is determined using either of the above methods. Different experiments are made using one by one reactant in small amount and rest all in excess. The sum of all the orders of reactants give order for reaction.

Reversible elementary reactions :

For reversible reaction $A \rightleftharpoons B$

Rate of reaction $= K_f[A] - K_b[B]$ ...(A)

First order opposed by first order :

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$t = 0$	$[A]_0$	0
$t = t$	$[A]_0 - X$	X
$t = eq.$	$[A]_0 - X_{eq.}$	$X_{eq.}$

We can integrate Eq. (A) to have

$$t = \frac{2.303}{(K_f + K_b)} \log \left[\frac{X_{eq.}}{X_{eq.} - X} \right]$$

If $[B] = [B]_0$ at $t = 0$,

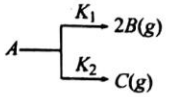
then $t = \frac{2.303}{K_f} \left[\frac{[B]_0 + X_{eq.}}{[A]_0 + [B]_0} \right] \log \left[\frac{X_{eq.}}{X_{eq.} - X} \right]$.

• NUMERICAL PROBLEMS •

1. The reaction $2NO + Br_2 \longrightarrow 2NOBr$, obeys the following mechanism.
   (i) $NO + Br_2 \overset{\text{Fast}}{\rightleftharpoons} NOBr_2$
   (ii) $NOBr_2 + NO \xrightarrow{\text{Slow}} 2NOBr$
   Suggest the rate expression.
2. The thermal decomposition of N_2O_5 occurs in the following steps:
   Step I $N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$
   Step II $N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$
   Overall reaction is $2N_2O_5 \longrightarrow 4NO_2 + O_2$
   Suggest the rate expression.
3. For the reaction $2NO_2 + F_2 \longrightarrow 2NO_2F$, the experimental rate law is $r = K[NO_2][F_2]$. Propose the mechanism of reaction.
4. The reaction $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$ has experimental data that rate $= K[NO_2Cl]$. Propose the mechanism.
5. The decomposition of A and B obeys I order with half-life 54.0 and 18.0 minutes respectively. If $[A]_0 = [B]_0$ then after how much time the ratio of concentration of A and B will be 4 : 1 and 1 : 4 respectively.
6. From the concentrations of R at different times given below, calculate the average rate of the reaction : $R \rightarrow P$ during different intervals of time.

t/s	0	5	10	20	30
$10^3 \times [R]$/ mol L^{-1}	160	80	40	10	2.5

7. The initial concentration of $[I^-]_0$ and $[ClO^-]_0$ are 0.075 M and 0.125 M to carry out a reaction :
   $$ClO^- + I^- \longrightarrow Cl^- + IO^-$$
   and rate $= K[ClO^-][I^-]$. Derive the rate expression in terms of concentration of ClO^- alone at any time.
8. The net rate of reaction for the change :
   $[Cu(NH_3)_4]^{2+} + H_2O \rightleftharpoons [Cu(NH_3)_3H_2O]^{2+} + NH_3$ is,
   $\frac{dx}{dt} = 2.0 \times 10^{-4}[Cu(NH_3)_4]^{2+} - 3.0 \times 10^5 [Cu(NH_3)_3H_2O]^{2+}[NH_3]$ calculate :
   (i) Rate expression for forward and backward reactions.
   (ii) The ratio of rate constant for forward and backward reactions.
   (iii) The direction of reaction in which the above reaction will be more predominant.
9. Gas $A(g)$ shows two parallel path I order reaction as:



   The initial pressure of $A(g)$ in a container of volume V litre is 1 atm. After 10 sec the pressure becomes 1.4 atm and after ∞ time it becomes 1.5 atm. Calculate K_1 and K_2.
10. For a reversible reaction $A \rightleftharpoons B$, if pre-exponential factor is same for both forward and backward reaction, show that $K_C = e^{-\Delta H/RT}$, where ΔH is heat of reaction.
11. The rate constant of a reaction is $1.5 \times 10^7 sec^{-1}$ at 50°C and $4.5 \times 10^7 sec^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a. **(IIT 1998)**
12. The specific rate constant for the decomposition of formic acid is $5.5 \times 10^{-4} sec^{-1}$ at 413 K. Calculate the specific rate constant at 458 K, if the energy of activation is 2.37×10^4 cal mol^{-1}.
13. For a reaction $A_2 + B_2 \longrightarrow 2AB$, evaluate the energy of activation from the following data :

T (in K)	$\frac{1}{T}(K^{-1})$	$\log_{10} K$
500	2×10^{-3}	3.0
200	5×10^{-3}	2.0

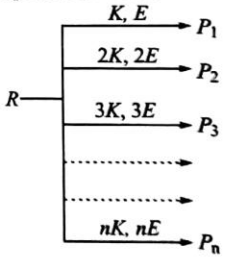
14. Calculate the rate constant and half-life period for first order reaction having the activation energy 39.3 kcal mol^{-1} at 300°C and the frequency constant $1.11 \times 10^{11} sec^{-1}$.
15. A reaction proceeds five times more at 60°C as it does at 30°C. Estimate energy of activation.
16. For two first order reactions having same concentration of A and B at $t = 0$, use the given data to calculate the temperature at which both occurs with same rate.
    Reaction I $A \longrightarrow Z$; $K_1 = 10^{16} e^{\left(-\frac{3000}{T}\right)}$
    Reaction II $B \longrightarrow Y$; $K_2 = 10^{15} e^{\left(-\frac{2000}{T}\right)}$
17. The rate constant of a reaction increases by 7% when its temperature is raised from 300 K to 310 K, while its equilibrium constant increases by 3%. Calculate the activation energy of the forward and reverse reactions.
18. For the reaction $A \rightleftharpoons B$, ΔE for the reaction is –33.0 kJ mol^{-1}. Calculate:
    (a) equilibrium constant K_C for the reaction at 300 K.
    (b) if E_f and E_b are in the ratio 20 : 31, calculate E_f, E_b at 300 K.
    Assuming pre-exponential factor same for forward and backward reactions.
19. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as

well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

20. Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate the activation energy.
21. A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minute, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. **(IIT 1993)**
22. A given sample of milk turns sour at room temperature (20°C) in 64 hour. In a refrigerator at 3°C, milk can be stored three times as long before it sours. Estimate (a) the activation energy for souring of milk, (b) how long it take milk to sour at 40°C?
23. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 s^{-1}$, calculate its rate constant at 318 K and also the energy of activation. **(IIT 1997)**
24. Calculate the factor by which the rate of I order reaction is increased for a temperature rise of 10°C from 25°C to 35°C. The energy of activation is 35 kcal mol^{-1}.
25. A Ist order reaction is 50% complete in 30 minute at 27°C and in 10 minute at 47°C. Calculate the :
    (a) rate constant for reaction at 27°C and 47°C.
    (b) energy of activation for the reaction.
    (c) energy of activation for the reverse reaction if heat of reaction is –50 kJ mol^{-1}.
26. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 minute. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. **(IIT 1995)**
27. The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C; other things being equal?
28. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction, if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1}. **(IIT 2000)**
29. The rate constant for the first order decomposition of a certain reaction is given by the equation,

$$\ln K(sec^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

Calculate :
    (a) the energy of activation.
    (b) the rate constant at 500 K.
    (c) at what temperature will its half-life period be 256 minute? **(IIT July 1997)**
30. For $A + B \longrightarrow C + D$; $\Delta H = 20$ kJ mol^{-1}; the activation energy of the forward reaction is 85 kJ/mol. Calculate activation energy of the reverse reaction.
31. Two reactions (I) $A \rightarrow$ Products (II) $B \rightarrow$ Products follow first order kinetics. The rate of the reaction (I) is doubled when temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minute. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (II) is half that of reaction (I) calculate the rate constant of reaction (II) at 300 K. **(IIT 1992)**
32. In the Arrhenius equation for a certain reaction, the values of A and E_a (energy of activation) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 10 minute? **(IIT 1990)**
33. A compound (R) undergoes parallel path reactions involving n steps as shown below :



Where K and E represents rate constant and energy of activations. Calculate the overall rate constant and overall energy of activation.

34. Two I order reactions having same reactant concentrations proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C.
35. The decomposition of ammonia on platinum surface follow the change,

$$2NH_3 \longrightarrow N_2 + 3H_2$$

    (a) What does $\frac{-d[NH_3]}{dt}$ denote?
    (b) What does $\frac{d[N_2]}{dt}$ and $\frac{d[H_2]}{dt}$ denote?
    (c) If the decomposition is zero order then what are the rate of production of N_2 and H_2, if $K = 2.5 \times 10^{-4} M\, s^{-1}$?

(d) If the rate obeys $-\frac{d[NH_3]}{dt}=\frac{K_1[NH_3]}{1+K_2[NH_3]}$, what will be the order for decomposition of NH_3, if (i) $[NH_3]$ is very very less and (ii) $[NH_3]$ is very very high? K_1 and K_2 are constants.

36. Dinitrogen pentaoxide decomposes as follows :

$$N_2O_5 \longrightarrow 2NO_2+\frac{1}{2}O_2.$$ If,

$$\frac{-d[N_2O_5]}{dt}=K_1[N_2O_5]$$

$$\frac{d[NO_2]}{dt}=K_2[N_2O_5]$$

$$\frac{d[O_2]}{dt}=K_3[N_2O_5]$$

Derive a relation between K_1, K_2 and K_3.

37. The decomposition of ozone occurs as $2O_3(g)\rightarrow 3O_2$, following the rate law :

$$-\frac{d[O_3]}{dt}=K\frac{[O_3]^2}{[O_2]}$$

what are the units of rate and rate constant?

38. The rate law has the form; rate $=K[A][B]^{3/2}$, can the reaction be an elementary process?

39. For the chemical reaction,

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

the rate expression is rate $=K[Br^-][BrO_3^-][H^+]^2$, calculate:

(a) order of reaction.

(b) apparent molecularity of reaction.

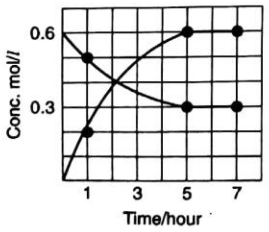
40. In a reaction, $2A\rightarrow$ Products, the concentration of A decreases from 0.5 mol litre^{-1} to 0.4 mol litre^{-1} in 10 minute. Calculate average rate during this interval.

41. The progress of the reaction $A \rightleftharpoons nB$ with time is presented in the figure. Determine :

(i) the value of n,

(ii) the equilibrium constant, K and

(iii) the initial rate of conversion of A. **(IIT 1994)**



42. A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate:

(i) the concentration of oxygen atom needed so that the reaction $O+O_3\rightarrow 2O_2$ having rate constant equal to 1.5×10^7 litre mol^{-1}sec^{-1} can proceed with a rate of 0.15 mol litre^{-1}sec^{-1}.

(ii) the rate of formation of oxygen under this condition.

43. The rate constant for the reaction :

$$CO_2 + OH^- \longrightarrow HCO_3^-$$

in the aqueous solution is 4×10^{-3} litre mol^{-1} sec^{-1}. Calculate the number of mole of CO_2 and OH^- used up per second when $[CO_2]$ and $[OH^-]$ are 10^{-6} and 10^{-1} mol litre^{-1}. Also predict the mole of HCO_3^- formed per second.

44. For a reaction $3A \longrightarrow$ Products, it is found that the rate of reaction doubles, if concentration of A is increased four times, calculate order of reaction.

45. The rate of a reaction starting with initial concentration of $2\times10^{-3}M$ and $1\times10^{-3}M$ are equal to 2.40×10^{-4} Ms^{-1} and 0.60×10^{-4} M sec^{-1} respectively. Calculate the order of reaction w.r.t. reactant and also the rate constant.

46. The reaction $2A+B+C \longrightarrow D+2E$ is found to be I order in A, II order in B and zero order in C.

(a) Write rate expression.

(b) What is the effect on rate on increasing the conc. of A, B and C two times?

47. For $2A+B+\underset{\text{(excess)}}{C} \longrightarrow$ Products, calculate the :

(a) rate expression.

(b) units of rate and rate constant.

(c) effect on rate, if concentration of A is doubled and of B is tripled.

48. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which reaction should be the fastest and is this true for all ranges of concentrations?

49. Find the order of reaction for the rate expression rate $=K[A][B]^{2/3}$. Also suggest the units of rate and rate constant for this expression.

50. The rate law of a chemical reaction given below :

$$2NO + O_2 \longrightarrow 2NO_2$$

is given as rate $=K[NO]^2[O_2]$. How will the rate of reaction change, if the volume of reaction vessel is reduced to 1/4th of its original value?

51. Calculate the order of reaction for which rate becomes half if volume of container having same amount of reactant is doubled. (Assume gaseous phase reaction)

52. The rate of a reaction is given by $\frac{dx}{dt}=\frac{K(a-x)}{1+bx}$, where a is the initial concentration of the reactant and K, b are constants. x is the concentration of product at time t. What is half-life of this reaction?

53. The rate of a first order reaction is 0.04 mol litre^{-1}sec^{-1} at 10 minute and 0.03 mol litre^{-1} at 20 minute after initiation. Find the half-life of the reaction. **(IIT 2001)**

54. The rate law for the following reaction;

Ester $+H^+ \longrightarrow$ Acid + Alcohol, is $\frac{dx}{dt} = K$ (ester) $[H_3O^+]^0$

What would be the effect on rate if :

(a) concentration of ester is doubled?

(b) concentration of H^+ ion is doubled?

55. The rate of change in concentration of C in the reaction $2A + B \longrightarrow 2C + 3D$ was reported as 1.0 mol litre^{-1} sec^{-1}. Calculate the reaction rate as well as rate of change of concentration of A, B and D.

56. Write the rate law expression and find the rate constant of the reaction $A + B \rightarrow$ Product. Also calculate half-life period. **(IIT 2004)**

$[A_0]$ mol litre^{-1}	$[B_0]$ mol litre^{-1}	Rate $[R_0]$ mol litre^{-1}sec^{-1}
0.1	0.2	0.05
0.2	0.2	0.10
0.1	0.1	0.05

57. For the reaction $A + B \longrightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is 1×10^{-4} mol litre^{-1}minute^{-1}. In the second experiment when the initial concentrations of A and B are 0.1 M and 0.3 M, the initial rate is 9.0×10^{-4}mol litre^{-1}minute^{-1}. In the third experiment when the initial concentrations of both A and B are $0.3M$, the initial rate is 2.7×10^{-3} mol litre^{-1}minute^{-1}.

(a) Write rate law for this reaction.

(b) Calculate the value of specific rate constant for this reaction. **(Roorkee 1987)**

58. For the reaction, $2NO + H_2 \rightarrow N_2O + H_2$, the value of $-\frac{dP}{dt}$ was found to be 1.5 Pa s^{-1} for a pressure of 359 Pa of NO and 0.25 Pa s^{-1} for a pressure of 152 Pa of NO. The pressure of H_2 being constant. If pressure of NO was kept constant, the value of $-\frac{dP}{dt}$ was found 1.60 Pa s^{-1} for a pressure of H_2 289 Pa and 0.79 Pa s^{-1} for a pressure of 147 Pa of H_2. Calculate the order of reaction.

59. The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

$[Cl_2]$	[NO]	Initial rate (mol litre^{-1}sec^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order with respect to NO and Cl_2 in the reaction?

(b) Write the rate expression.

(c) Calculate the rate constant.

(d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 M and 0.4 M respectively. **(Roorkee 1993)**

60. The following data are for the reaction $A + B \longrightarrow$ Products:

Conc. of A (M)	Conc. of B (M)	Initial rate (mol L^{-1}s^{-1})
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

(a) What is the order with respect to A and B for the reaction?

(b) Calculate the rate constant.

(c) Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M respectively. **(Roorkee 1995)**

61. The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is,

$2HgCl_2 + K_2C_2O_4 \longrightarrow 2KCl + 2CO_2 + Hg_2Cl_2$

The weights of Hg_2Cl_2 precipitated from different solutions in given time are as:

Time	$HgCl_2$ (mol litre^{-1})	$K_2C_2O_4$ (mol litre^{-1})	Hg_2Cl_2 formed (mol litre^{-1})
60	0.0418	0.404	0.0032
65	0.0836	0.404	0.0068
120	0.0836	0.202	0.0031

Calculate order of reaction.

62. For a gaseous reaction $2A + B_2 \longrightarrow 2AB$, the following rate data were obtained.

Rate of disappearance of B_2 mol litre^{-1}	$[A]$	$[B_2]$
1.8×10^{-3}	0.015	0.15
1.08×10^{-2}	0.090	0.15
5.4×10^{-3}	0.015	0.45

Calculate : (a) the rate constant, (b) rate of formation of AB when,

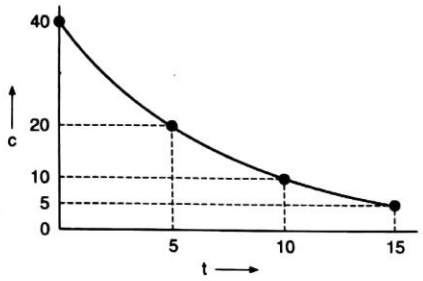
$[A] = 0.02$ and $[B_2] = 0.04$

63. For a reaction at 800°C, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, the following data were obtained.

	$[NO]\times10^{-4}$ mol litre^{-1}	$[H_2]\times10^{-3}$ mol litre^{-1}	$-\frac{1}{2}d[NO]/dt\times10^{-4}$ mol litre^{-1}min^{-1}
(i)	1.5	4.0	4.4
(ii)	1.5	2.0	2.2
(iii)	0.5	2.0	0.24

What is the order of this reaction with respect to NO and H_2? Also calculate rate constant.

64. For a reaction a graph was plotted between reactant concentration C and time t as shown in figure.



Identify the order of the reaction with respect to the reactant. Can the concentration of the reactant be theoretically zero after infinite time?

65. In the decomposition of N_2O_5, the plot between the reciprocal of concentration of the reactant and the time was found to be linear as shown in figure. Determine the order of reaction.

66. What will be the initial rate of a reaction if its rate constant is $10^{-3}\,min^{-1}$ and the concentration of reactant is 0.2 mol dm^{-3}? How much of reactant will be converted into products in 200 minute? **(Roorkee 1992)**

67. The rate constant for an isomerisation reaction, $A \rightarrow B$ is $4.5\times10^{-3}\,min^{-1}$. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 hr. **(IIT 1999)**

68. A substance reacts according to I order kinetics and rate constant for the reaction is $1\times10^{-2}\,sec^{-1}$. If its initial concentration is 1 M,

(a) What is initial rate?

(b) What is rate after 1 minute? **(Roorkee 1993)**

69. Show that for a first order reaction, time required for 99% completion is twice for the time required for the completion of 90% of the reaction.

70. Show that $t_{1/2}$ / $t_{3/4}$ for n^{th} order reaction is a function of 'n' alone. $t_{3/4}$ is the time required for concentration to become 1/4 of original concentration.

71. In a reaction, the decrease in reactant's concentration is 20% in 20 minute and 40% in 40 minute. Calculate order of reaction and rate constant.

72. The rate of a certain reaction depends on concentration according to the equation :

$-\frac{dC}{dt}=\frac{K_1C}{1+K_2C}$, what will be the order of reaction, where (a) concentration is very very high, (b) very very low?

73. The rate expression for a reaction is $\frac{-dC}{dt}=\frac{\alpha\cdot C}{1+\beta C}$ where $\alpha,\beta>0$. Calculate the $t_{1/2}$ for this reaction.

74. For a homogeneous gaseous phase reaction : $2A\rightarrow 3B+C$, the initial pressure of reactant was P° while pressure at time 't' was P. Find the pressure after time $2t$. Assume I order reaction.

75. If a reaction $A \longrightarrow$ Products, the concentrations of reactant A are $C_0, aC_0, a^2C_0, a^3C_0, \ldots$ after time interval, $0, t, 2t, 3t, \ldots$ where a is constant. Given $0<a<1$. Show that the reaction is of I order. Also calculate the relation in K, a and t.

76. Starting with one mole of a compound A, it is found that the reaction is 3/4 completed in 1 hour. Calculate the rate constant if the reaction is of:

(a) I order.

(b) II order.

77. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2(aq.) \longrightarrow N_2O(g)+H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate:

(i) time taken for NH_2NO_2 is decompose 99%.

(ii) volume of dry N_2O produced at this point measured at STP. **(Roorkee 1994)**

78. In I order reaction, the concentrations of reactants 10 and 20 minute after the beginning of reaction corresponds to 13.8 and 8.25 (arbitrary units). Calculate the initial concentrations of the reactants and the velocity constant.

79. Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minute and 73% in 100 minute. **(Roorkee 1990)**

(a) What is the order of reaction?

(b) Calculate velocity constant.

(c) How much will it decompose in 100 minute at the same temperature but at an initial pressure of 600 mm?

80. The decomposition of N_2O_5 according to equation $2N_2O_5(g) \longrightarrow 4NO_2(g)+O_2(g)$ is a first order reaction. After 30 minute from start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of reaction. **(IIT 1991)**

81. At 100°C, a gaseous reaction $A \longrightarrow B+2C$; is observed to be of I order. On starting with pure A, at the end of 14 minute, the total pressure was found to be 264 mm of Hg. After a long time the total pressure of the system was 450 mm of Hg. Calculate :

(a) initial pressure of A.

(b) rate constant of reaction.

(c) half-life period of reaction.

82. Arsine decomposes on heating to give As and H_2. The decomposition studied at constant volume and temperature gives the following data.

T in hr.	0	5.5	6.5	8
P in atm.	0.9654	1.06	1.076	1.1

Calculate velocity constant, assuming first order reaction.

83. The half-life period and initial concentration for a reaction are as follows. What is order of reaction?

Initial concentration	350	540	158
$t_{1/2}$	425	275	941

84. The inversion of cane sugar proceeds with constant half-life of 500 minute at pH = 5 for any concentration of sugar. However, if pH = 6, the half-life changes to 50 minute. Derive the rate law for inversion of cane sugar.

85. Hydrogenation of vegetable ghee at 25°C reduces the pressure of H_2 from 2 atm to 1.2 atm in 50 minute. Calculate the rate of reaction in terms of change of :

(a) pressure per minute.

(b) molarity per second.

86. The following data were obtained for the decomposition of NO in contact with gold surface at 900°C. Find the O.R.

Time (in minute)	15	30	45	65	80
% decomposition	17	32	44.5	57	65

87. Ethylene is produced by :

$$\underset{\text{Cyclobutane}}{C_4H_8} \xrightarrow{\Delta} 2C_2H_4$$

The rate constant is $2.48\times10^{-4}\,sec^{-1}$. In what time will the molar ratio of the ethylene to cyclobutane in reaction mixture attain the value (a) 1, (b) 100?

88. A drop of solution (volume 0.05 mL) contains 3.0×10^{-6} mole of H^+. If the rate constant of disappearance of H^+ is 1.0×10^{7} mol litre^{-1}sec^{-1}. How long would it take for H^+ in drop to disappear?

89. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is of I order. After 55 sec at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate :

(a) The rate constant.

(b) Pressure of Cl_2O_7 after 100 sec.

90. While studying the decomposition of $N_2O_5(g)$ it is observed that a plot of logarithm of its partial pressure *versus* time is linear. What kinetic parameter can be obtained from this?

91. The following data represent for the decomposition of NH_4NO_2 in aqueous solution.

Time in minute	10	15	20	25	∞
Volume of N_2 (in mL)	6.25	9.0	11.40	13.65	33.05

(a) Show that reaction is of I order.

(b) Calculate velocity constant.

92. Derive O.R. for the decomposition of H_2O_2 from the following data.

Time in minute	0	10	20	30
Volume of $KMnO_4$ needed for H_2O_2	25	16	10.5	7.09

93. Derive the O.R. for decomposition of H_2O_2 from the following data.

Time in minute	10	15	20	25	∞
Volume of O_2 given by H_2O_2	6.30	8.95	11.40	13.5	35.75

94. The kinetics of hydrolysis of methyl acetate in excess dilute HCl at 25°C were followed by withdrawing 2 mL of the reaction mixture at intervals of (t), adding 50 mL water and titrating with baryta water. Determine the velocity constant of hydrolysis.

t (in minute)	0	75	119	259	∞
Titre value (in mL)	19.24	24.20	26.60	32.23	42.03

95. In the inversion of cane sugar in presence of an acid, the following polarimeter readings are obtained.

Time in minute	0	30	90	230	∞
Rotation in degree	+46.75	+41.0	+30.75	+12.75	−18.75

Calculate rate constant.

96. The gas phase decomposition of dimethyl ether follows first order kinetics,

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 minute. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minute? Assume ideal gas behaviour. **(IIT 1993)**

97. The reaction $A + OH^- \longrightarrow$ Products, obeys rate law expression as,

$$\frac{-d[A]}{dt} = k[A][OH^-]$$

If initial concentrations of $[A]$ and $[OH^-]$ are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C, calculate the rate constant for the reaction.

98. For the non-equilibrium process, $A + B \rightarrow$ Products, the rate is first order with respect to A and second order reaction with respect to B. If 1.0 mole each of A and B are introduced into 1 litre vessel and the initial rate were 1.0×10^{-2} mol/litre-sec, calculate the rate when half of the reactants have been used.

99. Two reactants A and B separately shows two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half-lives, compare their rates (a) at the start of reaction (b) after the lapse of one half-life.

100. A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as:

$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$

The rate constant of decomposition is $4.78 \times 10^{-3}\,min^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hour of initiation of decomposition. Assume composition of gas present and gas diffused remains same.

101. Some $PH_3(g)$ is introduced into a flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant. **(Roorkee 2001)**

Time (sec.)	0	60	120	∞
P (mm Hg)	262.40	272.90	275.51	276.40

102. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volume was left open. Due to this some H_2O_2 decomposed. To determine the new volume strength after 6 hr, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.25 M $KMnO_4$ acidified solution. Calculate the rate constant for the decomposition of H_2O_2.

103. A certain reaction B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing agent which reacts only with B^{n+} and $B^{(n+4)+}$. In the process it converts B^{n+} to $B^{(n+2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of reagent consumed is 25 mL and at $t = 10$ minute, the volume used is 32 mL. Calculate the rate constant for the conversion of B^{n+} of $B^{(n+4)+}$ assuming it to be a first order reaction.

104. The reaction $CH_3COF + H_2O \rightarrow CH_3COOH + HF$ has been studied under the following initial conditions,

Case I	Case II
$[H_2O]_0 = 1.0\,M$	$[H_2O]_0 = 0.02\,M$
$[CH_3COF]_0 = 0.01\,M$	$[CH_3COF]_0 = 0.80\,M$

The variation of concentration with time were noted as:

Case I :		**Case II :**	
t/ min	$[CH_3COF]$	t/ min	$[H_2O]$
0	0.01000	0	0.0200
10	0.00857	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Determine the order of reaction and rate constant of reaction.

105. Two second order reactions given below having identical frequency factors :

(i) $A \longrightarrow$ Product

(ii) $B \longrightarrow$ Product

The E_a for first reaction is 10.46 kJ/mol^{-1} more than that of B. At 100°C, the reaction (i) is 30% completed after 60 minute when initial concentration of A is 0.1 mol dm^{-3}. How long will it take for reaction (ii) to reach 70% completion at the same temperature if initial concentration of B is 0.05 mol litre^{-1}?

106. The reaction : $OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^-$ takes place in following steps:

(i) $OCl^- + H_2O \underset{K_2}{\overset{K_1}{\rightleftharpoons}} HOCl + OH^-$ (fast)

(ii) $I^- + HOCl \xrightarrow{K_3} HOI + Cl^-$ (slow)

(iii) $OH^- + HOI \underset{K_2'}{\overset{K_1'}{\rightleftharpoons}} H_2O + OI^-$ (fast)

Write the rate expression in terms of rate of consumption of I^-.

107. The reaction : $CO + Cl_2 \longrightarrow COCl_2$ has the following mechanism. Derive the rate expression:

(i) $Cl_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast)

(ii) $Cl + CO \underset{K_2'}{\overset{K_1'}{\rightleftharpoons}} COCl$ (fast)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

108. What will be the order of reaction given below?

$NH_4CNO \longrightarrow NH_2CONH_2$

The reaction is completed in three steps as:

(i) $NH_4CNO \rightleftharpoons NH_4NCO$ (fast equilibrium)

(ii) $NH_4NCO \rightleftharpoons NH_3 + H-N=C=O$ (fast equilibrium)

(iii) $NH_3 + H-N=C=O \longrightarrow NH_2CONH_2$ (slow)

109. For the reversible reaction in equilibrium : $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$.

The values of K_1 and K_2 are 2×10^{-3} mol L^{-1}sec^{-1} and 3×10^{-3} sec^{-1} respectively. If we add 0.5 moles of B in the equilibrium mixture, initially containing 2 moles of A. Calculate the time taken for concentration of B to become equal to 3/4 of the concentration of A at initial equilibrium. The volume of mixture is 1 L and remains constant.

110. For a reversible first order reaction,

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B;\ K_f = 10^{-2}\,sec^{-1}$$

and $\frac{B_{eq.}}{A_{eq.}} = 4$; If $A_0 = 0.01\,ML^{-1}$ and $B_0 = 0$, what will be concentration of B after 30 sec?

111. 8 mole of an element undergoes decomposition in three parallel path following I order reaction giving three new elements B, C and D with rate constant 2×10^{-3}, 3×10^{-3} and 1.93×10^{-3} sec^{-1} respectively. What will be the mole of B after 100 sec.

112. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is : **[JEE (Advanced II) 2015]**

SOLUTIONS (Numerical Problems)

1. The rate expression is derived by (ii) step of mechanism, a slower step, thus,

$$\text{rate} = K[NOBr_2][NO] \quad \ldots(1)$$

However, $NOBr_2$ is an intermediate and thus its concentration should be replaced from Eq. (1)

For step (1), equilibrium constant $K_C = \dfrac{[NOBr_2]}{[NO][Br_2]}$

$$\therefore \quad [NOBr_2] = K_C[NO][Br_2] \quad \ldots(2)$$

Thus, by Eqs. (1) and (2)

$$\text{rate} = K \cdot K_C[NO]^2[Br_2]$$

$$\text{rate} = \boldsymbol{K'[NO]^2[Br_2]}$$

2. From the slow step, we can have

$$\text{rate} = \boldsymbol{K[N_2O_5]}$$

3. The rate $= K[NO_2][F_2]$ implies that slow step of reaction involves only one molecule of each reacting species, thus we can have the mechanism as :

$$NO_2 + F_2 \xrightarrow{\text{Slow}} NO_2F + F$$

$$NO_2 + F \xrightarrow{\text{Fast}} NO_2F$$

$$\therefore \text{Overall reaction is } 2NO_2 + F_2 \longrightarrow 2NO_2F$$

4.

$$NO_2Cl \xrightarrow{\text{Slow}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{\text{Fast}} NO_2 + Cl_2$$

$$\text{Overall reaction is } 2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

5.

$$[A]_t = [A]_0 \cdot e^{-K_1 t}$$

$$[B]_t = [B]_0 \cdot e^{-K_2 t}$$

$$\therefore \quad \frac{[A]_t}{[B]_t} = e^{(-K_1+K_2)\cdot t}$$

$$4 = e^{(K_2-K_1)\cdot t} \qquad \text{if } \frac{[A]_t}{[B]_t} = 4$$

or $(K_2 - K_1)\cdot t = \ln 4$

$$\therefore \quad t = \frac{\ln 4}{K_2 - K_1} = \frac{1.386}{\frac{0.693}{18} - \frac{0.693}{54}} = \boldsymbol{54 \text{ minute}}$$

$\dfrac{[A]_t}{[B]_t} = \dfrac{1}{4}$ is not possible because B decays fastly.

6. Average rate $= -\dfrac{[R_2 - R_1]\times 10^{-3}}{[t_2 - t_1]}$

After 5 sec $r_1 = -\dfrac{[80-160]\times 10^{-3}}{5} = \boldsymbol{16\times 10^{-3}\ ms^{-1}}$

After 10 sec $r_2 = -\dfrac{[40-80]\times 10^{-3}}{5} = \boldsymbol{8\times 10^{-3}\ ms^{-1}}$

After 20 sec $r_3 = -\dfrac{[10-40]\times 10^{-3}}{10} = \boldsymbol{3\times 10^{-3}\ ms^{-1}}$

After 30 sec $r_4 = -\dfrac{[2.5-10]\times 10^{-3}}{10} = \boldsymbol{0.75\times 10^{-3}\ ms^{-1}}$

7. The reaction suggest that 1 mole of ClO^- reacts with 1 mole of I^- at any time. Thus, at any time after the reaction begins

$$\Delta[I^-] = 0.075 - [I^-]_{left}$$

$$\Delta[ClO^-] = 0.125 - [ClO^-]_{left}$$

Also $\Delta[I^-] = \Delta[ClO^-]$ (∵ 1 : 1 ratio)

$$\therefore \quad 0.075 - [I^-]_{left} = 0.125 - [ClO^-]_{left}$$

or $[I^-]_{left} = [ClO^-]_{left} - 0.050$

Rate at any time $= K[ClO^-]_{left} \times [I^-]_{left}$

$$= K[ClO^-]_{left} \times ([ClO^-]_{left} - 0.050)$$

8. (i) Rate of forward reaction

$$= \boldsymbol{2.0\times 10^{-4}[Cu(NH_3)_4]^{2+}[H_2O]}$$

Rate of backward reaction

$$= \boldsymbol{3.0\times 10^{5}[Cu(NH_3)_3H_2O]^{2+}[NH_3]}$$

(ii) Also, $K_f = 2.0\times 10^{-4}$

$K_b = 3.0\times 10^5$

$$\frac{K_f}{K_b} = \frac{2.0\times 10^{-4}}{3.0\times 10^5} = \boldsymbol{6.6\times 10^{-10}}$$

(iii) More predominant reaction is **backward reaction.**

9.

$$\frac{-d[B]}{dt} = K_1[A]$$

$$\frac{-d[C]}{dt} = K_2[A]$$

$$\therefore \quad \frac{[B]}{[C]} = \frac{K_1}{K_2}$$

Let after ∞ time pressure equivalent to P' shows dissociation to B and $1-P'$ to C

$$\therefore \quad 2P' + 1 - P' = 1.5$$

$$\therefore \quad P' = 0.5 \text{ atm}$$

$$\therefore \quad \frac{K_1}{K_2} = \frac{2P'}{1-P'} = \frac{1}{0.5} = 2$$

i.e., 2 : 1 is the ratio for the decomposition to B : C.

Now,

A	$\longrightarrow$	$2B$	+	C
1		0		0
$1-a$		$\frac{2\times 2a}{3}$		$\frac{1\times a}{3}$

$$\therefore \quad 1 - a + \frac{4a}{3} + \frac{a}{3} = 1.4 \quad \therefore \quad a = 0.6$$

Also, $K_{av} = \dfrac{2.303}{10}\log\dfrac{1}{0.4} = 0.092$

$K_{av} = K_1 + K_2$

$0.092 = 2K_2 + K_2$

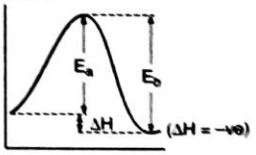
$$\therefore \quad K_2 = 0.03 \quad K_1 = 0.062$$

10.

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$K_f = Ae^{-E_a/RT}$

$K_b = Ae^{-E_b/RT}$



$\therefore \quad K_{eq.} = \dfrac{K_f}{K_b} = e^{(E_b - E_a)/RT} = e^{-\Delta H/RT}$

$(\because \Delta H = E_a - E_b)$

11. $2.303 \log_{10} \dfrac{K_2}{K_1} = \dfrac{E_a}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$\therefore \quad 2.303 \log_{10} \dfrac{4.5\times10^7}{1.5\times10^7} = \dfrac{E_a}{8.314}\left[\dfrac{373-323}{373\times323}\right]$

$\therefore \quad E_a = \mathbf{2.2\times10^4\ J\ mol^{-1}}$

Now, $K = Ae^{-E_a/RT} \quad \therefore \ 4.5\times10^7 = Ae^{-\frac{2.2\times10^4}{8.314\times373}}$

$\therefore \quad A = \mathbf{5.42\times10^{10}}$

12. Given,

$K_2 = ?, \qquad T_2 = 458\ K,$

$K_1 = 5.5\times10^{-4}, \qquad T_1 = 413\ K,$

$R = 1.987\ cal, \qquad E_a = 2.37\times10^4\ cal\ mol^{-1}$

$\because \quad 2.303 \log_{10} \dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2 - T_1]}{T_1 T_2}$

$2.303 \log_{10} \dfrac{K_2}{5.5\times10^{-4}} = \dfrac{2.37\times10^4}{1.987}\left[\dfrac{458-413}{458\times413}\right]$

$\therefore \quad K_2 = \mathbf{9.38\times10^{-3}\ sec^{-1}}$

13. $\because \quad \log_{10} K = \log_{10} A - \dfrac{E_a}{2.303RT}$

or $\log_{10}$ *vs.* $\dfrac{1}{T}$ graph is linear with slope, $-\dfrac{E_a}{2.303R}$

$\therefore \quad \text{Slope} = -\dfrac{E_a}{2.303\times R} = \dfrac{(3.0-2.0)}{(2\times10^{-3} - 5\times10^{-3})}$

or $\dfrac{E_a}{2.303\times2} = \dfrac{1}{3\times10^{-3}}$

or $E_a = \mathbf{1.54\times10^3\ cal = 15.4\ kcal}$

14. Given,

$A = 1.11\times10^{11}\ sec^{-1} \qquad E_a = 39.3\times10^3\ cal\ mol^{-1},$

$R = 1.987\ cal, \qquad T = 573\ K$

$\because \quad K = Ae^{-E_a/RT}$

$\therefore \quad \ln K = \ln A - \dfrac{E_a}{RT}$

or $\log_{10} K = \log_{10} A - \dfrac{E_a}{2.303RT}$

$\log_{10} K = \log_{10} 1.11\times10^{11} - \dfrac{39.3\times10^3}{2.303\times1.987\times573}$

$\therefore \quad K = \mathbf{1.14\times10^{-4}\ sec^{-1}}$

Also, $t_{1/2} = \dfrac{0.693}{1.14\times10^{-4}} = \mathbf{6078\ sec}$

15. Given, $T_2 = 60+273 = 333\ K, \quad T_1 = 30+273 = 303\ K,$

$R = 1.987\times10^{-3}$ kcal

$\because \quad r = k[\text{Reactant}]^n \qquad$ (at a temperature T)

$\therefore \quad \dfrac{r_2}{r_1} = \dfrac{K_2}{K_1} \qquad$ (at temp. T_2 and T_1)

$\because \quad \dfrac{r_2}{r_1} = 5 \qquad \therefore \ \dfrac{K_2}{K_1} = 5$

$\because \quad 2.303 \log_{10} \dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2 - T_1]}{T_1 T_2}$

$\therefore \quad 2.303 \log_{10} 5 = \dfrac{E_a}{10^{-3}\times1.987}\left[\dfrac{333-303}{333\times303}\right]$

$\therefore \quad E_a = \mathbf{10.757\ kcal\ mol^{-1}}$

16. $r_1 = K_1[A]$

and $r_2 = K_2[B]$

Since, $[A] = [B], \quad r_1 = r_2$ when $K_1 = K_2$

Thus, $10^{16} e^{\left(-\frac{3000}{T}\right)} = 10^{15} e^{\left(-\frac{2000}{T}\right)}$

or $16 - \dfrac{3000}{T\times2.303} = 15 - \dfrac{2000}{T\times2.303}$

$1 = \dfrac{1000}{T\times2.303}$

or $T = \dfrac{1000}{1\times2.303} = \mathbf{434.22\ K}$

17. Rate constant at 300 K = k

$\therefore \quad$ Rate constant at 310 K $= k + \left[k\times\dfrac{7}{100}\right] = 1.07k$

Thus, $2.303 \log \dfrac{k_2}{k_1} = \dfrac{E_a^f}{R}\dfrac{[T_2 - T_1]}{T_2 T_1}$

$2.303 \log \dfrac{1.07k}{k} = \dfrac{E_a^f}{2}\left[\dfrac{310-300}{310\times300}\right]$

$\therefore \quad E_a^f = \mathbf{1258.68\ cal}$

Now, equilibrium constant at 300 K = K'

Equilibrium constant at 310 K $= K' + \dfrac{3}{100}\times K' = 1.03\,K'$

Using $2.303 \log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$2.303 \log \dfrac{1.03K'}{K'} = \dfrac{\Delta H}{2}\left[\dfrac{310-300}{310\times300}\right]$

$\therefore \quad \Delta H = 549.89\ cal$

Since, $\Delta H = E_a^f - E_a^b$

$\therefore \quad 549.89 = 1258.68 - E_a^b$

$\therefore \quad E_a^b = \mathbf{708.79\ cal}$

18. Given, $\Delta H = E_f - E_b = -33\ kJ$



(a) $K_f = Ae^{-E_f/RT}$

$K_b = Ae^{-E_b/RT}$

$\therefore \quad K_C = \dfrac{K_f}{K_b} = e^{[E_b - E_f]/RT}$

$= e^{\frac{33\times10^3}{8.314\times300}}$

$= \mathbf{5.572\times10^5}$ at 300 K

(b) Given, $\dfrac{E_f}{E_b} = \dfrac{20}{31}$ and $E_f - E_b = -33\ kJ$

$\therefore \quad E_f - \dfrac{31}{20}E_f = -33\ kJ$

$\therefore \quad E_f = \dfrac{33\times20}{11} = \mathbf{60\ kJ}$ and $E_b = \mathbf{+93\ kJ}$

19. $K = Ae^{-E_a/RT}$

For methyl nitrite $K_1 = 10^{13}\ e^{[-152300/(8.314\times T)]}$

For ethyl nitrite $K_2 = 10^{14}\ e^{[-157700/(8.314\times T)]}$

if $K_1 = K_2$, then

$$10^{13}\ e^{[-152300/(8.314\times T)]} = 10^{14}\ e^{[-157700/(8.314\times T)]}$$

$$10 = e^{(+157700-152300)/(8.314\times T)}$$

or $$2.303\log_{10} = \frac{157700-152300}{8.314\times T} \quad \therefore\ T = \mathbf{282\ K}$$

20. Given, $\frac{K_2}{K_1} = 1.75$

$T_1 = 25°C = 25+273 = 298\ K$,

$T_2 = 35°\ C = 35+273 = 308\ K$

(Since, temperature coefficient is ratio of rate constants at 35°C and 25°C respectively.)

$$\because \quad 2.303\log_{10}\frac{K_2}{K_1} = \frac{E_a}{R}\frac{[T_2-T_1]}{T_1T_2}$$

$$\therefore \quad 2.303\log_{10}1.75 = \frac{E_a}{1.987}\frac{[308-298]}{308\times298}$$

$$\therefore \quad E_a = \frac{2.303\times308\times298\times1.987}{10}\times\log 1.75\ \text{cal mol}^{-1}$$

$$E_a = \mathbf{10.27\ kcal\ mol^{-1}}$$

21. Given, $A \longrightarrow B$

and 20% solution of A decomposes 25% in 20 minute at 25°C

$\therefore$ Initial amount $a = 20$

$\therefore$ Amount left $(a-x) = 20\times\frac{75}{100} = 15$

$$\therefore \quad K_{25} = \frac{2.303}{20}\log_{10}\frac{20}{15} \quad (\because\ t = 20\,\text{minute})$$

$$= 0.0144\ \text{minute}^{-1}$$

Now, $$2.303\log_{10}\frac{K_{40}}{K_{25}} = \frac{E_a}{R}\frac{[T_2-T_1]}{T_1T_2}$$

$$\therefore \quad 2.303\log_{10}\frac{K_{40}}{K_{25}} = \frac{70\times10^3}{8.314}\left[\frac{313-298}{313\times298}\right]$$

$$\frac{K_{40}}{K_{25}} = 3.872$$

$$\therefore \quad K_{40} = 0.05575\ \text{min}^{-1} \quad (\because\ K_{25} = 0.0144)$$

Now suppose amount m is left in 30% solution in 20 minute at 40°C.

$$K_{40} = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$0.05575 = \frac{2.303}{20}\log_{10}\frac{30}{m}$$

$$\therefore \quad m = 9.838$$

$$\therefore \quad \%\ \text{decomposition} = \frac{(a-m)}{a}\times100$$

$$= \frac{30-9.838}{30}\times100 = \mathbf{67.21\%}$$

22. Given, $\frac{K_{293}}{K_{276}} = 3$; $T_2 = 293\,K$ and $T_1 = 276\,K$

(a) $$2.303\log_{10}\frac{K_2}{K_1} = \frac{E_a}{R}\frac{[T_2-T_1]}{T_1T_2} \qquad (R = 2\,\text{cal})$$

$$\therefore \quad 2.303\log_{10}3 = \frac{E_a}{2}\frac{[293-276]}{293\times276}$$

$$\therefore \quad E_a = 10453.95\,\text{cal} = \mathbf{10.454\ kcal}$$

(b) Also, $$2.303\log_{10}\frac{K_3}{K_2} = \frac{E_a}{R}\frac{[T_3-T_2]}{T_3T_2}$$

This time, $E_a = 10.454$ kcal; $T_3 = 313\,K$ and $T_2 = 293\,K$

$$\therefore \quad 2.303\log_{10}\frac{K_3}{K_2} = \frac{10.454\times10^3}{2}\frac{[313-293]}{313\times293}$$

$$\therefore \quad \frac{K_3}{K_2} = 3.12$$

Now, $$\frac{K_3}{K_2} = \frac{t_2}{t_3} \quad \because\ K \propto \frac{1}{\text{time}}$$

Also if milk is not soured up to 64 hr at 20°C, it will not sour up to 192 hr at 3°C. Similarly we can have

$$t_3 = t_2\times\frac{K_2}{K_3} = 64\times\frac{1}{3.12} = \mathbf{20.5\ hr}$$

23. Given, $$t = \frac{2.303}{K_{298}}\log_{10}\frac{100}{90} = \frac{2.303}{K_{308}}\log_{10}\frac{100}{75}$$

$$\therefore \quad \frac{K_{308}}{K_{298}} = 2.73$$

Also, $$2.303\log_{10}\frac{K_{308}}{K_{298}} = \frac{E_a}{R}\frac{[T_2-T_1]}{T_1T_2}$$

$$\therefore \quad 2.303\log_{10}2.73 = \frac{E_a}{8.314}\times\frac{10}{298\times308}$$

$$\therefore \quad E_a = 76.6227\ \text{kJ mol}^{-1} = \mathbf{18.33\ kcal\ mol^{-1}}$$

Now, $$K = Ae^{-E_a/RT}$$

$$K_{318} = 3.56\times10^9\times e^{-76622.7/(8.314\times318)}$$

$$= 3.56\times10^9\times2.59\times10^{-13}$$

$$= \mathbf{9.22\times10^{-4}\ sec^{-1}}$$

24. Given,

$T_2 = 273+35 = 308\ K$, $T_1 = 273+25 = \mathbf{298\,K}$

$E_a = 35\times10^3\,\text{cal mol}^{-1}$, $R = 1.987$ cal

$$\because \quad 2.303\log_{10}\frac{K_2}{K_1} = \frac{E_a}{R}\frac{[T_2-T_1]}{T_1T_2}$$

$$\therefore \quad 2.303\log_{10}\frac{K_2}{K_1} = \frac{35\times10^3}{1.987}\frac{[308-298]}{308\times298}$$

$$\therefore \quad \frac{K_2}{K_1} = 6.812 \text{ or } K_2 = 6.812\times K_1$$

$\therefore$ The factor by which the rate constant changes is **6.812.**

$\because$ Rate $= K[\ ]$

$\therefore$ The factor by which rate changes is also **6.812.**

25. For I order reaction, $K = \frac{0.693}{t_{1/2}}$

(a) $\therefore$ At 27°C $K_1 = \frac{0.693}{30} = 2.31\times10^{-2}\ \text{minute}^{-1}$

At 47°C $K_2 = \frac{0.693}{10} = 6.93\times10^{-2}\ \text{minute}^{-1}$

(b) Now, $$2.303\log_{10}\frac{K_2}{K_1} = \frac{E_a}{R}\frac{[T_2-T_1]}{T_1T_2}$$

$\therefore\ 2.303\log_{10}\dfrac{6.93\times10^{-2}}{2.31\times10^{-2}}=\dfrac{E_a}{8.314}\times\dfrac{[320-300]}{320\times300}$

$\therefore\ E_a = 43850\ \text{J mol}^{-1}$ or $E_a = \mathbf{43.85\ kJ\ mol^{-1}}$

(c) For a reaction $E_{a\,F.R.} - E_{a\,B.R.} = \Delta H$

$\therefore\ 43.85 - E_{a\,B.R.} = -50.0$

or $E_{a\,B.R.} = 43.85 + 50.0 = \mathbf{93.85\ kJ\ mol^{-1}}$

26. $K_1 = 0.693/360\ \text{min}^{-1}$ at 653 K and

$E_a = 200\times10^3$ J, $K_2 = ?$ at 723 K, $R = 8.314$ J

$\therefore$ From $2.303\log_{10}(K_2/K_1) = (E_a/R)[(T_2-T_1)/(T_1T_2)]$

$K_2 = 0.068\ \text{min}^{-1}$

Now, $t = \dfrac{2.303}{0.068}\log_{10}\dfrac{100}{25} = \mathbf{20.39\ minute}$

27. $\because\ K = Ae^{-E_a/RT}$

Case I. $K_1 = Ae^{-100/RT}$

Case II. $K_2 = Ae^{-25/RT}$

$\therefore\ \dfrac{K_1}{K_2} = \dfrac{e^{-100/RT}}{e^{-25/RT}} = e^{-75/RT}$

or $\log_e\dfrac{K_2}{K_1} = \log e^{75/RT}$ (ΔH in kJ)

$\log_e\dfrac{K_2}{K_1} = \dfrac{75}{RT} = \dfrac{75\times10^3}{8.314\times293}$ (ΔH in J)

$\dfrac{K_2}{K_1} = 2.35\times10^{13}$

Since, $r = K[\ ]^n$ $\because$ n and [ ] are same for Case I and II.

$\therefore\ \dfrac{r_2}{r_1} = \dfrac{K_2}{K_1} = \mathbf{2.35\times10^{13}}$

28. Let E_a and E_a' be the energy of activation in presence and absence of catalyst for hydrogenation reaction, then

$K = Ae^{-E_a/RT}$

In presence of catalyst: $K_1 = Ae^{-E_a/(R\times500)}$

In absence of catalyst: $K_2 = Ae^{-E_a'/(R\times400)}$

Given, the two rates are same, *i.e.*, $r_1 = r_2$; $\therefore\ K_1 = K_2$

Therefore, $e^{-E_a/(R\times500)} = e^{-E_a'/(R\times400)}$

or $\dfrac{E_a}{R\times500} = \dfrac{E_a'}{R\times400}$

or $\dfrac{E_a}{500} = \dfrac{E_a-20}{400}$ $\because\ E_a - E_a' = 20$

$\therefore\ E_a = \mathbf{100\ kJ\ mol^{-1}}$

29. (a) Given, $\ln K = 14.34 - \dfrac{1.25\times10^4}{T}$

Also we have $\ln K = \ln A - \dfrac{E_a}{RT}$

Therefore, comparing these two

$\dfrac{E_a}{R} = 1.25\times10^4$

$\therefore\ E_a = 1.25\times10^4\times R\ \text{cal mol}^{-1}$

$= 1.25\times10^4\times1.987\ \text{cal mol}^{-1}$

$E_a = \mathbf{24.83\ kcal\ mol^{-1}}$

(b) $\ln K = 14.34 - \dfrac{1.25\times10^4}{500}$ (since $T = 500$ K)

$\therefore\ K = \mathbf{2.35\times10^{-5}\ sec^{-1}}$

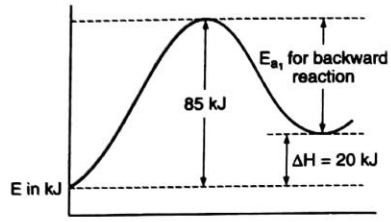
(c) $K = \dfrac{0.693}{256\times60}$

$\therefore\ \ln\dfrac{0.693}{256\times60} = 14.34 - \dfrac{1.25\times10^4}{T}$

or $-10.00 = 14.34 - \dfrac{1.25\times10^4}{T}$

$\therefore\ T = \mathbf{513\ K}$

30.



ΔH of forward reaction = 20 kJ mol^{-1}

Energy of activation for forward reaction

$(E_a) = 85$ kJ mol^{-1}

$\therefore$ Energy of activation for backward reaction

$= E_a - \Delta H$

$= 85 - 20 = \mathbf{65\ kJ\ mol^{-1}}$

31. (I) $A \longrightarrow$ Products

(II) $B \longrightarrow$ Products

$\because\ t_{1/2}$ for (I) at 310 K = 30 minute

$\therefore\ K_1 \text{ at } 310 = \dfrac{0.693}{30} = 0.0231\ \text{min}^{-1}$ ...(1)

$\because$ Rate $= K[\ ]$

and both reactions are of I order

Also given, $\dfrac{K_{\text{I}} \text{ at } 310}{K_{\text{I}} \text{ at } 300} = 2$ ...(2)

Also given, $\dfrac{K_{\text{II}} \text{ at } 310}{K_{\text{I}} \text{ at } 310} = 2$ ...(3)

Also we have, $\dfrac{E_{a_{\text{II}}}}{E_{a_{\text{I}}}} = \dfrac{1}{2}$ ...(4)

For I: $2.303\log_{10}\dfrac{K_{\text{I}} \text{ at } 310}{K_{\text{I}} \text{ at } 300} = \dfrac{E_{a_{\text{I}}}}{R}\left[\dfrac{310-300}{310\times300}\right]$ ...(5)

For II: $2.303\log_{10}\dfrac{K_{\text{II}} \text{ at } 310}{K_{\text{II}} \text{ at } 300} = \dfrac{E_{a_{\text{II}}}}{R}\left[\dfrac{310-300}{310\times300}\right]$ ...(6)

Dividing Eq. (5) by (6),

$\therefore\ \dfrac{\log_{10}\dfrac{K_{\text{I}} \text{ at } 310}{K_{\text{I}} \text{ at } 300}}{\log_{10}\dfrac{K_{\text{II}} \text{ at } 310}{K_{\text{II}} \text{ at } 300}} = \dfrac{E_{a_{\text{I}}}}{E_{a_{\text{II}}}} = 2$ By Eq. (4) ...(7)

or $\log_{10}\dfrac{K_{\text{I}} \text{ at } 310}{K_{\text{I}} \text{ at } 300} = 2\log_{10}\left[\dfrac{K_{\text{II}} \text{ at } 310}{K_{\text{II}} \text{ at } 300}\right]$

or $$\frac{K_I \text{ at } 310}{K_I \text{ at } 300} = \left[\frac{K_{II} \text{ at } 310}{K_{II} \text{ at } 300}\right]^2 \quad ...(8)$$

By Eqs. (2) and (8),

or $$\left[\frac{K_{II} \text{ at } 310}{K_{II} \text{ at } 300}\right]^2 = 2$$

or $$K_{II} \text{ at } 310\text{ K} = \sqrt{2} K_{II} \text{ at } 300\text{ K} \quad ...(9)$$

By Eqs. (3) and (9),

$$2 \times K_I \text{ at } 310\text{ K} = \sqrt{2}\,(K_{II} \text{ at } 300\text{ K}) \quad ...(10)$$

$$K_{II} \text{ at } 300\text{ K} = \frac{2 \times K_1 \text{ at } 310}{\sqrt{2}}$$

By Eqs. (1) and (10),

$$K_{II} \text{ at } 300\text{ K} = \sqrt{2} \times 0.0231$$

$$K_{II} \text{ at } 300\text{ K} = 3.27 \times 10^{-2} \text{ min}^{-1}$$

$$= \mathbf{0.0327\ min^{-1}}$$

32. Given,

$K = ?$ $\quad A = 4 \times 10^{13} \text{ sec}^{-1}$

$E_a = 98.6 \times 10^3 \text{ J mol}^{-1}$ $\quad t_{1/2} = 10 \times 60 \text{ sec}$

$\because \quad K = Ae^{-E_a/RT} \quad \therefore K = 4 \times 10^{13}\, e^{-(98.6 \times 10^3)/8.314 \times T}$

Now for I order reaction, $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{600} \text{ sec}^{-1}$

$$\therefore \quad \frac{0.693}{600} = 4 \times 10^{13}\, e^{-(98.6 \times 10^3)/8.314 \times T}$$

or $$\log_e \frac{0.693}{600} = \log_e 4 \times 10^{13} - \frac{98.6 \times 10^3}{8.314 \times T}$$

or $$\log_{10} \frac{0.693}{600} = \log_{10} 4 \times 10^{13} - \frac{98.6 \times 10^3}{8.314 \times 2.303 \times T}$$

$$\therefore \quad T = \mathbf{311.35\ K}$$

33. In parallel path reactions, rate constant are additive. Thus,

$$K_{AV} = K_1 + K_2 + ... + K_n$$

$$K_{AV} = K + 2K + ... + nK = \frac{n}{2}(n+1)K$$

$$\because \quad K = Ae^{-E_a/RT}$$

$$\therefore \quad K_{AV} = A_1 e^{-E/RT} + 2A_2 \times e^{-2E/RT} + ... + nA_n \times e^{-nE/RT} \quad ...(i)$$

$$A_{AV} \times e^{-E_{av}/RT} = A_1 e^{-E/RT} + 2A_2 \times e^{-2E/RT} + ... + nA_n \times e^{-nE/RT} \quad ...(ii)$$

On differentiating Eq. (ii)

$$A_{AV} \cdot \frac{E_{av}}{RT^2} \cdot e^{-E_{av}/RT} = A_1 \frac{E}{RT^2} \cdot e^{-E/RT} + 2A_2 \frac{2E}{RT^2} \times e^{-2E/RT} + ... + nA_n \times \frac{nE}{RT^2} \times e^{-nE/RT}$$

$$A_{AV} + E_{av} \cdot e^{-E_{av}/RT} = E \times A_1 \times e^{-E/RT} + 2E \times 2A_2 \times e^{-2E/RT} + ... + nE \times nA_n \times Ee^{-nE/RT}$$

$$E_{AV} \times K_{AV} = K \times E + 2K \times 2E + ... + nK \times nE = K \times E[1^2 + 2^2 + ... n^2]$$

$$E_{AV} \times \frac{n}{2}(n+1)K = K \times E\left[\frac{2n^3 + 3n^2 + n}{6}\right] = K \times E \times \left[\frac{n(2n+1) \times (n+1)}{6}\right]$$

$$\therefore \quad E_{AV} = \frac{E}{3} \times [2n + 1]$$

34. For I order reaction $r_1 = K\,[C]^1$

$$\therefore \quad \frac{R_1}{R_2} = K_1 / K_2 = \textbf{temperature coefficient}$$

Let temperature coefficient be a $\quad \frac{R_{35}}{R_{25}} = \frac{K_{35}}{K_{25}} = a$

$$\frac{R_{45}}{R_{35}} = \frac{K_{45}}{K_{35}} = a \quad \therefore \quad \frac{R_{45}}{R_{25}} = a \times a = a^2$$

Similarly, $\quad \frac{R_{75}}{R_{25}} = a^5$

For I reaction $(R_{75})_I = 2^5 \times (R_{25})_I$

For II reaction $(R_{75})_{II} = 3^5 \times (R_{25})_{II}$

$$\therefore \quad \frac{(R_{75})_{II}}{(R_{75})_I} = \frac{3^5}{2^5} = \mathbf{7.9537} \qquad [\because (R_{25})_I = (R_{25})_{II}]$$

35. (a) Rate of decomposition of NH_3.

(b) Rate of formation of N_2 and rate of formation of H_2.

(c) $$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = K\,[NH_3]^0$$

$$\therefore \quad \frac{d[N_2]}{dt} = K = 2.5 \times 10^{-4}\ \mathbf{Ms^{-1}}$$

$$\frac{d[H_2]}{dt} = 3K = 3 \times 2.5 \times 10^{-4} = \mathbf{7.5 \times 10^{-4}\ Ms^{-1}}$$

(d) $$-\frac{d[NH_3]}{dt} = \frac{K_1[NH_3]}{1 + K_2[NH_3]}$$

if $[NH_3]$ is very very low $[1 + K_2[NH_3] \simeq 1]$

or $$-\frac{d[NH_3]}{dt} = K_1[NH_3], \textit{i.e.}, \textbf{ Ist order reaction}$$

if $[NH_3]$ is very very high

$$-\frac{d[NH_3]}{dt} = \frac{K_1}{\frac{1}{[NH_3]} + K_2} = \frac{K_1}{K_2} = K'\left[\frac{1}{[NH_3]} + K_2 \simeq K_2\right]$$

i.e., **zero order.**

36. For the given change

$$\frac{-d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt}$$

On substituting values as given,

$$K_1[N_2O_5] = \frac{1}{2}K_2[N_2O_5] = 2K_3[N_2O_5]$$

or $$\mathbf{2K_1 = K_2 = 4K_3}$$

37. Unit of rate = mol litre^{-1} time^{-1}

Unit of rate constant = time^{-1}

The overall order for reactions is 1.

Thus, $\quad$ rate $= K\,[\text{Reactant}]^1$

or $$K = \frac{\text{rate}}{[\text{Reactant}]^1} = \frac{\text{mol litre}^{-1}\ \text{time}^{-1}}{\text{mol litre}^{-1}} = \textbf{time}^{-1}$$

38. Rate law with order equal to molecularity (necessarily integer) are elementary process. For the given reaction O.R. $= 1 + 3/2 = 5/2$. Since, molecularity can never be fractional and thus, for given reaction O.R. is not equal to molecularity.

Thus, given reaction is **not elementary process.**

39. Order of reaction = 1+1+2 = 4
Apparent molecularity = 5+1+6 = **12**

40. Rate of reaction = $\frac{1}{2}$ × rate of disappearance of A

$$= \frac{1}{2}\left(-\frac{\Delta[A]}{\Delta t}\right) = \frac{1}{2}\left[\frac{0.5-0.4}{10}\right] = \mathbf{0.005\ mol\ L^{-1}\ minute^{-1}}$$

41. Loss in concentration of A in Ist hour $= \frac{0.6-0.5}{1} = 0.1$

Gain in concentration of B in Ist hour $= \frac{0.2-0}{1} = 0.2$

(i) ∵ 0.1 mole of A changes to 0.2 mole of B in a given time and thus,

$$n = 2$$

(ii) Equilibrium constant, $K = \frac{[B]^n}{[A]} = \frac{[0.6]^2}{0.3}$

$$= 1.2 \text{ mol litre}^{-1}$$

(∵ Equilibrium is attained after 5 hr, where $[B] = 0.6$ and $[A] = 0.3$)

(iii) Initial rate of conversion of A = changes in conc. of A during Ist hour

$$= \frac{0.1}{1} = \mathbf{0.1\ mol\ litre^{-1}\ hour^{-1}}$$

42. (i) The unit of rate constant suggest the second order for reaction. Thus,

Rate of reaction = $K\,[O_3][O]$

or $0.15 = 1.5\times10^{7}\left[\frac{0.76}{0.0821\times298\times760}\right][O]$

$$\left(\because \frac{n}{V} \text{ for } O_3 = \frac{P}{RT} = \frac{0.76}{0.0821\times298\times760}\right)$$

$\therefore$ $[O] = 2.45\times10^{-4}$ or $\frac{n}{V}$ for $O = \mathbf{2.45\times10^{-4}}$

$\therefore$ $\frac{P}{RT}$ for $O = 2.45\times10^{-4}$

or $P_O = 2.45\times10^{-4}\times0.0821\times298$

$= 5.99\times10^{-3}$ atm

$= 5.99\times10^{-3}\times760$ mm $= 4.5$ mm

(ii) Also, rate of reaction

$$= \frac{1}{2}\frac{d[O_2]}{dt} = \frac{1}{2} \text{ rate of formation of } O_2$$

$\therefore$ Rate of formation of $O_2 = 2\times0.15 = \mathbf{0.30\ mol\ L^{-1}\ t^{-1}}$

43. Rate of reaction $= -\frac{d[CO_2]}{dt} = -\frac{d[OH^-]}{dt} = \frac{d[HCO_3]}{dt}$

Also the unit of K suggest it to be II order. Thus, rate of reaction

$$= K\,[CO_2][OH^-] = 4\times10^{-3}\times10^{-6}\times10^{-1}$$

$$= \mathbf{4\times10^{-10}\ mol\ L^{-1}\ sec^{-1}}$$

44. Rate = K [Reactant]^n if [Reactant] = a, rate = r_1

$r_1 = K[a]^n$ if [Reactant] = $4a$, rate = $2r_1$

$2r_1 = K[4a]^n$

$\therefore$ $\frac{1}{2} = \left[\frac{1}{4}\right]^n$ $\therefore$ $n = \frac{1}{2}$

45. $(r_0)_1 = K[A_0]_1^a$ (a is order of reaction)

$(r_0)_2 = K[A_0]_2^a$

$\therefore$ $\frac{(r_0)_1}{(r_0)_2} = \left\{\frac{[A_0]_1}{[A_0]_2}\right\}^a$

or $a = \frac{\log(r_0)_1 - \log(r_0)_2}{\log[A_0]_1 - \log[A_0]_2}$

$$= \frac{\log[2.40\times10^{-4}] - \log[0.60\times10^{-4}]}{\log[2\times10^{-3}] - \log[1\times10^{-3}]}$$

$$= \frac{-3.62+4.22}{-2.70+3} = 2$$

$\therefore$ $r = K[A]^2$

Also, $K = \frac{r}{[A]^2} = \frac{2.40\times10^{-4}}{[2\times10^{-3}]^2} = \mathbf{60\ mol^{-1}\ L\ sec^{-1}}$

46. (a) Rate = $K[A]^1[B]^2[C]^0$

(b) Let initial conc. of A, B and C be a, b, c mol litre^{-1}

Then, rate $r_1 = K\,a^1b^2c^0$ ...(1)

Now if conc. of A, B and C are doubled, *i.e.*, $2a$, $2b$ and $2c$ respectively, then,

$$r_2 = K(2a)^1(2b)^2(2c)^0 \quad ...(2)$$

By Eqs. (1) and (2), $\frac{r_1}{r_2} = \frac{1}{8}$ $\therefore$ $r_2 = 8r_1$

47. (a) Rate = $K[A]^2[B]^1[C]^0$

(b) Unit of rate = mol litre^{-1} time^{-1}

Unit of rate constant = $\mathbf{L^2\ mol^{-2}\ time^{-1}}$

(c) Let initial conc. of A, B and C be a, b, c respectively.

$\therefore$ $r_1 = K(a)^2(b)^1(c)^0$ ...(1)

Now, $[A] = 2a$; $[B] = 3b$

$\therefore$ $r_2 = K(2a)^2(3b)^1(c)^0$ ...(2)

By Eqs. (1) and (2), $\frac{r_1}{r_2} = \frac{1}{12}$ $\therefore$ $r_2 = 12\,r_1$

48. Consider a reaction $A \longrightarrow$ Product

$\therefore$ $r_1 = K[A]^1$ for I order ...(1)

$\therefore$ $r_2 = K[A]^2$ for II order ...(2)

$\therefore$ $r_3 = K[A]^3$ for III order ...(3)

∵ K is same in all.

If $[A] = 1$ $r_1 = r_2 = r_3$

If $[A] < 1$ $r_1 > r_2 > r_3$

If $[A] > 1$ $r_3 > r_2 > r_1$

49. Rate = $K[A][B]^{2/3}$

$\therefore$ O.R. $= 1+\frac{2}{3} = \frac{5}{3} = \mathbf{1.67}$

Unit of rate $\left(\frac{dx}{dt}\right)$ is $\mathbf{mol\ L^{-1}\ time^{-1}}$

Unit of rate constant : rate constant

$$(K)=\frac{dx/dt}{[\text{Reactant}]^{5/3}}=\frac{\text{mol litre}^{-1}t^{-1}}{\left(\frac{\text{mol}}{\text{litre}}\right)^{5/3}}$$

$$=\textbf{mol}^{-2/3}\textbf{L}^{+2/3}\textbf{time}^{-1}$$

50. For, $2NO+O_2 \longrightarrow 2NO_2$

$$\text{Rate}=K[NO]^2[O_2]$$

Let a mole of NO and b mole of O_2 be taken to start a reaction at any time in a vessel of V litre

$$\therefore \quad r_1=K\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right] \qquad ...(1)$$

if volume of vessel is reduced to $V/4$, then for same mole of NO and O_2

$$r_2=K\left[\frac{a}{V/4}\right]^2\left[\frac{b}{V/4}\right]$$

$$=64K\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right] \qquad ...(2)$$

By Eqs. (1) and (2),

$$\therefore \quad \frac{r_2}{r_1}=\textbf{64} \quad \text{or} \quad \textbf{r_2 is 64 times of r_1.}$$

51. $$\text{Rate}=K[\text{Reactant}]^n$$

For Case I : Let a mole of reactant in vessel of V litre

$$\therefore \quad r_1=K\left[\frac{a}{V}\right]^n \qquad ...(1)$$

For Case II : The volume is doubled, rate becomes half

$$\therefore \quad \frac{r_1}{2}=K\left[\frac{a}{2V}\right]^n \qquad ...(2)$$

$\therefore$ By Eqs. (1) and (2),

or $\quad 2=(2)^n \quad \therefore \quad n=1$

Note : The above fact is not valid for solution phase reactions.

52. $$\frac{dx}{dt}=K\left[\frac{a-x}{1+bx}\right]$$

On integrating

or $$\int dx\frac{(1+bx)}{(a-x)}=K\int dt$$

$$\int\frac{dx[1-b(a-x)+ab]}{(a-x)}=K\int dt$$

or $$\int dx\frac{(1+ab)}{(a-x)}-\int dx\cdot b=K\,dt$$

or $$-(1+ab)\log(a-x)-bx=Kt+C$$

at $t=0, x=0$

$$\therefore \quad C=-(1+ab)\log a$$

or $$-(1+ab)\log(a-x)-bx=Kt-(1+ab)\log a$$

or $$Kt=(1+ab)\log\left[\frac{a}{(a-x)}\right]-bx$$

at $t=t_{1/2}, x=\frac{a}{2}$

$$\therefore \quad Kt_{1/2}=(1+ab)\log\left[\frac{a}{a-a/2}\right]-\frac{ba}{2}$$

$$=(1+ab)\log 2-\frac{ab}{2}=\log 2+ab\log 2-ab\times 0.5$$

$$t_{1/2}=\frac{\textbf{log 2}+\textbf{ab(log 2}-\textbf{0.5)}}{K}$$

53. $$\text{Rate}=K\times[A]$$

$$0.04=K[A]_{10} \quad \text{and} \quad 0.03=K[A]_{20}$$

$$\frac{[A]_{10}}{[A]_{20}}=\frac{0.04}{0.03}=\frac{4}{3}$$

Also, $$t=\frac{2.303}{K}\log\frac{[A]_{10}}{[A]_{20}} \qquad \text{when } t=10\,\text{min.}$$

$$10=\frac{2.303}{K}\log\frac{4}{3} \quad \therefore \quad K=\frac{2.303}{10}\log\frac{4}{3}=0.0288\ \text{min}^{-1}$$

$$t_{1/2}=\frac{0.693}{K}=\frac{0.693}{0.0288}=\textbf{24.06 min}$$

54. $$\text{Rate}=K[\text{ester}]^1[H_3O^+]^0$$

(a) $$r_1=K[\text{ester}]^1[H_3O^+]^0$$

Let, initial conc. of ester $=a$, initial conc. of $H_3O^+=b$

$$\therefore \quad r_1=K[a]^1[b]^0$$

If conc. of ester is doubled, *i.e.*, [ester] $=2a$, then

$$r_2=K[2\times a]^1[b]^0$$

$$\therefore \quad \frac{r_1}{r_2}=\frac{1}{2} \quad \text{or} \quad r_2=\textbf{2}r_1$$

(b) $$r_1=K[a]^1[b]^0$$

If conc. of H_3O^+ is doubled, *i.e.*, $[H_3^+O]=2b$

$$r_3=[a]^1[2b]^0$$

$$\therefore \quad \frac{r_1}{r_3}=1 \quad \text{or} \quad r_1=r_3$$

55. We have,

$$-\frac{1}{2}\frac{d[A]}{dt}=-\frac{d[B]}{dt}=\frac{1}{2}\frac{d[C]}{dt}=\frac{1}{3}\frac{d[D]}{dt}=\text{rate of reaction}$$

$\because \quad \frac{d[C]}{dt}=1.0\ \text{mol litre}^{-1}\text{sec}^{-1}$

$$\therefore \quad -\frac{d[A]}{dt}=\frac{d[C]}{dt}=\textbf{1.0 mol L}^{-1}\textbf{sec}^{-1}$$

$$-\frac{d[B]}{dt}=\frac{1}{2}\frac{d[C]}{dt}=\frac{1}{2}=\textbf{0.5 mol L}^{-1}\textbf{sec}^{-1}$$

$$\frac{d[D]}{dt}=\frac{3}{2}\frac{d[C]}{dt}=\frac{3}{2}\times 1=\textbf{1.5 mol L}^{-1}\textbf{sec}^{-1}$$

Also, $\because \quad \text{Rate}=\frac{1}{2}\frac{d[C]}{dt}$

$$\therefore \quad \text{Rate}=\frac{1}{2}\times 1=\textbf{0.5 mol L}^{-1}\textbf{sec}^{-1}$$

56. $$\text{Rate}=K[A]^m[B]^n$$

For Case I : $0.05=K[0.1]^m[0.2]^n$ ...(1)

For Case II : $0.10=K[0.2]^m[0.2]^n$ ...(2)

For Case III : $0.05=K[0.1]^m[0.1]^n$ ...(3)

By Eqs. (1) and (2), $\frac{1}{2}=\left(\frac{1}{2}\right)^m \quad \therefore \quad m=1$

By Eqs. (1) and (3), $1=\left(\frac{1}{2}\right)^n$ $\therefore$ $n=0$

Thus, Rate $= K[A]^1[B]^0$ $\therefore$ O.R. $= 1+0=1$

Now $0.05 = K[0.1]^1\ [0.2]^0$

$\therefore$ $K=\frac{0.05}{0.1}=0.5\text{sec}^{-1}$

For I order reaction, $t_{1/2}=\frac{0.693}{K}=\frac{0.693}{0.5}=1.386\ \text{sec}^{-1}$

57. Let Rate $= K[A]^m[B]^n$

(a) $r_1 = 1\times10^{-4} = K[0.1]^m[0.1]^n$ ...(1)

$r_2 = 9\times10^{-4} = K[0.1]^m[0.3]^n$ ...(2)

$r_3 = 2.7\times10^{-3} = K[0.3]^m[0.3]^n$ ...(3)

By Eqs. (1) and (2), $\frac{r_1}{r_2}=\frac{1\times10^{-4}}{9\times10^{-4}}=\left(\frac{1}{3}\right)^n \Rightarrow n=2$

By Eqs. (2) and (3), $\frac{r_2}{r_3}=\frac{9\times10^{-4}}{27\times10^{-4}}=\left(\frac{1}{3}\right)^m \Rightarrow m=1$

$\therefore$ Rate $= K[A]^1[B]^2$

(b) Also, by Eq. (1), $1\times10^{-4} = K[0.1]^1[0.1]^2$

$K = 10^{-1} = 0.1\ \text{l}^2\text{mol}^{-2}\text{min}^{-1}$

58. Rate of reaction $= -\frac{1}{2}\frac{dP_{NO}}{dt}=-\frac{dP_{H_2}}{dt}$

For P_{H_2} constant :

$$-\frac{1}{2}\frac{dP_{NO}}{dt}=1.5=K(359)^m(P_{H_2})^n$$

$$-\frac{1}{2}\frac{dP_{NO}}{dt}=0.25=K(152)^m(P_{H_2})^n$$

$\therefore$ $\frac{1.5}{0.25}=\left(\frac{359}{152}\right)^m$ $\therefore$ $m=2$

For P_{NO} constant :

$$-\frac{dP_{H_2}}{dt}=1.60=(P_{NO})^m(289)^n$$

$$-\frac{dP_{H_2}}{dt}=0.79=(P_{NO})^m(147)^n$$

$\therefore$ $\frac{1.60}{0.79}=\left(\frac{289}{147}\right)^n$ $\therefore$ $n=1$

$\therefore$ Rate $= K[P_{NO}]^2[P_{H_2}]^1$

$\therefore$ Order of Reaction $= 2+1=3$

59. For the reaction $2NO+Cl_2 \longrightarrow 2NOCl$

Rate $= K[Cl_2]^m[NO]^n$ ...(1)

where, m and n are order of reaction with respect to Cl_2 and NO respectively.

From the given data :

$1\times10^{-3} = K[0.05]^m[0.05]^n$ ...(2)

$3\times10^{-3} = K[0.15]^m[0.05]^n$ ...(3)

$9\times10^{-3} = K[0.05]^m[0.15]^n$ ...(4)

By Eqs. (2) and (3), $m=1$

By Eqs. (2) and (4), $n=2$

(a) $\therefore$ Order w.r.t. NO is 2 and with respect to Cl_2 is 1.

(b) Also rate expression $r = K[Cl_2]^1[NO]^2$

(c) And rate constt, $K=\frac{r}{[Cl_2]^1[NO]^2}=\frac{1\times10^{-3}}{[0.05]^1[0.05]^2}$

$= 8\ \text{L}^2\ \text{mol}^{-2}\text{sec}^{-1}$

(d) Further, $r = K[Cl_2]^1[NO]^2$

$= 8[0.2]^1[0.4]^2 = 0.256\ \text{mol L}^{-1}\text{sec}^{-1}$

60. (a) Rate $= K[A]^2[B]^0$

(b) $K = 4\times10^{-2}\ \text{L mol}^{-1}\text{sec}^{-1}$

(c) Rate $= 16\times10^{-4}\ \text{mol L}^{-1}\text{sec}^{-1}$

61. Rate $= K[HgCl_2]^m[K_2C_2O_4]^n$

$\therefore$ $\frac{0.0032}{60}=K[0.0418]^m[0.404]^n$ ...(1)

$\frac{0.0068}{65}=K[0.0836]^m[0.404]^n$ ...(2)

$\frac{0.0031}{120}=K[0.0836]^m[0.202]^n$ ...(3)

Solving Eqs. (1), (2) and (3), we get

$m=1$

$n=2$

$\therefore$ O.R. $= m+n=1+2=3$

62. $\because$ Rate $= K[A]^m[B_2]^n$

$\therefore$ Rate of disappearance of $B_2 = K[A]^m[B_2]^n$

$r_1 = 1.8\times10^{-3} = K[0.015]^m[0.15]^n$ ...(1)

$r_2 = 1.08\times10^{-2} = K[0.09]^m[0.15]^n$ ...(2)

$r_3 = 5.4\times10^{-3} = K[0.015]^m[0.45]^n$ ...(3)

By Eqs. (1) and (2), $\frac{1.8\times10^{-3}}{1.08\times10^{-2}}=\left[\frac{0.015}{0.09}\right]^m$ $\therefore$ $m=1$

By Eqs. (1) and (3), $\frac{1.8\times10^{-3}}{5.4\times10^{-3}}=\left[\frac{0.15}{0.45}\right]^n$ $\therefore$ $n=1$

$\therefore$ Rate of disappearance of $B_2 = K[0.015]^1[0.15]^1$

$\therefore$ O.R. $= 2$

Also $1.8\times10^{-3} = K[0.015]^1[0.15]^1$

$K = 0.8\ \text{litre mol}^{-1}\text{time}^{-1}$

Now $\frac{1}{2}\frac{d[AB]}{dt}=-\frac{d[B_2]}{dt}$

$\therefore$ $\frac{d[AB]}{dt}=2\times\left(-\frac{d[B_2]}{dt}\right)$

$= 2\times K[A]^1[B_2]^1$

$= 2\times0.8\times(0.02)^1(0.04)^1$

$= 1.28\times10^{-3}$

63. Let rate expression be,

$r = K[NO]^m[H_2]^n$ ...(1)

Case I : $[NO]\times10^{-4} = 1.5$ $\therefore$ $[NO] = 1.5\times10^4$

$[H_2]\times10^{-3} = 4.0$ $\therefore$ $[H_2] = 4.0\times10^3$

$-\frac{1}{2}\frac{d[NO]}{dt}\times10^{-4} = 4.4$ $\therefore$ $-\frac{1}{2}\frac{d[NO]}{dt}=4.4\times10^4$

$\therefore$ By Eqs. (1), $4.4\times10^4 = K[1.5\times10^4]^m[4.0\times10^3]^n$ ...(2)

Similarly for case II and III, we can write

Case II : $2.2\times10^{4} = K[1.5\times10^{4}]^{m}[2.0\times10^{3}]^{n}$ ...(3)

Case III : $0.24\times10^{4} = K[0.5\times10^{4}]^{m}[2.0\times10^{3}]^{n}$ ...(4)

By Eqs. (2) and (3), $2 = (2)^{n}$ $\therefore n = 1$

By Eqs. (3) and (4), $9.16 = (3)^{m}$ $\therefore m = 2$

$\therefore$ O.R. with respect to NO is **2** and with respect to H_2 = **1**

For rate constt. use Eq. (2) with $m = 2$ and $n = 1$

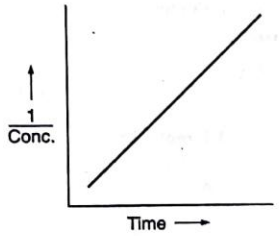
$$4.4\times10^{4} = K[1.5\times10^{4}]^{2}[4.0\times10^{3}]^{1}$$

$$\therefore \quad K = \mathbf{4.88\times10^{-8}\ mol^{-2}\,L^{2}\,min^{-1}}$$

64. From the graph it is evident that concentration of 40 reduces to 20 in 5 minute, 20 reduces to 10 in 5 minute and 10 reduces to 5 in again 5 minute, which shows that half life period is independent of concentration, a characteristic of a first order reaction. In a first order reaction the concentration of the reactant **can never be theoretically zero.**

65. The reaction is of second order, because for II order,

$$K = \frac{1}{t}\cdot\frac{x}{a(a-x)}$$



or $$t = \frac{1}{K}\cdot\frac{x}{a(a-x)}$$

or time (t) *vs.* $\frac{1}{\text{conc.}}$ graph is linear.

66. Since, K has unit min^{-1} and thus, given reaction is of I order

Now $\text{Rate} = K[\ ]^{1}$

$$\text{Rate} = 10^{-3}\times[0.2]^{1} = \mathbf{2\times10^{-4}\ mol\ dm^{-3}\,min^{-1}}$$

Also $$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$\therefore \quad 10^{-3} = \frac{2.303}{200}\log_{10}\frac{100}{(100-x)}$$

$$\therefore \quad x = \mathbf{18.12\%}$$

67. $A \longrightarrow B$ $K = 4.5\times10^{-3}\ min^{-1}$

$[A]_0 = 1\,M$

For I order reaction, $K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$

at $t = 60$ min, $(a-x) = ?$

$$4.5\times10^{-3} = \frac{2.303}{60}\log_{10}\frac{1}{(a-x)}$$

$$\therefore \quad (a-x) = 0.7634$$

Thus, rate after 60 minute $= K(a-x)$

$$= 4.5\times10^{-3}\times0.7634 = \mathbf{3.4354\times10^{-3}}$$

68. (a) Initial rate $= K[\ ]^{1} = 1\times10^{-2}[1] = 1\times10^{-2}$

$\therefore$ Rate $= \mathbf{1\times10^{-2}\ mol\ L^{-1}\,sec^{-1}}$

(b) Now $$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$10^{-2} = \frac{2.303}{1\times60}\log_{10}\frac{1}{(1-x)}$$

($\because t = 1$ minute $= 60$ sec)

$\therefore$ $(1-x) = 0.549$

$\therefore$ Rate after 1 minute $= K[\ ]$ after 1 minute $= K[0.549]$

$$= 10^{-2}[0.549]$$

Rate after 1 minute $= \mathbf{5.49\times10^{-3}\ mol\ L^{-1}\,sec^{-1}}$

69. $t_{99\%} = \frac{2.303}{K}\log_{10}\frac{100}{100-99}$ ...(1) ($\because a = 100; x = 99$)

$t_{90\%} = \frac{2.303}{K}\log_{10}\frac{100}{100-90}$ ...(2) ($\because a = 100; x = 90$)

$\therefore$ By Eqs. (1) and (2), $\frac{t_{99\%}}{t_{90\%}} = \frac{\log_{10}100}{\log_{10}10} = 2$

$\therefore$ $t_{99\%} = 2\times t_{90\%}$

70. $A \longrightarrow$ Products

$\therefore$ $$-\frac{dC_A}{dt} = KC_A^{n}$$ ($\because$ order is n)

On integrating $\frac{-(C_A)^{1-n}}{1-n} = Kt + \text{constant}$ ...(1)

at $t = 0, C_A = C_0$ $\therefore$ constant $= -\frac{C_0^{1-n}}{1-n}$ ...(2)

$\therefore$ By Eqs. (1) and (2), $-\frac{C_A^{1-n}}{1-n} = Kt - \frac{C_0^{1-n}}{1-n}$

or $$Kt = \frac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}]$$ ...(3)

if $C_A = \frac{C_0}{2}$ at $t = t_{1/2}$ then by Eq. (3)

$$Kt_{1/2} = \frac{1}{(n-1)}\left[\left(\frac{C_0}{2}\right)^{1-n} - (C_0)^{1-n}\right]$$

$$= \frac{1(C_0)^{1-n}}{(n-1)}\times[2^{n-1} - 1]$$ ...(4)

Similarly, if $C = \frac{C_0}{4}$ at $t = t_{3/4}$, then by Eq. (3)

$$Kt_{3/4} = \frac{C_0^{1-n}}{(n-1)}[4^{n-1} - 1]$$ ...(5)

By Eqs. (4) and (5), $\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1}-1}{4^{n-1}-1}$

Thus the ratio depends only on 'n'.

71. For zero order reaction : $t = \frac{x}{K}$ or $K = \frac{x}{t}$

If $t = t_{20\%} = 20$ minute, $x = 20$

Then $K = \frac{20}{20} = \mathbf{1\ mol\ L^{-1}\,time^{-1}}$

If $t = t_{40\%} = 40$ minute, $x = 40$

Then, $K = \frac{40}{40} = 1 \text{ mol L}^{-1} \text{time}^{-1}$

Thus, reaction is of **zero order.**

72. $$-\frac{dC}{dt} = \frac{K_1 C}{1+K_2 C} = \frac{K_1}{\frac{1}{C}+K_2}$$

(a) If C is very very high $1/C$ is smallest and thus negligible.

$$\therefore \quad -\frac{dC}{dt} = \frac{K_1}{K_2} = \text{constant}$$

Thus order of reaction is **zero.**

(b) If C is very very low. $1+K_2C = K'$

$$\therefore \quad -\frac{dC}{dt} = \frac{K_1 C}{K'} = K'' \cdot C$$

Thus order of reaction is **unity.**

73. $$\frac{-dC}{dt} = \frac{\alpha C}{1+\beta C}$$

or $$\frac{-dC(1+\beta C)}{C} = \alpha \cdot dt \quad \text{or} \quad \frac{-dC}{C} - dC \cdot \beta = \alpha \cdot dt$$

$$-\ln C - \beta C = \alpha t + \text{constant} \qquad \ldots(1)$$

at $t = 0, C = C_0$

$$\therefore \quad -\ln C_0 - \beta C_0 = \alpha 0 + \text{constant}$$

or $$\text{constant} = -\ln C_0 - \beta C_0$$

$\therefore$ By (1) $-\ln C - \beta C = \alpha t - \ln C_0 - \beta C_0$

or $$\ln \frac{C_0}{C} + \beta(C_0 - C) = \alpha \cdot t \qquad \ldots(2)$$

if $$t = t_{1/2}, \; C = \frac{C_0}{2}$$

$\therefore$ By Eq. (2) $$\ln \frac{C_0}{C_0/2} + \beta\left[C_0 - \frac{C_0}{2}\right] = \alpha t_{1/2}$$

or $$t_{1/2} = \frac{1}{\alpha} \ln 2 + \frac{\beta \cdot C_0}{2\alpha} \qquad \ldots(3)$$

74.

	$2A \longrightarrow$	$3B$	+ C
Initial pressure	$P°$	0	0
Pressure at $t = t$	$P°-2a$	$3a$	a
Pressure at $t = 2t$	$P°-2x$	$3x$	x

Given, $P°-2a+3a+a = P$

$$\therefore \quad P°+2a = P \qquad \ldots(1)$$

Now for I order reaction at time t

$$K = \frac{2.303}{t} \log \frac{P°}{P°-2a} = \frac{2.303}{t} \log \frac{P°}{2P°-P} \qquad \ldots(2)$$

Let total pressure at $t = 2t$ be A, then $P°-2x+3x+x = A$

or $P°+2x = A$

$$K = \frac{2.303}{2t} \log \frac{P°}{P°-2x} = \frac{2.303}{2t} \log \frac{P°}{2P°-A} \qquad \ldots(3)$$

$$K = \frac{2.303}{t} \log \left[\frac{P°}{2P°-A}\right]^{1/2} \qquad \ldots(4)$$

By Eqs. (2) and (4) $$\left[\frac{P°}{2P°-P}\right]^2 = \left[\frac{P°}{2P°-A}\right]$$

$$[2P°-A] \cdot P° = [2P°-P]^2$$

$$\therefore \quad P° \cdot A = 2(P°)^2 - (2P°-P)^2$$

$$\therefore \quad A = 2P° - \frac{(2P°-P)^2}{P°}$$

75. **For I order reaction :** $K = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

If $t = t, a = C_0$ and $(a-x) = aC_0$

$$K = \frac{2.303}{t} \log_{10} \frac{C_0}{aC_0} = \frac{2.303}{t} \log_{10} \frac{1}{a}$$

If $t = 2t, a = C_0$ and $(a-x) = a^2 C_0$

$$K = \frac{2.303}{2t} \log_{10} \frac{C_0}{a^2 C_0} = \frac{2.303}{t} \log_{10} \frac{1}{a}$$

If $t = 3t$, $$K = \frac{2.303}{3t} \log_{10} \frac{C_0}{a^3 C_0} = \frac{2.303}{t} \log_{10} \frac{1}{a}$$

K comes constant and thus, it is **I order reaction.**

Also, $$K = \frac{2.303}{t} \log_{10} \frac{1}{a}$$

76. Given, $a = 1$ mole, $x = 3/4$ mole, $t = 1$ hr

(a) **For I order :** $$K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$$K = \frac{2.303}{1} \log_{10} \frac{1}{1-\frac{3}{4}} = \frac{2.303}{1} \log_{10} 4$$

$$K = \mathbf{1.386 \text{ hr}^{-1}}$$

(b) **For II order :**

$$K = \frac{1}{t \times a} \cdot \frac{x}{(a-x)} = \frac{1}{1 \times 1} \cdot \frac{3}{4\left(1-\frac{3}{4}\right)} = 3$$

$$K = \mathbf{3 \text{ L mol}^{-1} \text{hr}^{-1}}$$

77. $\because$ $$t = \frac{2.303}{K} \log_{10} \frac{a}{(a-x)}$$

If $t = \frac{t}{2}$, $x = \frac{a}{2}$; $\therefore$ $$t_{1/2} = \frac{2.303}{K} \log_{10} \frac{a}{a-\frac{a}{2}} \qquad \ldots(1)$$

If $t = t_{99\%}$, $x = \frac{99a}{100}$; $$t_{99\%} = \frac{2.303}{K} \log_{10} \frac{a}{a-\frac{99a}{100}} \qquad \ldots(2)$$

By Eqs. (1) and (2),

$$t_{99\%} = \frac{\log_{10} 100}{\log_{10} 2} \times t_{1/2} = \frac{2}{0.3010} \times 2.1 = \mathbf{13.95 \text{ hour}}$$

Also, mole of N_2O formed $= \frac{99}{100} \times$ mole of NH_2NO_2 taken

$$= \frac{99}{100} \times \frac{6.2}{62} = 0.099$$

$\therefore$ Volume of N_2O formed at STP $= 0.099 \times 22.4 = \mathbf{2.217 \text{ L}}$

78. $t = 10$, $(a-x) = 13.8$

$t = 20$, $(a-x) = 8.25$

$t = 0$, a

$\because$ $$K = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$\therefore$ $$K = \frac{2.303}{10} \log_{10} \frac{a}{13.8} \qquad \ldots(1)$$

$$K = \frac{2.303}{20} \log_{10} \frac{a}{8.25} \qquad \ldots(2)$$

By solving Eqs. (1) and (2),

$$K = \mathbf{5.1 \times 10^{-2} \text{ minute}^{-1}}$$

$$a = \mathbf{23.09}$$

79. $\because \quad K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$ ...(1)

Case I : $a \propto 200\,\text{mm}$, $x \propto 200\times\frac{50}{100}$ or $x \propto 100\,\text{mm}$

$t_{1/2} = 53\,\text{minute}$

$\therefore \quad K_1 = \frac{2.303}{53}\log_{10}\frac{200}{200-100} = 1.307\times10^{-2}\,\text{minute}^{-1}$

Case II : $a \propto 200\,\text{mm}$, $x \propto 200\times\frac{73}{100}$

or $x \propto 146\,\text{mm}$

$t_{73\%} = 100\,\text{minute}$

$\therefore \quad K_2 = \frac{2.303}{100}\log_{10}\frac{200}{200-146} = 1.309\times10^{-2}\,\text{minute}^{-1}$

(a) The Eq. (1) gives same value of K and thus, reaction obeys **I order.**

(b) $K = \frac{K_1+K_2}{2} = \frac{(1.307+1.309)\times10^{-2}}{2}$

$= \mathbf{1.308\times10^{-2}\,minute^{-1}}$

(c) $t_{1/n} \propto (a)^0$ for first order reaction and thus, reaction will proceed to 73% completion in 100 minute if initial pressure is **600 mm.**

80.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Mole at $t=0$	a	0	0
$t=30$	$(a-x)$	$2x$	$x/2$
$t=\infty$	0	$2a$	$a/2$

$\because$ No. of mole $\propto$ pressure developed

$\therefore \quad a \propto P_0$ at $t=0$

$a+\frac{3x}{2} \propto 284.5$ at $t = 30\,\text{minute}$

$\frac{5a}{2} \propto 584.5$ at $t=\infty$

Thus, $a \propto \frac{2\times584.5}{5}$ or $x \propto 233.8$ at $t=0$

$x \propto 33.8$ at $t = 30$ minute

$a-x \propto 200.0$

$\because \quad K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$

$\therefore \quad K = \frac{2.303}{30}\log_{10}\frac{233.8}{200} = \mathbf{5.206\times10^{-3}\,minute^{-1}}$

81. Reaction mixture after a long time or on heating is supposed to show completion.

$$A \longrightarrow B + 2C$$

at $t=0$	a	0	0	Mole before dissociation
at $t=t$	$(a-x)$	x	$2x$	Mole after dissociation
at $t=\infty$	0	a	$2a$	Mole after complete dissociation

Let a mole of A are present and x mole of A dissociate in time t.

Also, Total mole at any time $\propto$ pressure at that time

$\therefore \quad a+2x \propto 264$ at $t = 14\,\text{minute}$ ...(1)

$\therefore \quad 3a \propto 450$ at $t=\infty$ ...(2)

and $a \propto P^\circ$ at $t=0$ ...(3)

Let P° is initial pressure

(a) By Eqs. (2) and (3),

$\therefore \quad P^\circ = \mathbf{150\,mm}$

(b) $K = \frac{2.303}{14}\log_{10}\frac{150}{150-57}$

$\because$ By Eqs. (1) and (2), $x \propto 57$

$= \mathbf{3.415\times10^{-2}\,minute^{-1}}$

(c) $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3.415\times10^{-2}} = \mathbf{20.29\,minute}$

82.

$$AsH_3(g) \longrightarrow As(s) + \frac{3}{2}H_2(g)$$

Mole at $t=0$	a	0	0
Mole at $t=t$	$a-x$	x	$\frac{3x}{2}$

$\because \quad$ Mole $\propto$ Pressure (at constant V and T)

Now $a \propto 0.9654$ at $t = 0$ hr

$a-x+\frac{3x}{2} \propto 1.06$ at $t = 5.5$ hr

$\therefore \quad x \propto 0.1892$ at $t = 5.5$ hr

As being solid and hence, its mole should not be counted for pressure.

$\because \quad K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$

$\therefore \quad K_1 = \frac{2.303}{5.5}\log_{10}\frac{0.9654}{0.9654-0.1892}$

$= \mathbf{3.96\times10^{-2}\,hr^{-1}}$

Similarly, $a \propto 0.9654$

$a-x+\frac{3x}{2} \propto 1.076$ at $t = 6.5$ hr

$\therefore \quad x \propto 0.2212$

$\therefore \quad K_2 = \frac{2.303}{6.5}\log_{10}\frac{0.9654}{0.9654-0.2212}$

$= \mathbf{4.00\times10^{-2}\,hr^{-1}}$

Similarly, $a \propto 0.9654$

$a-x+\frac{3x}{2} \propto 1.1$ at $t = 8$ hr

$\therefore \quad x \propto 0.2692$ at $t = 8$ hr

$\therefore \quad K_3 = \frac{2.303}{8}\log_{10}\frac{0.9654}{0.9654-0.2692}$

$= \mathbf{4.08\times10^{-2}\,hr^{-1}}$

$\therefore \quad K = \frac{K_1+K_2+K_3}{3} = \frac{(3.96+4.00+4.08)\times10^{-2}}{3}$

$= \mathbf{4.01\times10^{-2}\,hr^{-1}}$

83. $t_{1/2} \propto (a)^{1-n}$

For I $\therefore \quad 425 \propto (350)^{1-n}$ ...(1)

For II $\therefore \quad 275 \propto (540)^{1-n}$ ...(2)

For III $\therefore \quad 941 \propto (158)^{1-n}$ ...(3)

By Eqs. (1) and (2), $\frac{425}{275} = \left(\frac{350}{540}\right)^{1-n}$

Taking log, $\log\frac{425}{275} = (1-n)\log\frac{350}{540} \quad \therefore \; n = 2$

84. At pH = 5, the half life is 500 for all concentrations of sugar, *i.e.*, $t_{1/2} \propto [\text{sugar}]^0$. Thus, the reaction is I order with respect to sugar.

Now $\text{rate} = K[\text{sugar}]^1[H^+]^m$

Also for $[H^+]$ $\quad t_{1/2} \propto [H^+]^{1-m} \quad \therefore \quad 500 \propto [10^{-5}]^{1-m}$

$50 \propto [10^{-6}]^{1-m} \quad \therefore \quad 10 = (10)^{1-m}$

or $\quad 1-m=1 \quad \therefore \quad m=0$

Therefore, **rate** $= K\,[\text{sugar}]^1\,[H^+]^0$.

85. (a) Rate of reaction $= \dfrac{\text{Change in pressure}}{\text{Time in min}} = \dfrac{2-1.2}{50}$

$= \dfrac{0.8}{50} = \mathbf{1.6\times10^{-2}\ atm\ min^{-1}}$

(b) $\because$ Change in molarity may be derived by

$PV = nRT; \quad \dfrac{n}{V} = \dfrac{P}{RT}$

$\dfrac{n}{V} = \dfrac{0.8}{0.0821\times298} = 0.0327$

Rate of reaction $= \dfrac{\text{Change in molarity}}{\text{Time in second}} = \dfrac{0.0327}{50\times60}$

$= \mathbf{1.09\times10^{-5}\ mol\ L^{-1}\ sec^{-1}}$

86. $\because \quad K = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x} \quad \ldots(1)$

Case I: $K = \dfrac{2.303}{15}\log_{10}\dfrac{100}{100-17} = 1.24\times10^{-2}$

$\left(\begin{array}{l}\text{if } a=100\\ x=17 \text{ at } t=15\end{array}\right)$

Case II: $K = \dfrac{2.303}{30}\log_{10}\dfrac{100}{100-32} = 1.28\times10^{-2}$

$(x=32 \text{ at } t=30)$

Case III: $K = \dfrac{2.303}{45}\log_{10}\dfrac{100}{100-44.5} = 1.31\times10^{-2}$

$(x=44.5 \text{ at } t=45)$

Thus, all the values of K are same and hence equation (1) is valid, *i.e.*, **reaction obeys I order kinetics.**

87.

$$C_4H_8 \xrightarrow{\Delta} 2C_2H_4$$

Mole at $t=0$	a	0
Mole at $t=t$	$(a-x)$	$2x$

Case (a) When $\dfrac{2x}{a-x}=1$, then $x=\dfrac{a}{3}$

$\because \quad t = \dfrac{2.303}{K}\log_{10}\dfrac{a}{a-x}$

$= \dfrac{2.303}{2.48\times10^{-4}}\log_{10}\dfrac{a}{a-\frac{a}{3}} = 1635.2 \text{ second}$

$= \mathbf{27.25\ minute}$

Case (b) When $\dfrac{2x}{a-x}=100$, then $x=\dfrac{100}{102}a$

$t = \dfrac{2.303}{2.48\times10^{-4}}\log_{10}\dfrac{a}{a-\frac{100a}{102}} = 15856.9 \text{ sec}$

$= \mathbf{264.2\ minute}$

88. Since, rate constant $= 1.0\times10^7$ mol litre^{-1}sec^{-1}

$\therefore$ Zero order reaction.

For zero order: $\quad t = \dfrac{x}{K} = \dfrac{\text{concentration used}}{\text{rate constant}} \quad \ldots(1)$

$\because$ 0.05 mL has 3×10^{-6} mole of H^+

$\therefore$ 1000 mL has $\dfrac{3\times10^{-6}\times10^3}{0.05} = 0.6\times10^{-1}$ mol/litre of H^+

$\therefore$ By Eq. (1), $\quad t = \dfrac{0.6\times10^{-1}}{1\times10^7} = \mathbf{6\times10^{-9}\ second}$

89.

$$Cl_2O_7 \longrightarrow Cl_2 + \frac{7}{2}O_2$$

Mole at $t=0$	a	0	0
Mole at $t=55$ sec	$(a-x)$	x	$7x/2$

(a) Since, pressure of Cl_2O_7 is given and therefore,

$a \propto 0.062$

$(a-x) \propto 0.044$

$\because \quad K = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x} \quad \therefore K = \dfrac{2.303}{55}\log_{10}\dfrac{0.062}{0.044}$

$K = \mathbf{6.23\times10^{-3}\ sec^{-1}}$

(b) Let at $t=100$ sec, $(a-x) \propto P$

$\therefore \quad 6.23\times10^{-3} = \dfrac{2.303}{100}\log_{10}\dfrac{0.062}{P} \quad \therefore P = \mathbf{0.033\ atm}$

90. Consider I order reaction :

$$Kt = 2.303\log_{10}\frac{a}{(a-x)}$$

or $\quad Kt = 2.303\log_{10}a - 2.303\log_{10}(a-x) \quad \ldots(1)$

In terms of pressure Eq. (1) may be written as,

$\because \quad a \propto P_0$

$(a-x) \propto P$

$Kt = 2.303\log_{10}P_0 - 2.303\log_{10}P$

or $\quad \log_{10}P = -\dfrac{K}{2.303}t + \log_{10}P_0$

Thus, log P *vs.* time graph is linear with intercept equal to log P_0 and slope equal to $-\dfrac{K}{2.303}$. Since, linear results are given and thus, decomposition may be said **to be of I order.**

91.

$$NH_4NO_2(s) \longrightarrow N_2(g) + 2H_2O(l)$$

Mole at $t=0$	a	0	0
Mole at $t=t$	$(a-x)$	x	$2x$

The volume of N_2 formed at any time is proportional to the amount of NH_4NO_2 decomposed in that time.

	At $t=\infty$	$V_{N_2} = 33.05$ mL	$\therefore\ a \propto 33.05$
I	At $t=10$	$V_{N_2} = 6.25$ mL	$\therefore\ x \propto 6.25$
II	At $t=15$	$V_{N_2} = 9.0$ mL	$\therefore\ x \propto 9.0$
III	At $t=20$	$V_{N_2} = 11.40$ mL	$\therefore\ x \propto 11.40$
IV	At $t=25$	$V_{N_2} = 13.65$ mL	$\therefore\ x \propto 13.65$

Now use, $\quad K = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x}$

Case I $\quad K = \dfrac{2.303}{10}\log_{10}\dfrac{33.05}{33.05-6.25}$

$K = \mathbf{2.0\times10^{-2}\ min^{-1}}$

Similarly, calculate K for each case. The values of K come almost constant and thus, showing that reaction is I order. For K, take average of all values of K.

92. The volume of $KMnO_4$ used at any time is proportional to conc. of H_2O_2 at that time.

	At $t=0$	$V=25$	$\therefore \quad a \propto 25$
I	At $t=10$	$V=16$	$\therefore\ (a-x) \propto 16$
II	At $t=20$	$V=10.5$	$\therefore\ (a-x) \propto 10.5$
III	At $t=30$	$V=7.09$	$\therefore\ (a-x) \propto 7.09$

Now use, $K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$

For I $K_1 = \frac{2.303}{10}\log_{10}\frac{25}{16} = \mathbf{4.46\times10^{-2}\ minute^{-1}}$

For II $K_2 = \frac{2.303}{20}\log_{10}\frac{25}{10.5} = \mathbf{4.34\times10^{-2}\ minute^{-1}}$

For III $K_3 = \frac{2.303}{30}\log_{10}\frac{25}{7.09} = \mathbf{4.20\times10^{-2}\ minute^{-1}}$

The values of K come almost constant and thus, confirming I order reaction. For velocity constant, take average of all values of K.

93. Volume of O_2 at any time $\propto$ Mole of H_2O_2 decomposed

$\therefore \quad a \propto 35.75$

At $t = 10, x \propto 6.30$

$\therefore \quad K = \frac{2.303}{10}\log_{10}\frac{35.75}{35.75-6.30} = 1.94\times10^{-2}$

At $t = 15, x \propto 8.95$

$K = \frac{2.303}{15}\log_{10}\frac{35.75}{35.75-8.95} = 1.92\times10^{-2}$

At $t = 20, x \propto 11.40$

$K = \frac{2.303}{20}\log_{10}\frac{35.75}{35.75-11.40} = 1.92\times10^{-2}$

At $t = 25,\ x \propto 13.50$

$K = \frac{2.303}{25}\log_{10}\frac{35.75}{35.75-13.50} = 1.90\times10^{-2}$

Since, K values are constant using I order equation and thus, reaction **obeys I order kinetics.**

$K = \mathbf{1.92\times10^{-2}\ minute^{-1}}$

94. $\because$ Volume of alkali used $\propto$ Mole of acid at that time

$\therefore$ At $t = 0$, *i.e.*, $V_0 \propto$ Mole of HCl

$\therefore$ At $t = t$, *i.e.*, $V_t \propto$ Mole of HCl + Mole of CH_3COOH formed at $t = t$

At $t = \infty$, *i.e.*, $V_\infty \propto$ Mole of HCl + Total mole of CH_3COOH formed

$\therefore \quad a \propto V_\infty - V_0$ *i.e.*, total ester

$(a-x) \propto V_\infty - V_t$ *i.e.*, left ester at $t = t$

At $t = 75$,

$K_1 = \frac{2.303}{75}\log_{10}\frac{42.03-19.24}{42.03-24.20} = 3.27\times10^{-3}\ \text{min}^{-1}$

At $t = 119$,

$K_2 = \frac{2.303}{119}\log_{10}\frac{42.03-19.24}{42.03-26.60} = 3.28\times10^{-3}\ \text{min}^{-1}$

At $t = 259$,

$K_3 = \frac{2.303}{259}\log_{10}\frac{42.03-19.24}{42.03-32.23} = 3.26\times10^{-3}\ \text{min}^{-1}$

Since, K values are constant and thus, reaction **obeys I order kinetics.**

Also, $K = \frac{K_1+K_2+K_3}{3} = \mathbf{3.27\times10^{-3}\ min^{-1}}$

95. At $t = 0$, Rotation $r_0 \propto$ Mole of sugar + rotation due to external factor

At $t = t$, Rotation $r_t \propto$ Left sugar + rotation due to external factors

At $t = \infty$, Rotation $r_\infty \propto$ External factors

$\therefore \quad a =$ Mole of sugar $\propto r_0 - r_\infty$ at $t = 0$

$(a-x) =$ Left mole of sugar $\propto r_t - r_\infty$ at $t = t$

$\therefore \quad K_1 = \frac{2.303}{30}\log_{10}\frac{46.75+18.75}{41+18.75} = 3.06\times10^{-3}\ \text{min}^{-1}$

$K_2 = \frac{2.303}{90}\log_{10}\frac{46.75+18.75}{30.75+18.75} = 3.11\times10^{-3}\ \text{min}^{-1}$

$K_3 = \frac{2.303}{230}\log_{10}\frac{46.75+18.75}{12.75+18.75} = 3.18\times10^{-3}\ \text{min}^{-1}$

Since, K values are constant and thus, reaction **obeys I order kinetics.**

Also, $K = \mathbf{3.12\times10^{-3}\ min^{-1}}$

96. $CH_3\cdot O\cdot CH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

Initial P	0.40 atm			
Final P at 12 min.	$(0.40-P)$	P	P	P

For ideal gas behaviour, Mole $\propto$ Pressure (at constant V and T)

$\therefore \quad a \propto 0.40\ ; \quad (a-x) \propto (0.40-P)$

$\therefore \quad K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$

$\frac{0.693}{14.5} = \frac{2.303}{12}\log_{10}\frac{0.40}{(0.40-P)} \quad \therefore \ P = 0.175$ atm

$\therefore$ Pressure of ether decomposed $= 0.175$

Now, Total pressure $= 0.40-P+P+P+P$

$= 0.40+2P = 0.40+2\times0.175$

$= \mathbf{0.75\ atm}$

97.

	A	+	OH^-	$\longrightarrow$	Products
$t = 0$	0.002		0.3		
$t = 30$	$\left[0.002-\frac{0.002\times1}{100}\right]$		$\left[0.3-\frac{0.002\times1}{100}\right]$		

Using $K = \frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$

$$K = \frac{2.303}{30\times(0.002-0.3)}\log_{10}\frac{0.3\times\left[0.002-\frac{0.002\times1}{100}\right]}{0.002\left[0.3-\frac{0.002\times1}{100}\right]}$$

$K = \mathbf{1.12\times10^{-3}\ L\ mol^{-1}\ sec^{-1}}$

98. Rate $= K[A][B]^2$

$\therefore \quad 10^{-2} = K[1][1]^2$ or $K = 10^{-2}\ \text{litre}^2\text{mol}^{-2}\text{sec}^{-1}$

Now, $\text{rate}_{II} = 10^{-2}\times0.5\times(0.5)^2$

or New rate $= \mathbf{1.2\times10^{-3}\ mol/L\text{-}sec}$

99. **For A:** $\text{rate} = K_A[A]^1$ ...(1)

and $(t_{1/2})_A = \frac{0.693}{K_A}$ ...(2)

For B: $\text{rate} = K_B[B]^2$ ...(3)

and $(t_{1/2})_B = \frac{1}{a\cdot K_B}$ ...(4)

where a is initial concentration

(a) Initial rate of A, $r_A = K_A\times a$

Initial rate of B, $r_B = K_B\times a^2$

$\therefore \quad \frac{r_A}{r_B} = \frac{K_A}{K_B}\times\frac{1}{a}$ ...(5)

From Eqs. (2) and (4) if $(t_{1/2})_A = (t_{1/2})_B$,

then $$\frac{0.693}{K_A} = \frac{1}{K_B \cdot a}$$

or $$\frac{K_A}{K_B} = 0.693 \times a \qquad \ldots(6)$$

∴ From Eqs. (5) and (6)

$$\frac{r_A}{r_B} = \frac{0.693a}{a} = \mathbf{0.693}$$

(b) After lapse of I half-life the new rates are r'_A and r'_B

$$r'_A = K_A \times \frac{a}{2}$$

$$r'_B = K_B \times \left(\frac{a}{2}\right)^2$$

$$\therefore \quad \frac{r'_A}{r'_B} = \frac{K_A}{K_B} \times \frac{2}{a} \qquad \ldots(7)$$

$$\frac{r'_A}{r'_B} = 0.693 \times a \times \frac{2}{a} = \mathbf{1.386}$$

[From Eqs. (6) and (7)]

100. $CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$

Pressure at $t = 0$	0.4	0	0	0
Pressure at $t = 4.5$ hr	$0.4 - a$	a	a	a
	$= A$			

$$K = \frac{2.303}{t} \log \frac{0.4}{A}$$

$$4.78 \times 10^{-3} = \frac{2.303}{4.5 \times 60} \log \frac{0.4}{A} \quad \therefore \quad A = 0.110$$

$$\therefore \quad 0.4 - a = 0.110 \quad \text{or} \quad a = 0.29$$

Now molecular weight of mixture

$$= \frac{0.11 \times 46 + 0.29 \times 16 + 0.29 \times 28 + 0.29 \times 2}{0.98}$$

$$= 18.78$$

$$\therefore \quad \frac{r_0}{r_m} = \sqrt{\frac{18.78}{46}} \times \frac{0.4}{0.98} = \mathbf{0.261} \quad (P_0 = 0.4\,;\, P_m = 0.98)$$

101. $4PH_3(g) + \text{Inert gas} \longrightarrow P_4(g) + 6H_2(g) + \text{Inert gas}$

$t = 0$	P	P'	0	0	
$t = t$	$(P - A)$	P'	$\frac{A}{4}$	$\frac{6A}{4}$	P'
$t = \infty$	0	P'	$\frac{P}{4}$	$\frac{6P}{4}$	P'

$t = 0$ $\quad P = 262.40 = P_{PH_3} + P_{I(g)}$

$t = 60$ $\quad P = 272.90 = P_{PH_3(Left)} + P_{P_4(g)} + P_{H_2(g)} + P_{I(g)}$

$t = 120$ $\quad P = 275.51 = P_{PH_3(Left)} + P_{P_4(g)} + P_{H_2(g)} + P_{I(g)}$

$t = \infty$ $\quad P = 276.40 = P_{P_4(g)} + P_{H_2(g)} + P_{I(g)}$

$$\therefore \quad \frac{P}{4} + \frac{6P}{4} + P' = 276.40$$

$$\therefore \quad 7P + 4P' = (276.40) \times 4 \qquad \ldots(1)$$

Also, at $t = 0$, $\quad P + P' = 262.40 \qquad \ldots(2)$

$$\therefore \quad P = 18.66 \text{ mm}$$

$$P' = 243.74 \text{ mm}$$

At $t = 60$, Pressure $= 272.90 = (P - A) + P' + \frac{A}{4} + \frac{6A}{4}$

$$272.90 = 18.66 - A + 243.74 + \frac{7A}{4}$$

$$\therefore \quad A = 14.0 \text{ mm} \quad \therefore \quad K = \frac{2.303}{t} \log \frac{[P_{PH_3}]_0}{[P_{PH_3}]_{60}}$$

$$= \frac{2.303}{60} \log \frac{18.66}{(18.66 - 14)}$$

$$= \mathbf{2.31 \times 10^{-2}\ sec^{-1}}$$

At $t = 120$, Pressure $= 275.51 = P - A' + P' + \frac{A'}{4} + \frac{6A'}{4}$

$$275.51 = 18.66 - A' + 243.74 + \frac{7A'}{4}$$

$$\therefore \quad A' = 17.48 \text{ mm}$$

$$\therefore \quad K = \frac{2.303}{120} \log \frac{18.66}{(18.66 - 17.48)} = \mathbf{2.30 \times 10^{-2}\ sec^{-1}}$$

∴ Reaction is of first order.

102. **After 6 hour**

Meq. of H_2O_2 in 10 mL diluted solution

$$= 25 \times 0.025 \times 5 = 3.125$$

Meq. of H_2O_2 in 10 mL conc. solution

$$= 3.125 \times 10 = 31.25$$

Meq. of H_2O_2 in 10 mL of 20 volume H_2O_2 present initially

$$= \frac{68 \times 20 \times 10}{22400 \times 17} \times 1000 = 35.71$$

[∵ 22400 mL O_2 = 68 g H_2O_2

$$\therefore \quad 20 \text{ mL } O_2 = \frac{68 \times 20}{22400} \text{ g } H_2O_2 \text{ in 1 mL}$$

$$= \frac{68 \times 20 \times 10}{22400} \text{ g } H_2O_2 \text{ in 10 mL}]$$

$$\therefore \quad K = \frac{2.303}{6} \log \frac{35.71}{31.25} = \mathbf{0.022\ hr^{-1}}$$

103. $B^{n+} \longrightarrow B^{(n+4)+}$

Millimole at $t = 0$	a	0	$2e + B^{n+} \longrightarrow B^{(n+2)+}$
$t = t$	$(a - x)$	x	$5e + B^{(n+4)+} \longrightarrow B^{(n-1)+}$

Let normality be N for reducing agent.

Thus, at $t = 0$ $\quad a \times 2 = N \times 25 \quad \therefore \quad a = \frac{25}{2}N$

at $t = t$ $\quad (a - x) \times 2 \quad + \quad x \cdot 5 \quad = N \times 32$

For B^{n+} $\qquad$ for $B^{(n+4)+}$

$$\therefore \quad 3x = 7N \quad \text{or} \quad x = \frac{7}{3}N$$

Now, $$K = \frac{2.303}{10} \log \frac{25/2N}{\left(\frac{25}{2} - \frac{7}{3}\right)N} = \frac{2.303}{10} \log \frac{25 \times 6}{2 \times 61}$$

$$K = \mathbf{2.07 \times 10^{-2}\ min^{-1}}$$

104. Let rate $= K\,[CH_3COF]^a\,[H_2O]^b$

Case I: $[H_2O] >> [CH_3COF]$

Case II: $[H_2O] << [CH_3COF]$

According to Ostwald isolation method, we can assume $[H_2O]$ in excess in case I and $[CH_3COF]$ in excess in case II.

Case I: Using I order for CH_3COF (by hit and trial)

$$K_I = 2.303 \log \frac{a}{a - x}$$

$$K_1 = \frac{2.303}{10} \log \frac{0.01}{0.00857} = 0.0154$$

$$K_2 = \frac{2.303}{20}\log\frac{0.01}{0.00735} = 0.0154$$

Thus, $K_{av.} = 0.0154$

Thus order with respect to $[CH_3COF]$ is one or $a = 1$.

Case II : Using I order for H_2O

$$K_1' = \frac{2.303}{10}\log\frac{0.02}{0.0176} = 0.0128$$

$$K_2' = \frac{2.303}{20}\log\frac{0.02}{0.0156} = 0.0124$$

$$K_3' = \frac{2.303}{40}\log\frac{0.02}{0.0122} = 0.0124$$

$$K_{av.}' = 0.0125\ \text{min}^{-1}$$

Thus order with respect to $[H_2O]$ is one or $b = 1$.

Now, rate $= K_T[CH_3COF]^1[H_2O]^1$

Also, rate $= K_1[CH_3COF]$

$$\therefore \quad K_T = \frac{K_1}{[H_2O]} = \frac{0.0154}{1.0} = \mathbf{1.54\times10^{-2}\ min^{-1}}$$

105. **For I :** $K = \frac{1}{t}\frac{x}{a(a-x)}$ (II order equation)

Given, $a = 0.1M$, $x = \frac{0.1\times30}{100} = 0.03$, $t = 60$ min

$$\therefore \quad K_1 = \frac{1}{60\times0.1}\times\frac{0.03}{(0.1-0.03)} = 0.07\ \text{min}^{-1}$$

Also, for I : $K_1 = Ae^{-E_a/RT}$

For II : $K_2 = Ae^{-E_a'/RT}$

$$\therefore \quad \frac{K_1}{K_2} = e^{(E_a'-E_a)/RT} = e^{-10.46/RT} = e^{-10.46/8.314\times10^{-3}\times373}$$

or $K_2 = \dfrac{K_1}{e^{-10.46/8.314\times10^{-3}\times373}} = \dfrac{0.07}{0.034} = \mathbf{2.10\ min^{-1}}$

Now, for II: $K_2 = \frac{1}{t}\frac{x}{a(a-x)}$; $a = 0.05$;

$$x = \frac{0.05\times70}{100} = 0.035$$

$$\therefore \quad t = \frac{1}{2.10\times0.05}\times\frac{0.035}{\left(0.05-\frac{0.05\times70}{100}\right)}$$

$$= \mathbf{22.22\ min}$$

106. By Step (ii) $\dfrac{-d[I^-]}{dt} = K_3[I^-][HOCl]$ ...(a)

By step (i) $\dfrac{K_1}{K_2} = \dfrac{[HOCl][OH^-]}{[OCl^-][H_2O]}$ ...(b)

By step (iii) $\dfrac{K_1'}{K_2'} = \dfrac{[H_2O][OI^-]}{[OH^-][HOI]}$ ...(c)

By Eqs. (b) and (a)

$$\frac{-d[I^-]}{dt} = K_3[I^-].\frac{K_1}{K_2}\frac{[OCl^-][H_2O]}{[OH^-]}$$

$$= K_3\cdot\frac{K_1}{K_2}\frac{[OCl^-][I^-]}{[OH^-]}$$

[Since $[H_2O]$ is constant]

$$\therefore \quad \frac{-d[I^-]}{dt} = \boldsymbol{K}\frac{[OCl^-][I^-]}{[OH^-]}$$

107. By step (iii) $\dfrac{d[COCl_2]}{dt} = K_3[COCl][Cl_2]$ ...(a)

By step (i) $\dfrac{K_1}{K_2} = \dfrac{[Cl]^2}{[Cl_2]}$ ...(b)

By step (ii) $\dfrac{K_1'}{K_2'} = \dfrac{[COCl]}{[CO][Cl]}$ ...(c)

Thus from Eqs. (b) and (c)

$$[COCl] = \frac{K_1'}{K_2'}\cdot[CO]\times\sqrt{\frac{K_1}{K_2}\cdot[Cl_2]} \quad \text{...(d)}$$

From Eqs. (a) and (d)

$$\frac{d[COCl_2]}{dt} = K_3\frac{K_1'}{K_2'}\left(\frac{K_1}{K_2}\right)^{1/2}[CO][Cl_2]^{1/2}\cdot[Cl_2]$$

$$\boldsymbol{\frac{d[COCl_2]}{dt} = K\cdot[CO][Cl_2]^{3/2}}$$

108. The rate of formation of urea is given by Eq. (iii)

$$\frac{d[\text{urea}]}{dt} = K[NH_3][HNCO] \quad \text{...(a)}$$

By step (ii) we have : $\dfrac{[NH_3][HNCO]}{[NH_4NCO]} = K_{C_1}$ ...(b)

By step (i) we have : $\dfrac{[NH_4NCO]}{[NH_4CNO]} = K_{C_2}$ ...(c)

$\therefore$ By Eqs. (b) and (c)

$$[NH_3][HNCO] = K_{C_1}\cdot K_{C_2}[NH_4CNO] \quad \text{...(d)}$$

$\therefore$ By Eqs. (a) and (d)

$$\frac{d[\text{urea}]}{dt} = K\cdot K_{C_1}\cdot K_{C_2}[NH_4CNO]$$

$$\boldsymbol{\frac{d[\text{urea}]}{dt} = K'[NH_4CNO]}$$

109.

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

$t = 0$	2 mol litre^{-1}	0
At eq.	$(2-X)$ mol litre^{-1}	X

$K_1 = 2\times10^{-3}$ mol L^{-1}sec^{-1} (zero order)

$K_2 = 3\times10^{-3}$ sec^{-1} (Ist order)

$$\frac{dX}{dt} = K_1[A]^0 - K_2[B]^1$$

At equilibrium $\dfrac{dx}{dt} = 0 \quad \therefore \quad 0 = K_1 - K_2[X]_{eq.}$

$$\therefore \quad [X]_{eq.} = \frac{K_1}{K_2} = \frac{2\times10^{-3}}{3\times10^{-3}} = 0.66\ \text{mol litre}^{-1} = K_c$$

	A	$\rightleftharpoons$	B
Initial eq.	1.34		0.66
Moles added at eq.	1.34		0.66 + 0.5 = 1.16
Addition of B will bring backward reaction			
at time t	$(1.34 + X)$		$(1.16 - X)$

$\because \quad [B] = \frac{3}{4}[A]_{eq.} = \frac{3}{4}\times1.34 = 1.005$

$$(1.16 - X) = 1.005 \quad \therefore \quad X = 0.155$$

Now, $\frac{dX}{dt} = K_1 - K_2[X] = 0.66K_2 - K_2X = K_2[0.66 - X]$

$\therefore \quad \frac{dX}{(0.66-X)} = K_2 \cdot dt$

or $-2.303\log(0.66-X) = K_2 \cdot t + C$

at $t = 0, \quad X = 0$

$\therefore \quad C = -2.303\log 0.66 \quad \therefore \quad K_2 \cdot t = 2.303 \log \frac{0.66}{0.66-X}$

$\therefore \quad t = \frac{2.303}{3\times10^{-3}} \log \frac{0.66}{0.66-0.155} = \mathbf{89.24\ sec}$

110.

$$A_0 \longrightarrow B$$

$$0.01 \qquad 0$$

$$0.01 - x_{eq.} \qquad x_{eq.}$$

$$\frac{[B]_{eq.}}{[A]_{eq.}} = \frac{10^{-2}}{K_b} = 4 = \frac{[x]_{eq.}}{0.01-[x]_{eq.}}$$

$\therefore \quad K_b = 0.25\times10^{-2}$

and $\quad x_{eq.} = \frac{0.04}{5} = 0.008$

$$t = \frac{2.303}{(K_f + K_b)} \log \frac{[x]_{eq.}}{[x]_{eq.} - x}$$

$$30 = \frac{2.303}{1.25\times10^{-2}} \log \frac{0.008}{(0.008-x)}$$

$\therefore \quad \frac{0.008}{0.008-x} = 1.455$

$\therefore \quad x = \mathbf{2.50\times10^{-3}}$

111. $A \xrightarrow{0.002} B$, $A \xrightarrow{0.003} C$, $A \xrightarrow{0.00193} D$

What is pressure of B after 100 sec.

$K_{av} = 0.002 + 0.003 + 0.00193$

$= 0.00693$

Mole of (A) Left $Kt = 2.303 \log \frac{8}{[A]} = 0.00693 \times 100$

$= 2.303 \log \frac{8}{[A]}$

$\log \frac{8}{[A]} = \frac{0.00693\times100}{2.303} = 0.3010$

$\frac{8}{[A]} = 2$

$\therefore$ mole of (A) left $= 4$

$[A]$ decomposed $= 8 - 4 = 4$ mole

mole of B formed $= \frac{0.002}{0.00693} \times 4 \times 1 = \mathbf{1.154}$

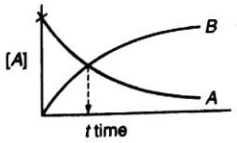
112. $MnO_4^- + [Fe(H_2O)_2(C_2O_4)_2]^{2-} + 8H^+ \longrightarrow Mn^{2+} + Fe^{3+} + 4CO_2 + 6H_2O$

$\because \quad -\frac{d[MnO_4^-]}{dt} = -\frac{1}{8}\frac{d[H^+]}{dt}$

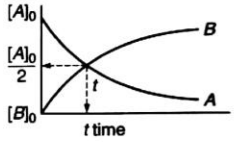
$\therefore \quad \frac{r_{H^+}}{r_{MnO_4^-}} = 8$

SINGLE INTEGER ANSWER PROBLEMS

1. The decomposition of equal mole of two reactants P and Q obey I order kinetics with half life 54 and 18 minute respectively. If both are allowed to run for 54 minute. The ratio of mole of P and Q left after decomposition will be.
2. A reaction obeys II order kinetics. If the half life period of the reaction is equal to its average life, then the value of reactant concentration at $t = 0$ is .....
3. A straight line with negative slope was found in graph of $\log_e K$ vs. $\frac{1}{T}$ with an angle of 45° with y-axis. The energy of activation is ..... cal.
4. A straight line was obtained on plotting $\log_{10}\frac{dx}{dt}$ vs. $\log_{10}(a-x)^n$ with an intercept on $\log\left(\frac{dx}{dt}\right)$ axis equal to 0.6021. The rate constant for the reaction is ..... litre^{n-1} mole^{1-n} t^{-1}.
5. Energy of activation for a reversible reaction is 6 kcal (E_a forward) and heat of reaction is –3 kcal. The energy of activation for backward reaction in kcal is .....
6. A reaction occurs in 'n' parallel paths. For each path having energy of activation as $E, 2E, 3E, \ldots nE$ and rate constant $K, 2K, 3K, \ldots nK$ respectively. If $E_{AV} = 3E$, then n is .....
7. If $\frac{d[NH_3]}{dt} = 34$ g hr^{-1} for the reaction
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
then $\frac{d[H_2]}{dt}$ is .....g hr^{-1}.
8. The half-life period of a reaction, becomes 16 times when reactant concentration is halved. The order of reaction is .....
9. The half lives of two parallel path reaction $A \begin{cases} \longrightarrow B \\ \longrightarrow C \end{cases}$ are 4 hrs and 12 hrs respectively. The average half-life for the decay of A is .....
10. The unit of rate constant for a reaction is litre^{2}mol^{-2} t^{-1}. The order of reaction is .....
11. For the I order reaction $3A \longrightarrow 2B$, the concentration of A and B at the intersection is given in figure.



if $[A]_0 = 20$ mol litre^{-1} then $[B]$ at time t is equal to .....
12. For the reaction : $2A + 3B \rightleftharpoons cC$ rate of formation of C is expressed as
$$\frac{d[C]}{dt} = -\frac{3[dA]}{dt}$$
The value of c is :
13. The order of reaction for $H_2 + Br_2 \longrightarrow 2HBr$ if it is carried over water is :
14. The decomposition of NH_3 on solid surface, *e.g.*, Pt shows the order of reaction equal to :
15. The time required to complete 99.9% decay is ..... times of the time required to complete 90% decay.
16. The rate of decomposition of a substance increases 2.25 times of concentration of reactant is increased by 1.5 times at same T. The order of reaction is :
17. For an elementary reaction $A \longrightarrow B$ shown in the figure.



The sum of slopes for curve A and B at the intersection point is:
18. In the above curve if rate constant for A is 0.34660, then t is:
19. The half life period for a reaction is 50 minute. If initial concentration is halved, the half life period is reduced to 25 minute. The order of reaction is :
20. For the reaction involving single reactant $C_o\sqrt{t_{1/2}}$ is found to be constant, where C_o is initial concentration and $t_{1/2}$ is half life. The order of reaction is .....
21. Energy of activation for free radical combination is .....
22. For the reaction
$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{CHBr}} \xrightarrow{OH^-} C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + Br^-,$$
rate law was found as :
$$\text{Rate} = 4.8\times10^{-5}[Br^-][OH^-] + 2.4\times10^{-6}[Br^-]$$
If the concentration of OH^- is 0.001 M, the % by which S_{N^2} path is followed is .....
23. A certain substance A is mixed with an equal amount of B. At the end of 1 hr, A is 70% reacted. How much % of A will be left unreacted at the end of 2.5 hr, if the reaction with respect to A is of 1 order ?
24. The rate of reaction depends on concentration as $-\frac{dC_A}{dt} = \frac{K_1C_A}{1+K_2C_A}$. If C_A being very high, then order of reaction is .....

25. A chemical reaction occurs in three paths having rate constants K_1, K_2 and K_3 respectively. If E_{a_1}, E_{a_2} and E_{a_3} are 5, 4, 8 kJ respectively and overall rate constant $K = \frac{K_1 K_3}{K_2}$. Assuming $A_{av} = \frac{A_1 A_3}{A_2}$ the overall energy of activation in kJ is .....
26. $t_{99.6\%} = t_{1/2} \times a$; the value of a is .....
27. Half-life of a reactant was found to be 9 hours, when 1.0 M reactant was allowed to carry out reaction. If 0.5 M reactant was taken then half-life was found 45 hours. The order of reaction is .....
28. For a consecutive I order reaction of both the steps $A \xrightarrow{K_1} B \xrightarrow{K_2} C$. If 20 M of A are taken and $K_2 = 2K_1$, the maximum concentration of B will be ..... M
29. Two first order reaction involving reactants A and B have the same frequency factor and activation energy of A is 10.46 kJ more than B. If A dissociates 30% in 60 minute at 100°C, the time taken in minute to dissociate 70% at the same temperature.
30. The rate of gaseous reaction expressed by $r = K[A][B]$. If pressure of gas A and B are doubled at the same conditions, the rate of reaction will be increased by ..... times.
31. 10 mole of a radioactive element undergoes decay follow I order to give three products B, C and D with rate constant 0.002, 0.003 and 0.00193 sec^{-1} respectively. How much mole are decayed in 100 sec.
32. For a given reaction $A \longrightarrow B$, temperature coefficient is constant. If $\frac{K_{55°C}}{K_{25°C}} = 8$ what is the value of $\frac{K_{65°C}}{K_{35°C}}$ in nearest possible integer. K is rate constant.
33. The rate of decomposition of HI is given by; rate = $K[HI]^2$. The rate constant K is 1×10^{-6} litre $mol^{-1} sec^{-1}$ at 600 K. Find out the number of moles of HI $\times 10^{-10}$ decomposed in first second when HI sample is taken in 1 litre container at 1 atm pressure.
34. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained.

$[R]$ (molar)	1.0	0.75	0.40	0.10
t (min.)	0.0	0.05	0.12	0.18

The order of reaction is: **(IIT 2010)**

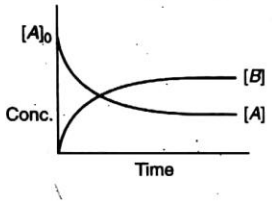
35. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10} 2 = 0.3$) **(IIT 2012)**

ANSWERS

1. Four 2. One 3. Two 4. Four 5. Nine 6. Four 7. Six 8. Five 9. Three 10. Three 11. Eight 12. Six
13. Zero 14. Zero 15. Three 16. Two 17. Zero 18. Two 19. Zero 20. Three 21. Zero 22. Two 23. Five 24. Zero
25. Nine 26. Eight 27. Zero 28. Five 29. Seven 30. Four 31. Five 32. Eight 33. Four 34. Zero 35. Nine

OBJECTIVE PROBLEMS (One Answer Correct)

1. The rate of combination of free radicals :
   (a) increases with increase in temperature
   (b) decreases with increase in temperature
   (c) dependent of temperature
   (d) altogether different for different reactions and independent of temperature
2. A consecutive reaction $P \xrightarrow{K_1} Q \xrightarrow{K_2} R$ leads to :
   (a) maxima in $[P]$ if $K_1 > K_2$
   (b) maxima in $[Q]$ if $K_1 > K_2$
   (c) maxima in $[Q]$ if $K_1 < K_2$
   (d) maxima in $[P]$ if $K_1 < K_2$
3. At the intersection point of two curves $nA \longrightarrow mB$, the concentration of B can be given by assume I order :

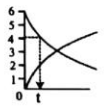


   (a) $\frac{m}{m+n}[A]_0$ (b) $\frac{m}{n}[A_0]$
   (c) $\frac{m}{m-n}[A_0]$ (d) $\frac{n}{m+n}[A_0]$
4. Select the incorrect statement :
   (a) Half-life period of all reactions decreases with increase in temperature.
   (b) Half life period of I order reaction is always constant.
   (c) Higher is rate constant of a reaction, lesser will be its energy of activation.
   (d) Rate of reaction whether exothermic or endothermic usually increases with temperature.
5. The rate constants of three reactions involving reactant A only obeying I, II, III order respectively is same. Which of the following is true ?
   (a) $r_3 > r_2 > r_1$ if $[A] > 1$ (b) $r_1 > r_2 > r_3$ if $[A] < 1$
   (c) $r_1 = r_2 = r_3$ if $[A] = 1$ (d) All of these
6. $\log_e K$ *vs.* $1/T$ plots shows a straight line having slope of 120° and intercepts on the Y-axis of 2, then :
   (a) $E_a = 8.0$ cal, $A = 100$
   (b) $E_a = 8.0$ cal, $A = 2$
   (c) $E_a = 3.46$ cal, $A = 7.38$
   (d) $E_a = 3.46$ cal, $A = 100$
7. The temperature coefficients of two reactions are 2 and 3 respectively. Which would be correct for these reactions?
   (a) $E_{a_1} < E_{a_2}$ (b) $E_{a_1} > E_{a_2}$
   (c) $E_{a_1} = E_{a_2}$ (d) Nothing can be said
8. A reaction occurs in three rate determining steps having rate constants K_1, K_2 and K_3 respectively and arrehenius factor A_1, A_2, A_3 respectively. The overall rate constant $K = \frac{K_1 K_2}{K_3}$. If energy of activations for each step is E_{a_1}, E_{a_2} and E_{a_3} respectively, then overall energy of actiavtion is :
   (a) $E_{a_1} + E_{a_2} + E_{a_3}$
   (b) $\frac{E_{a_1} \times E_{a_2}}{E_{a_3}}$
   (c) $E_{a_1} + E_{a_2} - E_{a_3}$
   (d) $K_3\left[\frac{E_{a_1}}{K_2} + \frac{E_{a_2}}{K_1} + \frac{K_3 E_{a_3}}{K_1 K_2}\right]$
9. For a I order reaction $-\frac{d[A]}{dt} = K[A]_0$. The reaction is carried out by taking 100 mol litre^{-1} of A, then concentration of A decayed after time $\frac{1}{K}$ is :
   (a) 53.21 mol litre^{-1} (b) 36.79 mol litre^{-1}
   (c) 61.21 mol litre^{-1} (d) 26.79 mol litre^{-1}
10. For two I order reactions : $A \longrightarrow B$; $K_1 = 10^{15} e^{\frac{2\times10^3}{T}}$
    $C \longrightarrow D$; $K_2 = 10^{14} e^{\frac{10^3}{T}}$
    The temperature at which both have same rate if $[A] = [C]$ is made initially :
    (a) 707.2°C (b) 434.2°C
    (c) 727°C (d) 707.2 K
11. H_2O and oxygen atoms react in upper atmospheric level bimolecularily to form two OH radicals having heat of reaction 72 kJ at 400 K and energy of activation being 77 kJ mol^{-1}. E_a for bimolecular combination of two OH radicals to form H_2O and O-atom is :
    (a) – 5 kJ (b) + 5 kJ
    (c) – 10 kJ (d) + 10 kJ
12. The rate of appearance of NO_2 (in atm m^{-1}) following the reaction, $N_2O_4 \longrightarrow 2NO_2$ when initial pressure of N_2O_4 is reduced from 0.50 atm to 0.25 atm in 5 minutes is :
    (a) 0.1 (b) 0.2
    (c) 0.25 (d) 0.3
13. At 3 km altitude, water boils at 90°C and 300 seconds are taken to cook a '3 minute egg'. The temperature coefficient for the process of cooking is :
    (a) 2.66 (b) 1.66
    (c) 3.66 (d) 0.6
14. The rate constant, the energy of activation and the Arrhenius parameter of a chemical reactions at 25°C are 3.0×10^{-4} sec^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{14} sec^{-1} respectively. The value of rate constant as $T \longrightarrow \infty$ is :
    (a) 2.0×10^{18} sec^{-1} (b) 6.0×10^{14} sec^{-1}
    (c) infinity (d) 3.6×10^{30} sec^{-1}

15. Select the incorrect statement :
(a) Rate of exothermic reactions increases with increase in temperature.
(b) Alkaline hydrolysis of ester is irreversible reaction.
(c) For $N_2 + 3H_2 \rightleftharpoons 2NH_3$; if rate of formation of NH_3 is 0.001 kg hr, than rate of consumption of H_2 is 0.0015 kg/hr.
(d) In Arrhenius equation :
$$K = Ae^{-Ea/RT}; \text{ if } T \to \infty \; K = A$$

16. A consecutive reaction : $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ shows a :
(a) Maxima in the concentration of A
(b) Maximum in the concentration of B
(c) Maxima in the concentration of C
(d) None of the above

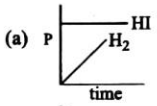
17. For the unimolecular reaction $A \to B$, the figure given below shows that at the time t curves represents :

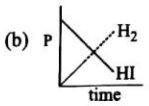


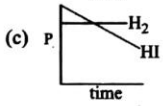
Thus t is :
(a) $t_{1/3}$ (b) $t_{1/2}$
(c) $t_{2/3}$ (d) $t_{1/4}$

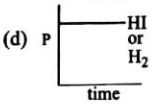
18. If c is the concentration of n mole of gas at pressure P and temperature T, then for the ideal gas reaction, the rate of reaction can be given by:
(a) $-\frac{d[A]}{dt}$ (b) $-\frac{1}{RT}\frac{dP}{dt}$
(c) $-\frac{1}{v}\frac{dn}{dt}$ (d) either of these

19. Decomposition of HI on gold surface is zero order reaction. Which of the following graph correctly represents this reaction?

(a) 

(b) 

(c) 

(d) 

20. The reaction $A \to B + C$ has rate constant 1×10^{-3} Ms^{-1}. If one starts the reaction with one mole of A than $t_{1/2}$ and completion of reaction time would be:
(a) 1000 s, 500 s (b) 500 s, 1000 s
(c) 750 s, 400 s (d) 400 s, 800 s

21. The half of a gaseous compound $(A_{(g)} \to B_{(s)})$ initially at 2 atm is 200 sec. If the initial pressure is taken as 1 atm, the half life reduces to 100 sec. The order of reaction is:
(a) 0 (b) 1
(c) 2 (d) 3

22. Which one is incorrect statement?
(a) Always $E_a > \Delta H$ for an endothermic reaction.
(b) $E_b < \Delta H$ for an endothermic reaction.
(c) $E_a \gtrless \Delta H$ for an exothermic reaction.
(d) Always $E_a < \Delta H$ for an exothermic reaction.

23. For a I order reaction which one is not correct?
(a) The concentration of product increases linearly with time
(b) The concentration of product increases exponentially with time
(c) The degree of dissociation 'α' is given by $1 - e^{-kt}$
(d) The reaction never goes for completion

24. Select the incorrect statement:
(a) A spontaneous reaction is not necessarily a fast reaction.
(b) Larger the activation energy, greater is the effect on rate constant with rise in temperature.
(c) The reactivity of bromine is more in liquid state than in vapour state.
(d) Reactions with low energy of activation are fast.

25. For the process :$2O_3 \to 3O_2$, mechanism is:
$$O_3 \overset{\text{fast}}{\rightleftharpoons} O_2 + O \quad ; \quad O + O_3 \xrightarrow{\text{slow}} 2O_2$$
The rate law is:
(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2 \cdot [O_2]^{-1}$
(c) $r = k[O_3] \cdot [O_2]$ (d) $r = k[O_3]^2 \cdot [O_2]^{-3}$

26. The rate constant of a reaction depends on :
(a) temperature
(b) initial concentration of the reactants
(c) time of reaction
(d) extent of reaction

27. The specific rate constant of a first order reaction depends on the:
(a) concentration of the reactant
(b) concentration of the product
(c) time required to complete half of the reaction
(d) none of these

28. For an endothermic reaction ΔH represents enthalpy of the reaction, the minimum value of the energy of activation will be:
(a) less than ΔH (b) zero
(c) more than ΔH (d) equal to ΔH

29. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{14} s^{-1} respectively. The value of the rate constant as $T \to \infty$ is,
(a) 2.0×10^{18} s^{-1} (b) 6.0×10^{14} s^{-1}
(c) infinity (d) 3.6×10^{30} s^{-1}

30. The variation of rate constant K for a given reaction with temperature is given by the expression :

$$\ln K_T = \ln K_0 + \left(\frac{\ln 3}{10}\right)T$$

The value of temperature coefficient is :

(a) 2 (b) 3

(c) 4 (d) 5

31. Reaction $2A + B \xrightarrow{K} C + D$, shows first order with respect to A and second order with respect to B. The reaction was allowed with molarity a_0 M of A and $2a_0$ M of B at $t = 0$. If after time $t = 30$ minute the molarity of C was $\frac{a_0}{4}$, the rate of reaction after 30 minutes can be written as :

(a) $r = \frac{7K a_0^3}{16}$ (b) $r = \frac{27K a_0^3}{32}$

(c) $r = \frac{247K a_0^3}{64}$ (d) $r = \frac{49K a_0^3}{32}$

32. The rate expression for a reaction is $-\frac{dc}{dt} = \frac{\alpha c}{1+\beta c}$ (α and $\beta > 0$). The half life of the reaction can be given by :

(a) $\frac{1}{\alpha}\ln 2 + \beta c_0$ (b) $\frac{1}{\alpha}\ln 2 + \frac{\beta c_0}{2\alpha}$

(c) $\ln 2 + \frac{\beta c_0}{2}$ (d) $\ln 2 + \frac{\beta c_0}{2\alpha}$

33. Rate constant for nth order reaction is given by :

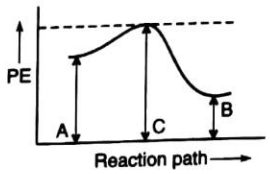
$$K \cdot t = \frac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}]$$

Thus, for a reaction of nth order, the ratio of $\frac{t_{1/2}}{t_{3/4}}$ is :

(a) 2^n (b) 2^{n-1}

(c) 2^{1-n} (d) $\frac{2^{n-1}-1}{4^{n-1}-1}$

34. With respect to the figure given below which of the following statements is correct?



(a) E_a for the forward reaction is $C - B$

(b) E_a for the forward reaction is $B - A$

(c) $E_{a\,(\text{forward})} < E_{a\,(\text{backward})}$

(d) E_a (for reverse reaction) $= C - A$

35. A consecutive reaction : $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ shows a :

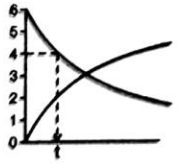
(a) maxima in the concentration of A

(b) maximum in the concentration of B

(c) maxima in the concentration of C

(d) none of the above

36. For the unimolecular reaction $A \longrightarrow B$, the figure given below shows that at the time t curves represents :



Thus t is given by :

(a) $t_{1/3}$ (b) $t_{1/2}$

(c) $t_{2/3}$ (d) $t_{1/4}$

37. The rate of a certain reaction depends on concentration according to the equation :

$$-\frac{dC}{dt} = \frac{K_1 C}{1 + K_2 C}$$

The order of reaction, where (i) concentration is very very high, (ii) very very low will be respectively :

(a) zero, 1 (b) 1, zero

(c) 1, 2 (d) 1, 1

38. The reaction : $CO + Cl_2 \longrightarrow COCl_2$ has the following mechanism.

(i) $Cl_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast)

(ii) $Cl + CO \underset{K_2'}{\overset{K_1'}{\rightleftharpoons}} COCl$ (fast)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

The rate expression will be :

(a) $r = K[CO][Cl_2]$ (b) $r = K[CO][Cl_2]^{3/2}$

(c) $r = K[CO]^2[Cl_2]$ (d) $r = [CO]^{3/2}[Cl_2]$

39. What will be the order of reaction given below ?

$$NH_4CNO \longrightarrow NH_2CONH_2$$

If the reaction is completed in three steps as :

(i) $NH_4CNO \rightleftharpoons NH_4NCO$ (fast equilibrium)

(ii) $NH_4NCO \rightleftharpoons NH_3 + H{-}N{=}C{=}O$ (fast equilibrium)

(iii) $NH_3 + H{-}N{=}C{=}O \longrightarrow NH_2CONH_2$ (slow)

(a) 2 (b) 3

(c) 1 (d) zero

40. The temperature coefficient of a reaction is 2. By what factor, the rate of reaction will increases when temperature is raised by 30°C :

(a) 21 (b) 6

(c) 8 (d) 16

41. Select the wrong statement :

(a) Rate of chain reaction involving nascent atoms and free radicals as intermediate depends on shape of the vessel

(b) Energy of activation is definitely +ve for unimolecular reactions
(c) Reaction having rate independent of concentration, never goes to completion
(d) Stoichiometry of reaction does not indicates its order

42. The *trans* → *cis* isomerisation of 1,2-dichloroethylene proceeds with an activation energy of 55.5 kcal mol^{-1}. The heat of reaction at constant pressure for above transformation is 1.0 k cal mol^{-1}. The activation energy for *cis* → *trans* transformation of 1,2-dichloroethylene is :
(a) 56.5 (b) 54.5
(c) 55.5 (d) none of these

43. The energy of activation for a reaction is 25 kJ mol^{-1}. To what temperature should it be raised from 300 K in order that the reaction rate increases 10 times.
(a) 389.5 K (b) 489.5 K
(c) 289.5 K (d) none of these

44. For the reaction $RX + OH^- \longrightarrow ROH + X^-$ at 50°C the rate expression is given as :
$$\text{rate} = 4.7 \times 10^{-5}[RX][OH^-] + 0.24 \times 10^{-5}[RX]$$
what percentage of *RX* reacts by the S_{N^2} mechanism when $[OH^-] = 0.001\ M$
(a) 0.192 (b) 0.0192
(c) 19.2 (d) 1.92

45. For a given reaction $A \longrightarrow$ Product, the graph plotted between $\log t_{1/2}$ *vs.* $\log [A]$ leads to an angle of 315°. The order of reaction is :
(a) 0 (b) 1
(c) 2 (d) 3

46. Find out ratio of two rates $\frac{r_1}{r_2}$ shown for the elementary reaction :

$$\underset{P_A}{A(g)} + \underset{P_B}{2B(g)} \longrightarrow C(g) + D(g)$$

r_1 for case I 6 atm 8 atm
r_2 for case II 6 atm 2 atm
(a) 8 (b) 16
(c) 32 (d) 64

47. Reactants *A* and *B* shows I order decomposition individually. If $[A_0] = 8[B_0]$ and $t_{1/2}$ for *A* and *B* are 10 and 20 minutes respectively then if both starts decomposing at the same time, after how much minute the concentration of both *A* and *B* will be same :
(a) 20 (b) 40
(c) 60 (d) 80

48. Mechanism of a hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ is given below :
(i) $X_2 \longrightarrow X + X$ (fast)
(ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow)
(iii) $X + Y \longrightarrow XY$ (fast)
The overall order of the reaction will be :
(a) 1 (b) 2
(c) 0 (d) 1.5

49. A first order reaction has a specific reaction rate of $10^{-2}\ sec^{-1}$. How much time will it take for 20 g of the reaction to reduce to 5g?
(a) 238.6 sec (b) 138.6 sec
(c) 346.5 sec (d) 693.0 sec

SOLUTIONS (One Answer Correct)

1. (d) $r = K[\ ]^n$ and $K = Ae^{-E_a/RT}$. $E_a = 0$ for free radical combination. K is constant with T.

2. (b) $[R]$ can be maximum only if its decay is slower than P, *i.e.*, $K_2 < K_1$.

3. (a) $[A]_{\text{left}} = [B]_{\text{formed}} = \frac{m}{n}[A]_{\text{decayed}}$,

$$[A_0]e^{-\lambda t} = \frac{m}{n}[1-e^{-\lambda t}][A_0]$$

$$\therefore \quad ne^{-\lambda t} = m - me^{-\lambda t} \text{ or } e^{-\lambda t} = \frac{m}{m+n}$$

$$\therefore \quad [B]_{\text{formed}} = \frac{m}{n}\left[1-\frac{m}{m+n}\right][A_0]$$

$$= \frac{m}{n}\left[\frac{m+n-m}{m+n}\right][A_0]$$

$$= \frac{m}{m+n}[A_0]$$

4. (c) $K = Ae^{-E_a/RT}$. K depends upon E_a, T and nature of reaction; but always increases with T. Thus rate always increases with T.

5. (d) $r_1 = K[A]^1$; $r_2 = K[A]^2$; $r_3 = K[A]^3$

6. (c) $\ln K = \ln A - \frac{E_a}{RT}$

Intercept $= \ln A = 2$;

Also $-\frac{E_a}{R} = \tan\theta (\tan 120 = -1.73)$

$2.303 \log [A] = 2$

$\log [A] = \frac{2}{2.303}$ $\therefore E_a = 1.73 \times 2 \text{cal} = 3.46 \text{ cal}$

$[A] = 7.38$

7. (a) Temperature coefficients are :

I. $\frac{K_1}{K_2} = \frac{E_{a_1}}{2.303R}\frac{[T_2 - T_1]}{T_1T_2} = 2$

II. $\frac{K_1'}{K_2'} = \frac{E_{a_2}}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] = 3$

if $\frac{K_1}{K_2} < \frac{K_1'}{K_2'}$ then $E_{a_2} > E_{a_1}$

8. (c) $$K = \frac{K_1K_2}{K_3} = \frac{A_1e^{-E_{a_1}/RT} \cdot A_2e^{-Ea_2/RT}}{A_3 \cdot e^{-E_{a_3}/RT}}$$

$$= \frac{A_1A_2}{A_3} \cdot e^{-\left[\frac{E_{a_1}}{RT} + \frac{E_{a_2}}{RT} - \frac{E_{a_3}}{RT}\right]}$$

$$K_{AV} = A_{AV} \cdot e^{-\frac{E_a}{RT}}$$

$\because \quad E_a = E_{a_1} + E_{a_2} - E_{a_3}$

9. (c) $[A] = [A]_0 e^{-Kt} = [100]e^{-K/K} = \frac{[100]}{e} = \frac{100}{2.718}$

$= 36.79$ mole litre^{-1}

$\therefore \quad [A]_{\text{decayed}} = 61.21$

10. (a) $r_1 = K_1[A]$ $\because$ $r_1 = r_2$ $\log_{10} K_1 = 15 - \frac{2000}{2.303T}$

$r_2 = K_2[C]$ $\therefore$ $K_1 = K_2$ $\log K_2 = 14 - \frac{1000}{2.303T}$

or $15 - \frac{2000}{T \times 2.303} = 14 - \frac{1000}{T \times 2.303}$

$\therefore \quad T = \frac{1000}{2.303} = 434.22 \text{K}$

11. (b) $H_2O + O \overset{E_a = 77 \text{kJ}}{\rightleftharpoons} 2OH$; $\Delta H = 72$ kJ

$2OH \longrightarrow H_2O + O$; $\Delta H = -72$ kJ

$E_{a(f)} - E_{a(b)} = \Delta H$.

$E_{a(f)} - 77 = -72$

$E_{a(f)} = +5$ kJ

12. (a) $r = -\frac{d[N_2O_4]}{dt} = -\frac{[0.50 - 0.25]}{5} = \frac{0.25}{5}$

$= 0.05$ atm min^{-1}

$\therefore \quad \frac{d[NO_2]}{dt} = 2 \times -\frac{d[N_2O_4]}{dt} = 2 \times 0.05$

$= 0.1$ atm min^{-1}

13. (b) Temperature coefficient

$= \frac{K_{373}}{K_{363}} = \frac{(t)_{363}}{(t)_{373}} = \frac{300}{180} = 1.66$ $\left(K \propto \frac{1}{t}\right)$

14. (b) $K = Ae^{-E_a/RT}$ if $T \longrightarrow \infty$, $e^{-E_a/RT} = 1$, or $K = A$

15. (c) $-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

$\therefore \quad -\frac{d[H_2]}{dt} = \frac{3}{2} \times \frac{0.001}{17 \times 10^{-3}}$ mol/hr

$= \frac{3}{2} \times \frac{0.001}{17 \times 10^3} \times 2$ g/hr

$= 3 \times \frac{0.001 \times 10^3}{17 \times 10^3}$ kg/hr

$= 1.76 \times 10^{-4}$ kg/hr

16. (b) Maximum in the concentration of B.

17. (a) Two mole of A are decayed out of six in time t.

18. (d) The rate of reaction $= -\frac{dc}{dt} = -\frac{1}{V}\frac{dn}{dt} = -\frac{1}{RT}\frac{dP}{dt}$.

19. (b) For zero order reaction: $P_{HI} = P_{HI}^0 - Kt$. Also P_{H_2} continuously increases.

20. (b) This is zero order reaction from the values of K (Ms^{-1})

$\therefore \quad t_{1/2} = \frac{(A_0)}{2K} = \frac{1}{2 \times 10^{-3}} = 500$ sec

and $t_{1/2} = \frac{[A_0]}{K} = \frac{1}{10^{-3}} = 1000$ sec

21. (a) $t_{1/2} \propto (P)^{1-n}$

$200 \propto (2)^{1-n}$

$100 \propto (1)^{1-n}$

$\therefore \quad 2 = 2^{1-n}$

$\therefore \quad 1 = 1-n \qquad \therefore \quad n = 0$

22. (d) $E_a - E_b = \Delta H$

In exothermic reaction $E_a \gtrless \Delta H$ depending upon the nature of reaction.

23. (a) $X = a(1-e^{-Kt})$



24. (c) Vapour state of Br_2 is more reactive as it possesses higher energy level and more collision frequency.

25. (b) $r = K[O_3][O]$

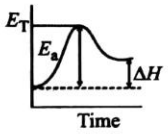
Also $K_c = \dfrac{[O_2][O]}{[O_3]} \qquad \because \quad [O] = \dfrac{K_c[O_3]}{[O_2]}$

$\therefore \quad r = K[O_3]^2 \cdot [O_2]^{-1}$

26. (a) $K = Ae^{-E_a/RT}$

27. (d) $K = \dfrac{0.693}{t_{1/2}}$

28. (c)



$E_a > \Delta H$ but for exothermic reactions $E_a >$ or $< \Delta H$

29. (b) $K = Ae^{-E_a/RT}$ at $T \to \infty$, $K = A$

30. (b) $\ln K_{T_1} = \ln K_0 + \left[\dfrac{\ln 3}{10}\right] T_1$

$\ln K_{T_2} = \ln K_0 + \left[\dfrac{\ln 3}{10}\right] T_2$

$\therefore \quad \ln K_2 - \ln K_1 = \left[\dfrac{\ln 3}{10}\right](T_2 - T_1)$

or $\ln \dfrac{K_2}{K_1} = \left[\dfrac{\ln 3}{10}\right] \times (T_2 - T_1)$

if $T_2 - T_1 = 10^\circ$ C, then temperature coefficient $= \dfrac{K_2}{K_1}$

or $\ln \dfrac{K_2}{K_1} = \left[\dfrac{\ln 3}{10}\right] \times 10$

or $\dfrac{K_2}{K_1} = 3$

31. (d)

	$2A$	+ B	$\longrightarrow$ C	+ D
$t = 0$	a_0	$2a_0$	0	0
$t = 30$	$\left(a_0 - \frac{a_0}{2}\right)$	$\left(2a_0 - \frac{a_0}{4}\right)$	$\frac{a_0}{4}$	$\frac{a_0}{4}$

After $t = 30$ rate $= K[A][B]^2$

$\therefore \quad \text{rate} = K\left[a_0 - \dfrac{a_0}{2}\right]^1 \left[2a_0 - \dfrac{a_0}{4}\right]^2$

$= K\dfrac{a_0}{2} \times \dfrac{49a_0^2}{16} = \dfrac{49Ka_0^3}{32}$

32. (b) $-\dfrac{dc}{dt} = \dfrac{\alpha c}{1+\beta c}$

$\dfrac{-dc(1+\beta c)}{c} = \alpha \cdot dt$

$-\dfrac{dc}{c} - dc \cdot \beta = \alpha \cdot dt$

on integration $\quad -\ln c - c\beta = \alpha t + \text{constant}$

at $t = 0, c = c_0$

$\therefore \quad -\ln c_0 - c_0\beta = \text{constant}$

Therefore $\quad -\ln c - c\beta = \alpha t - \ln c_0 - c_0\beta$

$\ln \dfrac{c_0}{c} + \beta(c_0 - c) = \alpha t$

at $t = t_{1/2}$; $c = \dfrac{c_0}{2}$

$\therefore \quad \ln \dfrac{c_0}{\frac{c_0}{2}} + \beta\left(c_0 - \dfrac{c_0}{2}\right) = \alpha t_{1/2}$

or $\ln 2 + \dfrac{c_0\beta}{2} = \alpha t_{1/2}$

$t_{1/2} = \dfrac{1}{\alpha}\left[\ln 2 + \dfrac{c_0\beta}{2}\right]$

33. (d) $A \longrightarrow$ Product

$\therefore \quad -\dfrac{dC_A}{dt} = KC_A^n \qquad (\because \text{ order is } n)$

On integrating $\dfrac{-(C_A)^{1-n}}{1-n} = Kt + \text{constant} \qquad \ldots(1)$

at $t = 0, C_A = C_0 \quad \therefore \quad \text{constant} = -\dfrac{C_0^{1-n}}{1-n} \qquad \ldots(2)$

$\therefore$ By Eqs. (1) and (2), $\quad -\dfrac{C_A^{1-n}}{1-n} = Kt - \dfrac{C_0^{1-n}}{1-n}$

or $\quad Kt = \dfrac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}] \qquad \ldots(3)$

if $C_A = \dfrac{C_0}{2}$ at $t = t_{1/2}$ then by Eq. (3)

$Kt_{1/2} = \dfrac{1}{(n-1)}\left[\left(\dfrac{C_0}{2}\right)^{1-n} - (C_0)^{1-n}\right]$

$= \dfrac{(C_0)^{1-n}}{(n-1)} \times [2^{n-1} - 1] \qquad \ldots(4)$

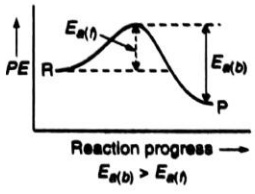
Similarly, if $C = \dfrac{C_0}{4}$ at $t = t_{3/4}$, then by Eq. (3)

$Kt_{3/4} = \dfrac{C_0^{1-n}}{(n-1)}[4^{n-1} - 1] \qquad \ldots(5)$

By Eqs. (4) and (5),

$\dfrac{t_{1/2}}{t_{3/4}} = \dfrac{2^{n-1} - 1}{4^{n-1} - 1}$

34. (c)



$E_{a(b)} > E_{a(f)}$

35. (b) Maximum in the concentration of B.

36. (a) Two moles of A are decayed out of six in time t.

37. (a) $$-\frac{dC}{dt}=\frac{K_1C}{1+K_2C}=\frac{K_1}{\frac{1}{C}+K_2}$$

(i) If C is very very high $1/C$ is smallest and thus negligible.

$$\therefore \quad -\frac{dC}{dt}=\frac{K_1}{K_2}=\text{constant}$$

Thus order of reaction is **zero.**

(ii) If C is very very low. $1+K_2C=K'$

$$\therefore \quad -\frac{dC}{dt}=\frac{K_1C}{K'}=K''\cdot C$$

Thus, order of reaction is **unity.**

38. (b) By step (iii) $\frac{d[COCl_2]}{dt}=K_3[COCl][Cl_2]$ ... (a)

By step (i) $\frac{K_1}{K_2}=\frac{[Cl]^2}{[Cl_2]}$ ... (b)

By step (ii) $\frac{K_1'}{K_2'}=\frac{[COCl]}{[CO]\,[Cl]}$ ... (c)

Thus from Eqs. (b) and (c)

$$[COCl]=\frac{K_1'}{K_2'}\cdot[CO]\times\sqrt{\frac{K_1}{K_2}\cdot[Cl_2]} \quad \text{... (d)}$$

From Eqs. (a) and (d)

$$\frac{d[COCl_2]}{dt}=K_3\frac{K_1'}{K_2'}\left(\frac{K_1}{K_2}\right)^{1/2}[CO][Cl_2]^{1/2}[Cl_2]$$

$$\frac{d[COCl_2]}{dt}=K[CO][Cl_2]^{3/2}$$

39. (c) The rate of formation of urea is given by Eq. (iii)

$$\frac{d[\text{urea}]}{dt}=K[NH_3][HNCO] \quad \text{... (a)}$$

By step (ii) we have: $\frac{[NH_3][HNCO]}{[NH_4NCO]}=K_{C_1}$ ... (b)

By step (i) we have: $\frac{[NH_4NCO]}{[NH_4CNO]}=K_{C_2}$ ... (c)

$\therefore$ By Eqs. (b) and (c)

$$[NH_3][HNCO]=K_{C_1}\cdot K_{C_2}[NH_4CNO] \quad \text{... (d)}$$

$\therefore$ By Eqs. (a) and (d)

$$\frac{d[\text{urea}]}{dt}=K\cdot K_{C_1}\cdot K_{C_2}[NH_4CNO]$$

$$\frac{d[\text{urea}]}{dt}=K'[NH_4CNO]$$

40. (c) $\frac{K_{T+10}}{K_T}=2$; $\frac{K_{T+20}}{K_{T+10}}=2$; $\frac{K_{T+30}}{K_{T+20}}=2$

On multiplying $\frac{K_{T+30}}{K_T}=2\times2\times2=8$

41. (c) Zero order reaction takes place at constant rate and goes for completion.

42. (b) $$\Delta H=E_{a_f}-E_{a_b}$$

$$\therefore \quad E_{a_b}=E_{a_f}-\Delta H=55.5-1.0=54.5$$

43. (a) $$\frac{K_T}{K_{300}}=10$$

$$2.303\log\frac{K_T}{K_{300}}=\frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$2.303\log 10=\frac{25\times10^3}{8.314}\left[\frac{T_2-300}{T_2\times300}\right]$$

$$T_2=389.5\text{ K}$$

44. (d) The rate expression involves S_{N^1} and S_{N^2} steps as

$$RX+OH^-\longrightarrow R^++X^-\xrightarrow{OH^-}ROH+X^-$$

$$RX+OH^-\longrightarrow HO\text{----}R\text{----}X^-\longrightarrow HOR+X^-$$

$$\text{rate}=4.7\times10^{-5}\underset{S_{N^2}}{[RX][OH^-]}+0.24\times10^{-5}\underset{S_{N^1}}{[RX]}$$

$$\%\,S_{N^2}=\left[\frac{r_{S_{N^2}}}{r_{S_{N^1}}+r_{S_{N^2}}}\right]\times100$$

$$=\left[\frac{4.7\times10^{-5}[RX][OH^-]}{0.24\times10^{-5}[RX]+4.7\times10^{-5}[RX][OH^-]}\right]\times100$$

$$=\left[\frac{4.7\times10^{-5}[OH^-]}{0.24\times10^{-5}+4.7\times10^{-5}[OH^-]}\right]\times100$$

$$=\left[\frac{4.7\times10^{-5}\times0.001}{0.24\times10^{-5}+(4.7\times10^{-5}\times0.001)}\right]\times100$$

$$=1.92$$

45. (c) $$t_{1/2}\propto[A]^{1-n}=K[A]^{1-n}$$

$$\log t_{1/2}=\log K+(1-n)\log[A]$$

$$1-n=\tan 315=-1$$

$$\therefore \quad n=2$$

46. (b) For case I: $r_1=K(P_A)(P_B)^2$

$$=K\times6\times8^2=384\text{ K}$$

For case II: $r_2=K\times6\times(2)^2=24\text{ K}$

$$\therefore \quad \frac{r_1}{r_2}=\frac{384\text{ K}}{24\text{ K}}=16$$

47. (c) $$\frac{N_{0A}}{N_A}=e^{K_At}$$

$$\frac{N_{0B}}{N_B}=e^{K_Bt}$$

Given $N_{0B}=\frac{N_{0A}}{8}$ and after time t, $N_A=N_B$

$$\therefore \quad \frac{\frac{N_{0A}}{N_A}}{\frac{N_{0B}}{N_B}}=e^{(K_A-K_B)t}$$

$$\frac{\frac{N_{0A}}{N}}{\frac{N_{0A}}{\frac{8}{N}}}=e^{(K_A-K_B)t}$$

or $$\ln 8=[K_A-K_B]t=\left[\frac{0.693}{10}-\frac{0.693}{20}\right]t$$

or $$2.08=\frac{0.693}{20}\times t$$

$$t=\frac{2.08\times20}{0.693}=60\text{ minutes}$$

48. (b) **Solution 1:** (a)

Rate determining step is not applicable when slow reaction is reversible and thus steady state approximation concept should be used.

According to steady state approximation concentration of intermediate remains constant most of the time so rate of reaction with respect to intermediate is taken to be zero.

$$X_2 \xrightarrow{k_1} 2X$$

$$X + Y_2 \xrightarrow{k_2} XY + Y$$

$$Y + XY \xrightarrow{k_3} X + Y_2$$

$$X + Y \xrightarrow{k_4} XY$$

At steady state approximation, rate of formation of intermediate = rate of disappearance of intermediate or rate of reaction for intermediate = 0

$$r = \frac{d[X]}{dt}$$

$$= 2k_1[X_2] - k_2[X][Y_2] + k_3[XY][Y] + k_4[X][Y]$$

$$= 0 \quad \ldots(i)$$

$$r = \frac{d[Y]}{dt}$$

$$= k_2[X][Y_2] - k_3[Y][XY] - k_4[X][Y]$$

$$= 0 \quad \ldots(ii)$$

$$k_2[X][Y_2] = k_3[Y][XY] + k_4[X][Y] \quad \ldots(iii)$$

on substituting the value of equation (iii) into equation (i) :

$$r = 2k_1[X_2]^1$$

So order of reaction is 1.

Solution 2 (d)

On the basis of rate determining step.

(i) $X_2 \longrightarrow X + X$ (fast)

(ii) $X + Y_2 \longrightarrow XY$ (slow)

(iii) $X + Y \longrightarrow XY$ (fast)

Note that $X + Y_2 \rightleftharpoons XY$ cannot be slow as it involves equilibrium. So mechanics of this reaction may be taken as

(i) $X_2 \rightleftharpoons X + X$ (fast)

(ii) $X + Y_2 \longrightarrow XY$ (slow)

(iii) $X + Y \longrightarrow XY$ (fast)

So step (ii) is rate determining step

$$r = k[X][Y_2] \quad \ldots(i)$$

X can be replaced by fast equilibrium given in step (i)

$$K = \frac{[X]^2}{[X_2]}$$

$$[X]^2 = k[X_2]$$

$$[X] = [k[X_2]]^{1/2} \quad \ldots(ii)$$

If value of equation (ii) is placed in equation (i) then

$$r = k[Y_2][k[X_2]]^{1/2}$$

So order of reaction is 1.5.

49. (b) $$K = 10^{-2} = \frac{0.693}{t/2}$$

So, $$\frac{t}{2} = \frac{0.693}{10^{-2}} = 69.3 \text{ sec}$$

For the reduction of 20 g of reactant into 5 g two half lives will be used.

So, time required = 2 × 69.3 = 138.6 sec

PREVIOUS YEARS PROBLEMS

1. The rate constant for the reaction;
$2N_2O_5 \longrightarrow 4NO_2 + O_2$ is 3.0×10^{-5} sec^{-1}. If the rate is 2.40×10^{-5} M sec^{-1}, then the concentration of N_2O_5 (in M) is: **(IIT 2000)**
(a) 1.4 (b) 1.2
(c) 0.04 (d) 0.8

2. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process $AB + h\nu \longrightarrow AB^x$, the rate of formation of AB^x is directly proportional to : **(IIT 2001)**
(a) C (b) I
(c) I^2 (d) $C \cdot I$

3. Consider the chemical reaction;
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. The rate of this reaction can be expressed in terms of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ as: **(IIT 2002)**
(a) Rate $= \frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$
(b) Rate $= \frac{-d[N_2]}{dt} = \frac{3d[H_2]}{dt} = \frac{2d[NH_3]}{dt}$
(c) Rate $= \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$
(d) Rate $= \frac{-d[N_2]}{dt} = \frac{-d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

4. In a first order reaction, the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant in sec^{-1} is : **(IIT 2003)**
(a) 2×10^4 (b) 3.45×10^{-5}
(c) 1.386×10^{-4} (d) 2×10^{-4}

5. The reaction : $X \longrightarrow$ Product, follows first order kinetics. In 40 minutes, the concentration of X changes from 0.1 M to 0.025 M, then rate of reaction when concentration of X is 0.01 M is : **(IIT 2004)**
(a) 1.73×10^{-4} M/min (b) 3.47×10^{-5} M/min
(c) 3.47×10^{-4} M/min (d) 1.73×10^{-5} M/min

6. Which one of the following statement for order of reaction is not correct? **(IIT 2005)**
(a) Order can be determined experimentally.
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
(c) It is not affected with stoichiometric coefficient of the reactants.
(d) Order cannot be fractional.

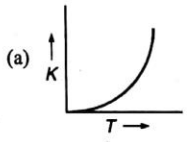
7. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]; K_1 = 6.8 \times 10^{-3}$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+; K_2 = 1.6 \times 10^{-3}$
then the formation constant of $[Ag(NH_3)_2]^+$ is: **(IIT 2006)**
(a) 6.8×10^{-6} (b) 1.08×10^{-5}
(c) 1.08×10^{-6} (d) 6.8×10^{-5}

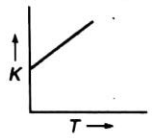
8. Consider a reaction. $aG + bH \longrightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases 8 times. However, when concentration of G is doubled, keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is: **(IIT 2007)**
(a) 0 (b) 1
(c) 2 (d) 3

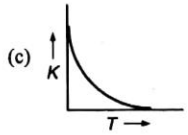
9. Under the same reaction conditions, the initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through I order and zero order kinetics. Ratio $\left(\frac{K_1}{K_0}\right)$ of the rate constants for I order (K_1) and zero order (K_0) of the reaction is : **(IIT 2008)**
(a) 0.5 mol^{-1}dm^{-3} (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1}dm^3

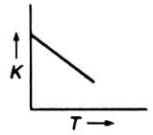
10. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (K) was found to follow the equation:
$$\log K = -\frac{2000}{T} + 6.0$$
The pre-exponential factor A and the activation energy E, respectively are : **(IIT 2009)**
(a) 1.0×10^6s^{-1} and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.66 kJ mol^{-1}
(c) 1.0×10^6s^{-1} and 16.66 kJ mol^{-1}
(d) 1.0×10^6s^{-1} and 38.3 kJ mol^{-1}

11. Plots of variation of the rate constant 'K' with temperature (T) are given below. The plot that follows Arrhenius equation is : **(IIT 2010)**

(a) 

(b) 

(c) 

(d) 

12. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be :

($R = 8.314\ JK^{-1}\ mol^{-1}$ and $\log_{10}2 = 0.301$)

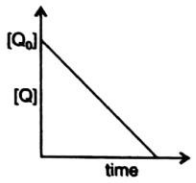
[JEE (Main) 2013]

(a) 58.5 kJ mol^{-1} (b) 60.5 kJ mol^{-1}

(c) 53.6 kJ mol^{-1} (d) 48.6 kJ mol^{-1}

13. In the reaction,

$$P+Q \longrightarrow R+S$$



the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is :

[JEE (Advanced-I) 2013]

(a) 2 (b) 3

(c) 0 (d) 1

14. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is :

[JEE (Advanced-II) 2014]

(a) 4 (b) 3

(c) 2 (d) 1

15. For the non-stoichiometre reaction $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C ($mol\ L^{-1}\ s^{-1}$)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is :

[JEE (Main) 2014]

(a) $\frac{d[C]}{dt} = k[A][B]$ (b) $\frac{d[C]}{dt} = k[A]^2[B]$

(c) $\frac{d[C]}{dt} = k[A][B]^2$ (d) $\frac{d[C]}{dt} = k[A]$

16. Higher order (> 3) reactions are rare due to :

[JEE (Main) 2015]

(a) low probability of simultaneous collision of all the reacting species

(b) increase in entropy and activation energy as more molecules are involved

(c) shifting of equilibrium towards reactants due to elastic collisions

(d) loss of active species on collision

17. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be : **[JEE (Main) 2016]**

(a) 6.93×10^{-4} mol min^{-1} (b) 2.66 L min^{-1} at STP

(c) 1.34×10^{-2} mol min^{-1} (d) 6.93×10^{-2} mol min^{-1}

18. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to :

($R = 8.314\ J\ mol^{-1}\ K^{-1}$) **[JEE (Main) 2017]**

(a) 8 (b) 12

(c) 6 (d) 4

SOLUTIONS (Previous Year Problems)

1. (d) $r = K[N_2O_5]$ I order as unit of $K = sec^{-1}$

$$2.40\times10^{-5} = 3.0\times10^{-5}[N_2O_5]$$

$$\therefore \quad [N_2O_5] = \frac{2.40}{3.0} = 0.8M$$

2. (d) In photo initiated primary process rate of reaction is directly proportional to intensity of light used. In case of pure solids rate $\propto I$ (Lamberts law). In case of solution rate $\propto I \cdot C$ (Bear's law).

3. (a) Follow text.

4. (c) $$K = \frac{2.303}{t}\log\frac{C_0}{C}$$

$$= \frac{2.303}{2\times10^4}\log\frac{800}{50} = 1.386\times10^{-4}\,sec^{-1}$$

5. (c) $$K = \frac{2.303}{40}\log\frac{0.1}{0.025} = 0.0347$$

$$\text{Rate} = K\times[X] = 0.0347\times0.01 = 3.47\times10^{-4}\ M\ min^{-1}$$

6. (d) Order can be fractional.

7. (b) Formation constant of $[Ag(NH_3)_2]^+$

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ = K$$

$$\therefore \quad K = K_1 \times K_2$$

$$= 6.8\times10^{-3}\times1.6\times10^{-3} = 1.08\times10^{-5}$$

8. (d) $r = K[G]^a [H]^b$ ...(i)

$8r = K[2G]^a [2H]^b$ ...(ii)

$2r = K[2G]^a [H]^b$ ...(iii)

By Eqs. (ii) and (iii)

$\therefore \quad 4 = 2^b$

$\therefore \quad b = 2$

By Eqs. (i) and (ii) $8 = 2^{a+b} = 2^{a+2}$

$\therefore \quad a = 1$

$\therefore$ O.R. $= a + b = 1 + 2 = 3$

9. (a) For I order : $K_1 = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{40}$

For zero order : $K_0 = \dfrac{a}{2t_{1/2}} = \dfrac{1.386}{2\times 20}$

$\therefore \quad \dfrac{K_1}{K_0} = \dfrac{0.693}{1.386} = 0.5$

10. (d) $\log_e K = -\dfrac{E_a}{RT} + \log_e A$

or $\log_{10} K = -\dfrac{E_a}{RT\times 2.303} + \log_{10} A$

$\therefore \quad \log_{10} A = 6, \quad A = 10^6$

Also $\dfrac{E_a}{R\times 2.303} = 2000$

$\therefore \quad E_a = 2.303\times 8.314\times 2000\,\text{J}$

$= 38294.28\,\text{J} = 38.3\,\text{kJ}$

11. (a) Since, $K = Ae^{-E_a/RT}$ and thus, K increases exponentially with rise in temperature.

12. (c) $\because \dfrac{r_2}{r_1} = \dfrac{k_2}{k_1} = 2$

Now $2.303 \log_{10} \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$2.303 \log_{10} 2 = \dfrac{E_a}{8.314} \times \left[\dfrac{310-300}{310\times 300}\right]$

$\therefore \quad E_a = \dfrac{2.303\times 0.301\times 8.314\times 310\times 300}{10} = 53598.6\,\text{J}$

$= 53.6\,\text{kJ mol}^{-1}$

13. (d) $P + Q \longrightarrow R + S$

Given : $T_{75\%} = 2\times T_{50\%}$ (for P)

Since $t_{1/2}$ is independent of concentration and thus it is first order for P.

From graph it is clear that reaction is of zero order with respect to Q

$[Q]_t = [Q]_0 - Kt$

so overall order will be = 1 + 0 = 1

14. (b) Consider, rate $(r) = K[M]^n$ where n is order of reaction

$$\frac{r_1}{r_2} = \frac{1}{8} = \frac{[M]^n}{[2M]^n} \Rightarrow n = 3$$

15. (d) Let rate expression be $r = K[A]^m [B]^n$

$\therefore \quad 1.2\times 10^{-3} = K(0.1)^m (0.1)^n$ ...(i)

$1.2\times 10^{-3} = K(0.1)^m (0.2)^n$ ...(ii)

$2.4\times 10^{-3} = K(0.2)^m (0.1)^n$ ...(iii)

By (i) and (ii) $n = 0$

By (i) and (iii) $m = 1$

$\therefore \quad \dfrac{dc}{dt} = K[A]^1$

16. (a) It is the reason for given fact.

17. (a) In 50 minutes, concentration of H_2O_2 becomes $\frac{1}{4}$ of initial *i.e.*, two half lives are used.

or $2\times t_{1/2} = 50$ minutes

or $t_{1/2} = 25$ minutes

$\therefore \quad K = \dfrac{0.693}{25}$ per minute

$r_{H_2O_2} = K\times[H_2O_2]$

$r_{H_2O_2} = \dfrac{0.693}{25}\times 0.05$

$= 1.386\times 10^{-3}$ mol litre^{-1} minute^{-1}

$2H_2O_2 \longrightarrow 2H_2O + O_2$

$r_{O_2} = \dfrac{1}{2}\times r_{H_2O_2} = \dfrac{1}{2}\times 1.386\times 10^{-3}$

$r_{O_2} = 0.693\times 10^{-3}$

$r_{O_2} = 6.93\times 10^{-4}$ mol litre^{-1} minute^{-1}

Note : The framing of question is not correct. The units for concentration of H_2O_2 is given as mol/litre whereas O_2 is reported in mol/minute. It has not been given that volume of solution is 1 litre.

18. (d) $k_1 = Ae^{-E_{a_1}/RT}$; $k_2 = Ae^{-E_{a_2}/RT}$

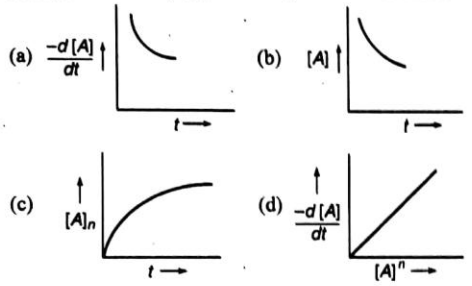
$\dfrac{k_2}{k_1} = e^{\frac{1}{RT}(E_{a_1} - E_{a_2})}$

$\ln \dfrac{k_2}{k_1} = \dfrac{E_{a_1} - E_{a_2}}{RT} = \dfrac{10\times 10^3}{8.314\times 300} \approx 4$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which of the following statements are correct?
   (a) Zero order reactions are complex reactions.
   (b) A reaction having I order may be either elementary reaction or complex reaction.
   (c) A reaction having II order reaction must have molecularity = 2.
   (d) A reaction with molecularity = 2 must be a II order reaction.

2. Which of the following plots are correctly made for the reaction $nA \rightleftharpoons (A)_n$, if it obeys I order reaction?



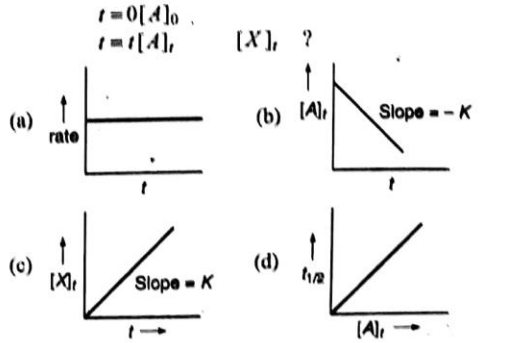
3. Select the correct statements :
   (a) Order of a reaction may be changed with change in the experimental conditions.
   (b) Rate of reaction either exothermic or endothermic both decrease with decrease in temperature.
   (c) A reaction mixture thermodynamically stable should be kinetically unstable.
   (d) A negative catalyst increases the energy of activation.

4. For a gaseous reaction : $A_{(g)} \longrightarrow B_{(g)}$, the rate expression may be given as :
   (a) $-\frac{d[A]}{dt} = K[A]^n$ (b) $-\frac{1}{V}\frac{dn_A}{dt} = K[A]^n$
   (c) $-\frac{1}{RT}\frac{dP_A}{dt} = K[A]^n$ (d) $-\frac{dP}{dt} = K(P_A)^n$

5. For which of the conditions K = Arrhenius factor?
   (a) $E_a = 0$
   (b) Free radical combinations
   (c) $T = \infty$
   (d) $T = 0$

6. Which of the following relations are correct if ΔH represents only magnitude?
   (a) Exothermic reactions : $E_{a(f)} + \Delta H = E_{a(b)}$
   (b) Endothermic reactions : $E_{a(f)} = E_{a(b)} + \Delta H$
   (c) Exothermic reactions : $\Delta H > E_a$
   (d) Endothermic reactions : $\Delta H < E_a$

7. Which of the following graphs represent zero order if
   $A \longrightarrow P$



8. Which one is correct according to collision theory of rate of reaction?
   (a) Threshold energy level is a characteristic of reaction
   (b) Energy of activation decreases with rise in temperature
   (c) The energy of adsorbed activated complex is lower than simple activated complex
   (d) The energy of activated complex (both activated or adsorbed) is higher than reactant or product

9. The rate expression for the reaction :
   $NH_4CNO \rightleftharpoons NH_2CONH_2$
   can be derived from the mechanism :
   (i) $NH_4CNO \underset{K_2}{\overset{K_1}{\rightleftharpoons}} NH_4NCO$ (Fast)
   (ii) $NH_4NCO \xrightarrow{K_3} NH_3 + HNCO$ (Fast)
   (iii) $NH_3 + HNCO \xrightarrow{K_4} NH_2CONH_2$ (Slow)
   Which of the following statements are correct about rate expression?
   (a) $\frac{d_{[urea]}}{dt} = \frac{K_1 K_3}{K_2}[NH_4NCO]$
   (b) $\frac{d_{[urea]}}{dt} = \frac{K_1 K_3}{K_2 K_4}[NH_4NCO]$
   (c) $\frac{d_{[urea]}}{dt} = K[NH_4NCO]$
   (d) $\frac{d_{[urea]}}{dt} = \frac{K_1 \times K_2}{K_3 \times K_4}[NH_4NCO]$

10. The rate of formation for $C_6H_6 + 3H_2 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} C_6H_{12}$ for the forward reaction is first order with respect to C_6H_6 and H_2 each. Which are correct?
    (a) $K_c = \frac{K_f}{K_b}$ (b) $K_c = \frac{[C_6H_{12}]}{[C_6H_6][H_2]^3}$
    (c) $r_f = K_f[C_6H_6][H_2]$ (d) $r_b = K_b[C_6H_{12}][H_2]^3$

11. The rate law for the reaction:

$$RCl + NaOH(aq) \rightarrow ROH + NaCl$$

is given by, Rate= $k_1[RCl]$. The rate of the reaction will be :

(a) doubled on doubling the concentration of sodium hydroxide

(b) halved on reducing the concentration of alkyl halide to one half

(c) increased on increasing the temperature of the reaction

(d) unaffected by increases the temperature of the reaction.

12. For a I order reaction

(a) The degree of dissociation is equal to $(1 - e^{-kt})$

(b) A plot of reciprocal of reactants, concentration *vs* time gives a straight line

(c) The time taken for completion of 75% reaction in thrice to that of $t_{1/2}$ of the reaction

(d) The pre exponential factor in the Arrhenius equation has the dimension of time T^{-1}.

13. The rate constant of a reaction becomes equal to A, then which are not correct?

(a) $-\frac{E_a}{RT} = 0$ (b) $E_A = -RT$

(c) $T = 0$ (d) $T = \infty$

14. Two first order exothermic reactions : $A \xrightarrow{K_1} B$ and $P \xrightarrow{K_2} Q$ at T K have their rate constants such that $K_1 > K_2$. If temperature is increased to T_2K($T_2 > T$), the rate constant K_1 changes to K_3 and K_2 to K_4. Select the correct statements.

(a) $K_1 < K_3$ (b) $K_2 < K_4$

(c) $K_3 > K_4$ (d) $K_4 > K_3$

15. For the first order reaction,

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ **[IIT 2011]**

(a) the concentration of the reactant decreases exponentially with time

(b) the half-life of the reaction decreases with increasing temperature

(c) the half-life of the reaction depends on the initial concentration of the reactant

(d) the reaction proceeds to 99.6% completion in eight half-life duration

16. According to the Arrhenius equation:

[JEE (Advanced) I 2016]

(a) A high activation energy usually implies a fast reaction

(b) Rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy

(c) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant

(d) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy

17. For 'invert sugar', the correct statement(s) is (are):

(Given : specific rotations of (+)-sucrose, (+)-maltose, *L*-(–)-glucose and *L*-(+)-fructose in aqueous solution are + 66°, + 140°, – 52° and + 92°, respectively)

[JEE (Advanced) II 2016]

(a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose

(b) 'invert sugar' is an equimolar mixture of *D*-(+)-glucose and *D*-(–)-fructose

(c) specific rotation of 'invert sugar' is –20°

(d) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products

18. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is (are) :

[JEE (Advanced) II 2017]

(a) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(b) The activation energy of the reaction is unaffected by the value of the steric factor

(c) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used

(d) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

SOLUTIONS (More Than One Answer Correct)

1. (a,b) Only elementary bimolecular reaction have order reaction = 2

2. (a,b,c,d) $-\frac{d[A]}{dt} = K[A]^n$

3. (a,b) Kinetic stability and thermodynamic stability has no relation. Also the function of negative catalyst to slow down the speed of reaction is not at all related with energy of activation.

4. (a,b,c,d) Rate of reaction

$$= \frac{d[A]}{dt} = K[A]^n \text{ or } -\frac{dP_A}{dt} = K(P_A)^n$$

$$= -\frac{1}{V}\frac{dn_A}{dt} = K[A]^n \qquad \because [A] = \frac{n_A}{V}$$

$$= -\frac{1}{RT}\frac{dP_A}{dt} = K[A]^n \qquad \because [A] = \frac{P_A}{RT}$$

5. (a,b,c) $K = Ae^{-E_a/RT}$; $E_a = 0$ for free radical combinations.

6. (a,b,d) For any reaction : $\Delta H = E_{a(f)} - E_{a(b)}$

Also, for exothermic reaction $\Delta H \gtrless E_a$

7. (a,b,c,d) $t_{1/2} \propto (a)^{1-n}$; $[A]_t - Kt$ and $X = Kt$ are integrated form of zero order.

8. (a,b,c,d) For basic concept follow **concepts of physical chemistry by Dr. P. Bahadur; Prakash Publications Muzaffarnagar**. Adsorption is always exothermic.

9. (a,c) $\frac{d}{dt}[NH_2CONH_2] = K_4[NH_3][HNCO]$ from (iii)

Applying steady state approximation to HNCO or NH_3

$$\frac{d[HNCO]}{dt} = 0 = K_3[NH_4NCO] - K_4[NH_3][HNCO]$$

$$\therefore \quad \frac{K_3}{K_4} = \frac{[NH_3][HNCO]}{[NH_3CNO]}$$

$$\frac{d[\text{urea}]}{dt} = K_4 \times [NH_3][HNCO] = K_4 \times \frac{K_3}{K_4}[NH_4NCO]$$

Also, $[NH_4NCO] = \frac{K_1}{K_2} \times [NH_4CNO]$

$$\therefore \quad \frac{d[\text{urea}]}{dt} = K_3 \times \frac{K_1}{K_2}[NH_4CNO]$$

$$= K[NH_4CNO]$$

10. (a,b,c,d) $K_c = \frac{K_f}{K_b} = \frac{[C_6H_{12}]}{[C_6H_6][H_2]^3} = \frac{[C_6H_{12}]}{[C_6H_6][H_2][H_2]^2}$

$r_f = K_f \times [C_6H_6][H_2]$

$r_b = K_b \times \text{Unknown}$

at eq. $r_f = r_b$

$\therefore \quad K_f[C_6H_6][H_2] = K_b \times \text{Unknown}$

$\therefore \quad \text{Unknown} = \frac{K_f}{K_b} \times [C_6H_6][H_2]$

$r_b = K_b \times \text{Unknown}$

$r_b = K_b \times \frac{K_f}{K_b} \times [C_6H_6][H_2]$

$= K_f \times [C_6H_6][H_2]$

$= K_b \times [C_6H_{12}][H_2]^{-2}$

11. (b, c) The reaction shows I order. Also rate of reaction increases with temperature.

12. (a, d) $N = N_0 \cdot e^{-\lambda t}$

$$\propto = \frac{N_0 - N}{N_0} = \frac{N_0[1 - e^{-\lambda t}]}{N_0} = 1 - e^{-\lambda t}$$

Also $A = Ke^{-E_a/RT}$

13. (b, c) $K = Ae^{-E_a/RT}$ if $-\frac{Ea}{RT} = 0$.

Also if $T = \infty$, then E_a approaches zero therefore $K = Ae^0 = A$

14. (a, b, c) Rate constant of a reaction whether exothermic or endothermic increases with temperature.

15. (a, b, d) For the first order reaction

(i) $N = N_0 e^{-kt}$; thus concentration of reactant decreases exponentially with time.

(ii) $t_{1/2} \propto [N_0]^0$ at constant temperature and thus half life is independent of initial concentration of reactant.

(iii) Also $t_{1/2} = \frac{0.693}{k}$

The rate of reaction and rate constant increase with temperature and thus $t_{1/2}$ decreases with temperature.

(iv) $t_{99.6\%} = \frac{2.303}{k}\log\frac{100}{0.4} = \frac{2.303}{k}\log 250$

$$t_{1/2} = \frac{0.693}{k}$$

$$\therefore \quad t_{99.6} = t_{1/2} \times \frac{2.303}{0.693}\log 250 = t_{1/2} \times 3.323 \times 2.40$$

$$= 8 \times t_{1/2}$$

16. (b, c, d) $K = Ae^{-E_a/RT}$

(Higher is E_a, lesser is rate constant, lesser is rate of reaction)

$$\frac{dK}{dT} = A\frac{E_a}{RT^2}$$

$$\frac{dK}{dT} \propto E_a$$

A is frequency factor *i.e.*, no. of collisions per unit time per unit volume.

17. (b, c) Sucrose ($C_{12}H_{22}O_{11}$) undergoes hydrolysis to form glucose and fructose and the process is known as inversion of sugar.

$$\text{Sucrose} \xrightarrow{\text{Hydrolysis}} D(+)\text{-glucose} + D(-)\text{ fructose}$$

$$[\alpha] = +52^\circ \qquad [\alpha] = -92^\circ$$

$$[\alpha]_{mix} = 0.5 \times (+52^\circ) + 0.5 \times (-92^\circ) = -20^\circ$$

$[\alpha]$ for L-(−)-glucose = −52°

$\therefore$ $[\alpha]$ for D(+)-glucose = +52°

Similarly for fructose $[\alpha] = -92^\circ$

Glucose with Br_2 water a weak oxidant will give gluconic acid. Strong oxidant will lead for saccharic acid.

18. (b, d)

Although Arrhenius factor or pre exponential factor (A) was theoretically proposed by Arrhenius in his equation : $K = Ae^{-Ea/RT}$. He could not consider the specific orientation of molecules at the time of collision which usually predominate in bimolecular reaction. If specific orientation of bimolecular reaction is taken in account, then Arrhenius equation can be modified by putting a term 'p' known as stearic factor as :

Arrhenius equation :

$$k = A_{\text{Arr.}} \times e^{-Ea/RT}$$

If p is stearic factor.

$$k = p \cdot A_{\text{Arr.}} \times e^{-Ea/RT}$$

Collision theory :

$$p \cdot A_{\text{Arr.}} = Z$$

where Z is experimentally determined frequency factor.

$$\frac{Z_{\text{actual}}}{A_{\text{Arr.}}} = p$$

Since p is usually less than unity the $Z_{\text{actual}} < A_{\text{Arr}}$. But here $p = 4.5$.

Thus, $Z_{\text{actual}} > A_{\text{Arr.}}$

it means that reaction occures more quickly than particles collide.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : From the following data form the reaction between A and B,

$[A]\times10^4$ mol litre^{-1}	$[B]\times10^5$ mol litre^{-1}	Initial rate mol litre^{-1}sec^{-1}	
		$r\times10^4$ 300 K	$r\times10^3$ 320 K
2.5	3.0	5.0	2.0
5.0	6.0	4.0	—
1:0	6.0	1.6	—

[1] The order of reaction with respect to A and with respect to B, respectively are :

(a) 2, 1 (b) 1, 2

(c) 2, 2 (d) 2, 3

[2] The rate constant at 300 K:

(a) 2.66×10^{-8} (b) 1.33×10^{-8}

(c) 2.66×10^{8} (d) 1.33×10^{8}

[3] The energy of activation:

(a) 55.3 kJ (b) 65.44 kJ

(c) 44.5 kJ (d) 75.44 kJ

[4] The pre-exponential factor:

(a) 1.140×10^{8} (b) 1.140×10^{10}

(c) 1.140×10^{18} (d) 1.140×10^{-18}

Comprehension 2: For the reaction $A \longrightarrow B$, the rate law expression is $-\frac{d[A]}{dt} = K[A]^{1/2}$. If initial concentration of A is A_0.

[1] Integrated form of the rate expression:

(a) $Kt = 2[A_0^{1/2} - A^{1/2}]$ (b) $Kt = 2[A_0^{-1/2} - A^{-1/2}]$

(c) $Kt = 1/2[A_0^{1/2} - A^{1/2}]$ (d) $Kt = 1/2[A^{-1/2} - A^{-1/2}]$

[2] Slope and intercept of the plots of $\log\sqrt{A}$ *vs.* t are respectively:

(a) $-\frac{K}{2}, A_0^{-1/2}$ (b) $-\frac{K}{2}, A_0^{1/2}$

(c) $2K, A_0^{1/2}$ (d) $-K, 2A_0$

[3] The half-life of the reaction is given by:

(a) $\frac{\sqrt{2}(\sqrt{2}-1)}{K}\cdot A_0$ (b) $\frac{\sqrt{2}(\sqrt{2}-1)A_0^{1/2}}{K}$

(c) $\frac{2\cdot A_0}{K}$ (d) $\frac{(\sqrt{2}-1)A_0^{1/2}}{2K}$

SOLUTIONS

Comprehension 1

Let rate expression be $r = K[A]^m[B]^n$

[1] (a) $\therefore \quad 5.0\times10^{-4} = K[2.5\times10^{-4}]^m[3.0\times10^{-5}]^n$ ...(1)

$4.0\times10^{-3} = K[5.0\times10^{-4}]^m[6.0\times10^{-5}]^n$ ...(2)

$1.6\times10^{-2} = K[1.0\times10^{-3}]^m[6.0\times10^{-5}]^n$ ...(3)

By Eqs. (2) and (3), $m = 2$ ...(4)

By Eqs. (1) and (4), $n = 1$

$\therefore$ Rate $= K[A]^2[B]^1$

or order with respect to A and B are **2 and 1** respectively.

[2] (c) By Eq. (1),

$$5.0\times10^{-4} = K[2.5\times10^{-4}]^2[3\times10^{-5}]^1$$

$$\therefore \quad \boldsymbol{K = 2.66\times10^{8}\ L^2\ mol^{-2}\ sec^{-1}} \quad (\text{at } 300\text{ K})$$

[3] (a) $\because \quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2 - T_1]}{T_1T_2}$

$$\left[\because \frac{r_2}{r_1} = \frac{K_2}{K_1}\right]$$

$$\because \quad 2.303\log_{10}\frac{2.0\times10^{-3}}{5.0\times10^{-4}} = \frac{E_a}{8.314}\left[\frac{320-300}{300\times320}\right]$$

$$\because \quad \boldsymbol{E_a = 55.33\ kJ}$$

[4] (c) Also, $2.303\log_{10}K = 2.303\log_{10}A - \dfrac{E_a}{RT}$

$$2.303\log_{10}2.66\times10^{8} = 2.303\log_{10}A - \frac{55.33\times10^3}{8.314\times300}$$

$$\therefore \quad \boldsymbol{A = 1.140\times10^{18}}$$

Comprehension 2

[1] (a) $-\dfrac{d[A]}{dt} = K[A]^{1/2}$ or $-\dfrac{dA}{[A]^{1/2}} = Kdt$

On integrating $-\int[A]^{-1/2}dA = K\int dt$

$$-2A^{1/2} = Kt + C \quad \text{...(1)}$$

at $t = 0$; $A = A_0$ $\therefore$ $C = -2A_0^{1/2}$ ...(2)

By Eqs. (2) and (1), $-2A^{1/2} = Kt - 2A_0^{1/2}$

or $$Kt = 2[A_0^{1/2} - A^{1/2}] \quad \text{...(3)}$$

[2] (b) Plot of $A^{1/2}$ *vs.* t will be **linear** because Eq. (3) yields,

$$2A^{1/2} = -Kt + 2A_0^{1/2}$$

or $A^{1/2} = -\dfrac{K}{2}t + A_0^{1/2}$ (similar to $y = mx + C$)

[3] (b) If $t = t_{1/2}$, $A = A_0/2$

$\therefore$ By Eq. (3),

$$Kt_{1/2} = 2\left[A_0^{1/2} - \left(\frac{A_0}{2}\right)^{1/2}\right] = 2A_0^{1/2}\left[1 - \frac{1}{\sqrt{2}}\right]$$

$$Kt_{1/2} = \frac{2[\sqrt{2}-1]}{\sqrt{2}}\cdot A_0^{1/2} = \sqrt{2}(\sqrt{2}-1)A_0^{1/2}$$

$$\therefore \quad t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{K}A_0^{1/2}$$

STATEMENT-EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. The molecularity of first step is 1 and of second step is 2.
   S : For the reaction given below, the molecularity of first step is 1 and of second step is 2.
   $$2O_3(g) \longrightarrow 3O_2(g)$$
   Step 1 $O_3(g) \rightleftharpoons O_2(g) + O(g)$
   Step 2 $O_3(g) + O \xrightarrow{\text{slow}} 2O_2(g)$
   E : $O(g)$ is an intermediate and rate of reaction is $K[O_3]^2[O_2]^{-1}$ and order of reaction is 1.

2. **S :** Observed rate constant of the given reaction given below decreases with temperature.
   $$NO + NO \underset{K_b}{\overset{K_f}{\rightleftharpoons}} N_2O_2$$
   $$N_2O_2 + O_2 \xrightarrow[\text{slow}]{K} 2NO_2$$
   $$2NO + O_2 \longrightarrow 2NO_2$$
   E : K_c of the reaction being exothermic and decrease in K_c overweigh increase in K with increase in temperature.

3. **S :** The plots of $\log t_{1/2}$ *vs.* $\log[A]_0$ gives a straight line with slope $(1 - n)$.
   E : $t_{1/2} \propto [A]_0^{1-n}$

4. **S :** Larger is the activation energy, lesser is the effect of a given temperature rise on rate constant 'K'.
   E : $K = Ae^{-E_a/RT}$

5. **S :** For a free radical combination, $K = A$.
   E : E_a is zero for free radical combination.

6. **S :** Every collision of reactant molecule is not successful.
   E : Every collision of reactant molecule with proper orientation is successful one.

7. **S :** A plot of $\log \frac{dX}{dt}$ *vs.* $\log(a - x)$ leads to value of K as antilog (intercept) and slope equal to order of reaction.
   E : $\frac{dX}{dt} = K(a - x)^n$

8. **S :** For a IInd order reaction $A + B \rightarrow$ Product, the rate can be given as : $K[A]^2$ or $K[A][B]$ or $K[B]^2$.
   E : Either $[A]$ or $[B]$ may or may not influence the rate of reaction.

9. **S :** The acid hydrolysis of ester takes place more rapidly in D_2O than H_2O.
   E : D_3O^+ is stronger acid than H_3O^+ or H_2D^+O.

10. **S :** Emission of light as a result of exposure of P to air in night is called phosphorescence.
    E : Phosphorus burns in O_2 to give P_2O_5 and conversion of chemical energy into light energy producing cold light and the phenomenon is called chemi-luminescence.

11. **S :** Activation energy always increases the potential energy of reaction system.
    E : The minimum kinetic energy that a molecule must possess in order to react on collision is called its activation energy.

12. **S :** The rate of reaction whether exothermic or endothermic, increases with temperature.
    E : The rate of reaction = K [reactant]^n and K increases with temperature.

13. **S :** A catalyst always lower the energy of activation.
    E : The catalyst-reactant interaction forms activated adsorbed complex and adsorption is always exothermic.

14. **S :** A catalyst does not affect the heat of reaction.
    E : It increases the rate of reaction.

15. **S :** The elementary reaction is single step reaction and does not possess mechanism.
    E : An elementary reaction has order of reaction and molecularity same.

16. **S :** Temperature coefficient is the ratio of two rate constants preferally at 35°C and 25°C.
    E : It can also be given as $e^{-\frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$

17. **S :** The rate expression of $2NO_2 + F_2 \longrightarrow 2NO_2F$ is $r = K[NO_2][F_2]$.
    E : The reaction has the mechanism
    $$NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F$$
    $$NO_2 + F \xrightarrow{\text{fast}} NO_2F$$

18. **S :** For the reaction $2O_3 \longrightarrow 3O_2$,
    the rate = $K[O_3]^2[O_2]^{-1}$.
    E : The reaction has –ve order for O_2

19. **S :** Threshold energy of a reaction is dependent of temperature.
    E : The energy of activation decreases with increase in temperature.

20. S : The emission of light during burning of P in O_2 is called chemi-luminescence.
E : The chemical energy is converted into light energy.

21. S : Photosynthesis in plants involves reaction of CO_2 and H_2O in presence of light and chlorophyll.
E : It is chlorophyll which absorbs light and passes this energy to reactant molecules.

22. S : Order of reaction can never be fractional for an elementary reaction.
E : An elementary reaction takes place by one step mechanism.

23. S : Every collision between molecules leads to a chemical reaction.
E : Only those molecules react during collisions which acquire threshold energy level.

24. S : For each ten degree rise of temperature the specific rate constant is nearly doubled.
E : Energy-wise distribution of molecules in a gas is an exponential function of temperature.

25. S : The instantaneous rate of reaction can be studied in chemical kinetics.
E : Ionic reactions occur instantaneously.

26. S : All catalytic reactions show zero order for catalyst used.
E : The rate of reaction does not depend on concentration of catalyst.

ANSWERS (Statement Explanation Problems)

1. (c) $K_c = \dfrac{[O_2][O]}{[O_3]}$

$$\text{rate} = K[O_3][O] = \frac{K_c[O_3]\times[O_3]}{[O_2]} = \frac{K^1[O_3]^2}{[O_2]}$$

2. (c) $\text{Rate} = K[N_2O_2][O_2]$

and $K_c = \dfrac{[N_2O_2]}{[NO]^2}$

$\therefore$ $\text{rate} = K \cdot K_c[NO]^2[O_2] = K_{obs}[NO]^2[O_2]$

3. (c) $\log t_{1/2} = \log\left[\dfrac{2^{n-1}-1}{K(n-1)}\right] + (1-n)\log[A]_0$

4. (b) Higher activation energy, greater is the effect of given temperature rise on rate constant 'K'.

5. (c) $K = Ae^{-E_a/RT}$, if $E_a = 0$ then $K = A$

6. (a) A successful collision leads to a chemical reaction when the reactant molecules collide with proper orientation and attain threshold energy level.

7. (c) $\log\dfrac{dX}{dt} = \log K + n\log(a-x)$

8. (c) In each case order is IInd.

9. (c) Explanation is correct reason for statement.

10. (b) The phenomenon is called chemi-luminiscence.

11. (d) Both are facts.

12. (c) Explanation is correct reason for statement.

13. (c) Explanation is correct reason for statement.

14. (d) Both statement and explanation are correct.

15. (c) Explanation is correct reason for statement.

16. (d) Both statement and explanation are correct.

17. (c) Explanation is correct reason for statement.

18. (d) Both statement and explanation are correct.

19. (d) Both statement and explanation are correct.

20. (c) Chemiluminesence refers for emission of light as a result of chemical change.

21. (c) Chlorophyll acts as photosensitizer. Neither CO_2 nor H_2O absorbs light.

22. (c) An elementary reaction is one step reaction and in such reactions order of reaction and molecularity are same. Note that molecularity can never be fractional.

23. (b) Explanation is correct and suggests that statement is wrong.

24. (c) Explanation is correct reason for statement.

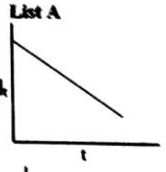
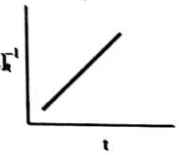
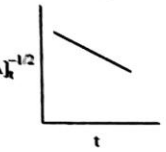
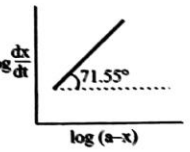
25. (b) Ionic reactions are not studied in kinetics as their $t_{1/2}$ is 10^{-2} sec.

26. (c) Explanation is correct reason for statement.

MATCHING TYPE PROBLEMS

Type I : Only One Match is Possible

1.

List A		List B
(a) $[A]_t$ 		(i) O.R.= 1/2
(b) $[A]_t^{-1}$ 		(ii) O.R.= zero
(c) $[A]_t^{-1/2}$ 		(iii) O.R.= 2
(d) $\log\frac{dx}{dt}$ 		(iv) O.R.= 3

2.

List A	List B
(a) Elementary reactions	1. No energy of activation
(b) Complex reactions	2. Low energy of activation
(c) Free radical combinations	3. High energy of activation
(d) Slow reactions	4. Several elementary steps
(e) Fast reactions	5. Single step

3.

List I	List II
A. Flash photolysis	p. Intensity of light
B. Rate of photochemical reaction	q. Fast reactions
C. Chemiluminescence	r. $4P + 5O_2 \longrightarrow 2P_2O_5$
D. Phosphorescence	s. ZnS

Type II : Only One Match From Each List

4.

List A	List B	List C
A. Rate of reaction	1. $-\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$	a. ΔH = +ve or − ve
B. Rate constant of a reaction	2. $V_t = V_0$	b. ΔH = −ve
C. Equilibrium constant	3. $V_t \neq V_0$	c. $t \to 0$
D. $V_t = \frac{V_0 \cdot T}{273}$	4. Increases	d. $\Delta t \to 0$
E. $V_t = V_0 + \frac{V_0 \cdot t}{273}$	5. Decreases	e. $T \to 0$

5.

Linear plots	Slope	Order
(A) $\ln\left(\frac{dx}{dt}\right)$ vs $\ln[A]_t$	1. $-k$	a. Two
(B) $[A]_t$ vs time	2. $\frac{-E_a}{R}$	b. Zero
(C) $\frac{1}{[A]_t}$ vs time	3. $1-n$	c. One
(D) $\log_e k$ vs T	4. Zero	d. n
(E) $\log[A]_t$ vs time	5. k	e. Any order
(F) $\log t_{1/2}$ vs $\log[A]_0$	6. n	f. 1− slope

ANSWERS

1. a – ii; b – iii; c – i; d – iv
2. a – 5; b – 4; c – 1; d – 3; e – 2
3. A – q; B – p; C – r; D – s
4. A – 1 – d; B – 4 – a; C – 5 – b; D – 3 – e; E – 2 – c
5. A – 6 – d; B – 1 – b; C – 5 – a; D – 2 – e; E – 1 – c; F – 3 – f

12 Chemical Equilibrium

Chemical Equilibrium

1. The state at which concentration of reactants or products do not change with time.

2. It is attained when rate of forward reaction becomes equal to rate of backward reaction.

3. A dynamic equilibrium, attained from either side.

Irreversible and reversible reactions

Irreversible reactions	Reversible reactions
1. Unidirectional	1. Both directional
2. Go for completion	2. Never go for completion
3. No equilibrium is attained	3. Attains equilibrium
4. A reaction is said to be irreversible when either of the product is settled down as solid or escapes out as gas, *e.g.*, $BaCl_2 + Na_2SO_4 \longrightarrow \underset{\text{(insoluble)}}{BaSO_4} + 2NaCl$	4. Otherwise the reaction is reversible, *e.g.*, $CaCO_3 \rightleftharpoons CaO + CO_2$ (in closed container)

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

Law of mass action : Guldbarg and Waage proposed that, "The rate at which a substance reacts is directly proportional to its active mass and the rate of a chemical reaction is directly proportional to product of active masses of reactants."

Active mass :

Active mass of a reactant = Concentration of reactant × activity coefficient

$$a = f \times \text{molarity} = \gamma \times \text{molality}$$

where f and γ are activity coefficients. For dilute solution f and γ are unity.

$\therefore$ $a = \text{Molarity} = \text{Molality}$

Formulation of law of mass action :

Consider a reversible reaction

$$m_1A + m_2B + \ldots \rightleftharpoons n_1Z + n_1Y + \ldots$$

$\therefore$ Rate of forward reaction $\propto (a_A)^{m_1}(a_B)^{m_2}$

$$= K_f(a_A)^{m_1}(a_B)^{m_2}$$

and Rate of backward reaction $\propto (a_Z)^{n_1}(a_Y)^{n_2}\ldots\ldots$

$$= K_b(a_Z)^{n_1}(a_Y)^{n_2}$$

where K_f and K_b are rate constants for forward and backward reactions respectively.

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$\therefore$ $K_f(a_A)^{m_1}(a_B)^{m_2}\ldots\ldots = K_b(a_Z)^{n_1}(a_Y)^{n_2}\ldots$

$\therefore$ $\dfrac{K_f}{K_b} = \dfrac{(a_Z)^{n_1}(a_Y)^{n_2}\ldots}{(a_A)^{m_1}(a_B)^{m_2}\ldots}$ or $K_a = \dfrac{(a_Z)^{n_1}(a_Y)^{n_2}\ldots}{(a_A)^{m_1}(a_B)^{m_2}\ldots}$ ...(1)

Since, $a = f \times \text{molarity}$

$\therefore$ By Eq. (1). $K_a = \dfrac{[f_z \cdot [Z]]^{n_1} \cdot [f_Y \cdot [Y]]^{n_2}\ldots}{[f_A \cdot [A]]^{m_1} \cdot [f_B \cdot [B]]^{m_2}\ldots}$

or $K_a \cdot \dfrac{(f_A)^{m_1}(f_B)^{m_2}}{(f_z)^{n_1}(f_B)^{n_2}} = \dfrac{[Z]^{n_1}[Y]^{n_2}\ldots}{[A]^{m_1}[B]^{m_2}\ldots}$

or $K_C = \dfrac{[Z]^{n_1}[Y]^{n_2}\ldots}{[A]^{m_1}[B]^{m_2}\ldots}$ ...(2)

where $[Z]$, $[Y]$, $[A]$ and $[B]$ are concentration of respective species at equilibrium.

In case of gaseous phases, $a \propto$ Partial pressure of gas, at constant T

$\therefore$ $K_P = \dfrac{(P_Z)^{n_1}(P_Y)^{n_2}\ldots}{(P_A)^{m_1}(P_B)^{m_2}\ldots}$ ...(3)

or $K_P = \dfrac{[n_Z]^{n_1}[n_Y]^{n_2}\ldots}{[n_A]^{m_1}[n_B]^{m_2}\ldots} \times \left[\dfrac{P}{RT}\right]^{\Delta n}$

where $\Delta n = [m_1 + m_2 + \ldots] - [n_1 + n_2 + \ldots]$

where P_Z', P_Y', P_A' and P_B' are partial pressures of respective species 234at equilibrium.

where K_a, K_C and K_P are equilibrium constants in terms of active mass, concentration and partial pressure respectively.

NOTE: 1. Normally 'f' values are not given in numericals and thus K_C and K_P are evaluated and not K_a.

2. Reaction Quotient Q for the reaction :

$m_1A + m_2B + \ldots\ldots \rightleftharpoons n_1Z + n_2Y + \ldots\ldots$, can be written as

$$Q = \frac{[Z]^{n_1}[Y]^{n_2}\ldots\ldots}{[A]^{m_1}[B]^{m_2}\ldots\ldots}$$

or $$Q = \frac{[P_z']^{n_1}[P_y']^{n_2}\ldots\ldots}{[P_A']^{m_1}[P_B']^{m_2}\ldots\ldots}$$ (for gaseous phase reaction)

where $[Z]$,$[Y]$, $[A]$, $[B]$ are concentration at $t = 0$ and P_Z',P_Y',P_A' and P_B' are partial pressures at $t = 0$.

The reaction Quotient helps in predicting the direction of reaction *i.e.*, is $Q > K$ backward direction

$Q < K$ forward direction

$Q = K$ At equilibrium

Relation in between K_P and K_C

$$K_P = K_C(RT)^{\Delta n} \quad \ldots(4)$$

where Δn = No. of mole of product – No. of mole of reactant

For Δn, one should remember,

(1) Δn may be zero, +ve or –ve integers or fractions.

(2) Only gaseous phases are to be taken in account.

(3) If $\Delta n = 0$, $K_P = K_C$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta n = -2$

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad \Delta n = 0$

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\quad \Delta n = +1$

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ $\quad \Delta n = +\frac{1}{2}$

Units of K_P and K_C

Unit of K_P = (Unit of pressure)$^{\Delta n}$ = (atm)$^{\Delta n}$

Unit of K_C = (Unit of concentration)$^{\Delta n}$ = (mol litre^{-1})$^{\Delta n}$

if $\Delta n = 0$, no unit of K_P or K_C.

Note : Now-a-days equilibrium constant is expressed as dimensionless quantity by specifying the standard state of reactants and products. For example standard state for pure gas is 1 bar and the partial pressures are expressed with respect to this standard *e.g.*, a pressure of 2 bar in terms of standard state is $\frac{2\text{bar}}{1\text{bar}}$ *i.e.*, 2 a dimension less quantity.

Similarly for solution species, the standard state is 1 *M*.

Factors influencing equilibrium constant :

(1) Temperature

The variation of K_C or K_P with temperature has been expressed in terms of :

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\frac{[T_2 - T_1]}{T_1T_2}$$

or $$2.303\log_{10}\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\frac{[T_2 - T_1]}{T_1T_2} \quad \ldots(5)$$

[Integrated form of van't Hoff isochore for two temperature limits.]

or $$K = Ae^{-\Delta H^\circ/RT} \quad \ldots(6)$$

[For one temperature limit]

where K is equilibrium constant; T represents temperature; ΔH° is heat of reaction; A is frequency factor; R is molar gas constant.

Case I : For endothermic reaction ΔH° = +ve and if $T_2 > T_1$

Then by Eq. (5), $\log_{10}\frac{K_2}{K_1}$ = +ve $\therefore$ $\log_{10}K_2 > \log_{10}K_1$

or $K_2 > K_1$

i.e., **Equilibrium constant increases with increase in temperature for endothermic reaction.**

Case II : For exothermic reaction ΔH° = –ve and if $T_2 > T_1$

Then by Eq. (5),

$\log_{10}\frac{K_2}{K_1}$ = –ve or $\log_{10}K_2 < \log_{10}K_1$ or $K_2 < K_1$

i.e., **Equilibrium constant decreases with increase in temperature for exothermic reactions.**

NOTE : Put R in the same unit in which ΔH° is given or desired.

(2) Stoichiometry of change

The numerical values of K_C or K_P change with stoichiometry, *e.g.*,

$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$
$K_{C_1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$	$K_{C_2} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

$$K_{C_1} = [K_{C_2}]^2 \quad \ldots(7)$$

(3) The mode of representing the change

The numerical values of K_P or K_C also change with method of representing equilibrium, *e.g.*,

$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$2NH_3 \rightleftharpoons N_2 + 3H_2$
$K_{C_1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$	$K_{C_3} = \frac{[N_2][H_2]^3}{[NH_3]^2}$

$$K_{C_1} = \frac{1}{K_{C_3}} \quad \ldots(8)$$

By Eqs. (7) and (8), $K_{C_1} = (K_{C_2})^2 = \frac{1}{K_{C_3}}$

(4) Units in which pressures or concentrations are expressed

(a) If $\Delta n = 0$; K_P or K_C values do not change with change in units of P or C.

(b) If $\Delta n \neq 0$; K_P or K_C values change with change in units of P or C.

NOTE : When a reaction takes place in more than one step, there can be a relationship among the equilibrium constants of the overall reaction and those of the step reactions.

The reaction, $H_2O_2 + 2H^+ + 2I^- \rightleftharpoons I_2 + 2H_2O$

for which $K = \frac{[I_2][H_2O]^2}{[H_2O_2][H^+]^2[I^-]^2}$ takes place in the following steps,

$$H_2O_2 + I^- \rightleftharpoons OH^- + HOI; \quad K_1 = \frac{[OH^-][HOI]}{[H_2O_2][I^-]}$$

$$H^+ + OH^- \rightleftharpoons H_2O; \quad K_2 = \frac{[H_2O]}{[H^+][OH^-]}$$

and $$HOI + H^+ + I^- \rightleftharpoons I_2 + H_2O; \quad K_3 = \frac{[I_2][H_2O]}{[HOI][H^+][I^-]}$$

Multiplying equations for K_1, K_2 and K_3, we see that,

$$K = K_1 \cdot K_2 \cdot K_3 \quad ...(9)$$

Thus, when a reaction takes place in more than one step, the equilibrium constant of the overall reaction is equal to the product of the equilibrium constants of each step.

Degree of dissociation and its use

$$2HI \rightleftharpoons H_2 + I_2$$

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Mole dissociated}}{\text{Total mole present before dissociation}}$$

The use of 'α' should be made very cautiously.

The reaction ratio is $HI : H_2 : I_2 :: 2 : 1 : 1$

(i) *e.g.,*

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Mole at $t = 0$	1		0		0
Mole at equilibrium	$1-x$		$x/2$		$x/2$

$\therefore \quad \alpha = \frac{x}{1} = x$

(ii)

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Mole at $t = 0$	1		0		0
Mole at equilibrium	$1-2x$		x		x

$\therefore \quad \alpha = \frac{2x}{1}$

(iii)

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Mole at $t = 0$	a		0		0
Mole at equilibrium	$a-x$		$x/2$		$x/2$

$\therefore \quad \alpha = \frac{x}{a}$

(iv)

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Mole at $t = 0$	a		0		0
Mole at equilibrium	$a-2x$		x		x

$\therefore \quad \alpha = \frac{2x}{a}$

(v)

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Mole at $t = 0$	a		0		0
Mole at equilibrium	$(a-ax)$		$\frac{ax}{2}$		$\frac{ax}{2}$
or	$a(1-x)$				

$\therefore \quad \alpha = \frac{ax}{a} = x$

Select either of the case and derive K_C or K_P accordingly as reported earlier, following step by step.

Factors influencing equilibrium concentrations

(1) Temperature. (a) An increase in temperature for exothermic reactions decreases the concentration of products at equilibrium and *vice-versa.*

(b) An increase in temperature for endothermic reactions increases the concentration of products at equilibrium and *vice-versa.*

(2) Pressure. An increase in pressure to an equilibrium favours the reaction where number of mole or volume shows a decrease and *vice-versa.*

(3) Addition of inert gas. (a) Addition of inert gas to an equilibrium (if, $\Delta n = 0$) has no effect.

(b) Addition of inert gas to an equilibrium (if, $\Delta n \neq 0$) has no effect, if addition is made at constant volume but addition at constant pressure will favour the direction of reaction where total number of mole at equilibrium show an increase.

Equilibrium Constant and Standard Free Energy Change

$$\Delta G = \Delta G^\circ + 2.303\, RT \log Q$$

where Q represents the reaction quotient. At equilibrium, $\Delta G = 0$ and $Q = K_P$ or K_C as the standard state is referred in terms of partial pressure or concentration.

Thus, the equilibrium constant K_P is related to standard free energy change (ΔG°) by the relation;

$$\Delta G^\circ = -2.303\, RT \log_{10} K_P$$

Also, $$\Delta G^\circ = -2.303\, RT \log_{10} K_C$$

Since, ΔG° can be obtained from independent measurements, *e.g.,* from thermal and spectroscopic data, it is possible to calculate K_P. The ΔG° value for a spontaneous or feasible reaction is always negative. From equation, ΔG° is obtained in the same energy unit in which value of R is introduced, provided, the equilibrium constant K_P is just a pure number or it is calculated by taking partial pressure in atmosphere.

From equation we may conclude that

When $\Delta G^\circ = -ve$ or $K > 1$;

Forward reaction is feasible at unit concentration (or partial pressure)

When $\Delta G^\circ = +ve$ or $K < 1$;

Reverse reaction is feasible.

Also, is $\Delta G^\circ = 0$ then $K = 1$;

• NUMERICAL PROBLEMS •

1. State which one is homogeneous or heterogeneous ?
   (a) $S_{Rhombus} \rightleftharpoons S_{Monoclinic}$
   (b) $H_2O(l) \rightleftharpoons H_2O(v)$
   (c) $H_2O(s) \rightleftharpoons H_2O(l)$
   (d) $C_{Diamond} \rightleftharpoons C_{Amorphous}$
   (e) $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$
   (f) $CuSO_4(s)+3NH_3(l) \rightleftharpoons CuSO_4 \cdot 3NH_3(l)$
   (g) $CaCO_3(g) \rightleftharpoons CaO(s)+CO_2(g)$
2. Write equilibrium constants for each ;
   (a) $KClO_3(s) \rightleftharpoons KCl(s)+\frac{3}{2}O_2$
   (b) $H_2(g)+3Fe_2O_3(s) \rightleftharpoons H_2O(g)+2Fe_3O_4(s)$
   (c) $CaC_2(s)+5O_2(g) \rightleftharpoons 2CaCO_3(s)+2CO_2(g)$
   (d) $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$
   (e) $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$
   (f) $CH_3COOH(l)+CH_3OH(l) \rightleftharpoons CH_3COOCH_3(l)+H_2O(l)$
3. If a mixture of 3 mole of H_2 and one mole of N_2 is completely converted into NH_3, what would be the ratio of the initial and final volume at same temperature and pressure ?
4. Calculate the equilibrium constant for the reaction
   $$H_2(g)+CO_2(g) \rightleftharpoons H_2O(g)+CO(g)$$
   at 1395 K, if the equilibrium constants at 1395 K for the following are ;
   $2H_2O(g) \rightleftharpoons 2H_2+O_2(g)$ $\quad K_1=2.1\times10^{-13}$
   $2CO_2(g) \rightleftharpoons 2CO(g)+O_2(g)$ $\quad K_2=1.4\times10^{-12}$
5. The equilibrium constant of the reaction,
   $$SO_3(g) \rightleftharpoons SO_2(g)+\frac{1}{2}O_2(g)$$
   is 0.15 at 900 K. Calculate equilibrium constant for
   $$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$$
6. Following two equilibria exist together
   $$2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} I \underset{K_4}{\overset{K_3}{\rightleftharpoons}} B+C$$
   Show that equilibrium constant for overall reaction $K_C=\frac{K_1K_3}{K_2K_4}$.
7. K_C for the reaction, $N_2+3H_2 \rightleftharpoons 2NH_3$ is 0.5 mol^{-2} $litre^{-2}$ at 400 K. Find K_P. Given $R=0.082$ litre atm $degree^{-1}$ mol^{-1}.
8. For the reaction $A+B \rightleftharpoons 3C$ at 25°C, a, 3 litre vessel contains 1, 2, 4 mole of A, B and C respectively. Predict the direction of reaction if :
   (a) K_C for the reaction is 10.
   (b) K_C for the reaction is 15.
   (c) K_C for the reaction is 10.66.
9. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction : $2AB_2(g) \rightleftharpoons 2AB(g)+B_2(g)$ with a degree of dissociation 'x' which is small compared to unity. Deduce the expression for 'x' in terms of the equilibrium constant K_P and the total pressure P. **(IIT 1994)**
10. In which case does the reaction go farthest to completion : $K=1; K=10^{10}; K=10^{-10}$ and why?
11. The equilibrium constant K_C for $A(g) \rightleftharpoons B(g)$ is 1.1. Which gas has a molar concentration greater than 1 ?
12. The equilibrium constant for the polymerisation of HCHO to $C_6H_{12}O_6$ in aqueous solution is 6×10^{22}. If 1 M solution of glucose was to reach the equilibrium according to :
    $$6HCHO \rightleftharpoons C_6H_{12}O_6 \qquad K_C=6\times10^{22}$$
    find out the concentration of formaldehyde in solution.
13. In an equilibrium $A+B \rightleftharpoons C+D$; A and B are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium has reached, concentration of C was thrice the equilibrium concentration of B. Calculate K_C.
14. The K_C for $A_2(g)+B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If one litre flask containing one mole of A_2 is connected with a two litre flask containing 2 mole of B_2, how many mole of AB will be formed at 100°C ?
15. For a gaseous phase reaction,
    $$A+2B \rightleftharpoons AB_2, K_C=0.3475 \text{ litre}^2 \text{ mol}^{-2}$$
    at 200°C. When 2 mole of B are mixed with one mole of A, what total pressure is required to convert 60% of A in AB_2?
16. For a gaseous phase reaction, $2HI \rightleftharpoons H_2+I_2$, at equilibrium 7.8 g, 203.2 g and 1638.4 g of H_2, I_2 and HI respectively were found in 5 litre vessel. Calculate K_C. If all the reactants and products are transferred to a 2 litre *vessel*, what will be the amount of reactants and products at equilibrium?
17. 60 mL of H_2 and 42 mL of I_2 are heated in a closed vessel. At equilibrium the vessel contains 28 mL HI. Calculate degree of dissociation of HI.
18. In the dissociation of HI, 20% of HI is dissociated at equilibrium.
    Calculate K_P for $HI(g) \rightleftharpoons \frac{1}{2}H_2(g)+\frac{1}{2}I_2(g)$.
19. The value of K_P for dissociation of $2HI \rightleftharpoons H_2+I_2$ is 1.84×10^{-2}. If the equilibrium concentration of H_2 is 0.4789 mol $litre^{-1}$, calculate the concentration of HI at equilibrium.

20. The K_P value for the reaction ; $H_2 + I_2 \rightleftharpoons 2HI$, at 460°C is 49. If the initial pressure of H_2 and I_2 is 0.5 atm respectively, determine the partial pressure of each gas at equilibrium. **(Roorkee 1999)**

21. One mole of H_2, two mole of I_2 and three mole of HI are injected in one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 500°C? K_C for reaction ; $H_2 + I_2 \rightleftharpoons 2HI$ is 45.9

22. 0.96 g of HI were heated to attain equilibrium $2HI \rightleftharpoons H_2 + I_2$. The reaction mixture on titration requires 15.7 mL of N/10 *hypo* solution. Calculate degree of dissociation of HI.

23. The degree of dissociation of HI at a particular temperature is 0.8. Calculate the volume of $2M$ $Na_2S_2O_3$ solution required to neutralise the iodine present in a equilibrium mixture of a reaction when 2 mole each of H_2 and I_2 are heated in a closed vessel of 2 litre capacity.

24. The activation energy of $H_2 + I_2 \rightleftharpoons 2HI$ in equilibrium for the forward reaction is 167 kJ mol^{-1} whereas for the reverse reaction is 180 kJ $mole^{-1}$. The presence of catalyst lowers the activation energy by 80 kJ mol^{-1}. Assuming that the reactions are made at 27°C and the frequency factor for forward and backward reactions are 4×10^{-4} and 2×10^{-3} respectively, calculate K_C.

25. A reversible reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ in equilibrium has $[H_2]=0.5$, $[I_2]=0.5$ and $[HI]=1.23$ in one litre flask. If suddenly 0.6 mole of HI is removed, find out the new equilibrium concentrations.

26. At 700 K, hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8. Calculate the mole of H_2, Br_2 and HBr at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of Br_2 is heated to 700 K. **(Roorkee 1995)**

27. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

was established with an equilibrium constant $K_C = 2.1\times10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2. **(IIT May 1997)**

28. K_C for $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 986°C is 0.63. A mixture of 1 mole $H_2O(g)$ and 3 mole $CO(g)$ is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.
(i) How many mole of H_2 are present at equilibrium ?
(ii) Calculate partial pressure of each gas at equilibrium
(Roorkee 1992)

29. An equilibrium mixture of

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

present in a vessel of one litre capacity at 815°C was found by analysis to contain 0.4 mole of CO, 0.3 mole of H_2O, 0.2 mole of CO_2 and 0.6 mole of H_2.
(a) Calculate K_C.
(b) If it is derived to increase the concentration of CO to 0.6 mole by adding CO_2 to the vessel, how many mole must be added into equilibrium mixture at constant temperature in order to get this change ?

30. A mixture of one mole of CO_2 and one mole of H_2 attains equilibrium at a temperature of 250°C and a total pressure of 0.1 atm for the change $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$. Calculate K_P if the analysis of final reaction mixture shows 0. 16 volume per cent of CO.

31. At 700 K, CO_2 and H_2 react to form CO and H_2O. For this purpose K_C is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K.
(a) Find out mole of each gas at equilibrium.
(b) When equilibrium has been reached, another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find composition of mixture at new equilibrium.

32. At a certain temperature, K_C for

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

is 16. If we take one mole of each of all the four gases in one litre container, what would be the equilibrium concentrations of NO and NO_2?

33. A mixture of SO_3, SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a temperature at which K_C for the reaction,
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 100 mol^{-1} litre. At equilibrium.
(a) If no. of mole of SO_3 and SO_2 in flask are same, how many mole of O_2 are present ?
(b) If no. of mole of SO_3 in flask are twice the no. of mole of SO_2, how many mole of O_2 are present ?

34. At 627°C and one atmosphere pressure SO_3 is partially dissociated into SO_2 and O_2 by $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$. The density of the equilibrium mixture is 0.925 g/litre. What is the degree of dissociation ?

35. The equilibrium constant K_P of the reaction :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 atm and 2 atm respectively is heated at constant volume to equilibriate. Calculate partial pressure of each gas at 800 K at equilibrium.

36. The equilibrium mixture for

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

present in 1 litre vessel at 600°C contains 0.50, 0.12 and 5.0 mole of SO_2, O_2 and SO_3 respectively.

(a) Calculate K_C for the given change at 600°C.
(b) Also calculate K_P.
(c) How many mole of O_2 must be forced into the equilibrium vessel at 600°C in order to increase the concentration of SO_3 to 5.2 mole ?

37. At 273 K and one atm, 'a' litre of N_2O_4 decomposes to NO_2 according to equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. To what extent has the decomposition proceeded when the original volume is 25% less than that of existing volume ?

38. The K_P for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 640 mm at 775 K. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm. At what pressure, the dissociation will be 50% ? **(Roorkee 1997)**

39. 0.1 mole of $N_2O_4(g)$ was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of $NO_2(g)$ present, if the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g), \qquad (K_P = 0.14)$$

is reached after sometime.

40. The degree of dissociation of N_2O_4 into NO_2 at one atmosphere and 40°C is 0.310. Calculate its K_P at 40°C. Also report the degree of dissociation at 10 atm pressure at same temperature.

41. At 340 K and one atmospheric pressure, N_2O_4 is 66% dissociated into NO_2. What volume of 10 g N_2O_4 occupy under these conditions ?

42. N_2O_4 dissociates as $N_2O_4 \rightleftharpoons 2NO_2$. At 55°C and one atmosphere, % decomposition of N_2O_4 is 50.3%. At what P and same temperature, the equilibrium mixture will have the ratio of $N_2O_4 : NO_2$ as 1 : 8 ?

43. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases. **(Roorkee 1991)**

44. At 25°C and 1 atmospheric pressure, the partial pressures in equilibrium mixture of gaseous N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and a total pressure of 10 atm.

45. An equilibrium mixture of N_2O_4 (0.98 mole) and NO_2 (0.06 mole) in a 0.750 litre flask at 27°C is expanded through an evacuated flask of 2.250 litre at 27°C. What are the new concentrations of N_2O_4 and NO_2 in equilibrium ?

46. Prove $\alpha = \sqrt{\left(\frac{K_P}{P + K_P}\right)}$ for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; where α is degree of dissociation at temperature when equilibrium constant is K_P.

47. How much PCl_5 must be added to a one litre vessel at 250°C in order to obtain a concentration of 0.1 mole of Cl_2? K_C for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 0.0414 mol/litre.

48. At 540 K, 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_P and K_C for the reaction. **(Roorkee 1998)**

49. At some temperature and under a pressure of 4 atm. PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same. **(Roorkee 1996)**

50. The degree of dissociation of 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atmosphere. (Atomic mass of P = 31.0 and Cl = 35.5)

51. The equilibrium concentration of the reactants and products for the given equilibrium in a two litre container are shown below :

$$\underset{2M}{PCl_3(g)} + \underset{1M}{Cl_2(g)} \rightleftharpoons \underset{4M}{PCl_5(g)}$$

(i) If 2 mole of Cl_2 are added in the container, find the new equilibrium concentration of each.
(ii) If the equilibrium mixture reported initially is transferred into 4 litre vessel, what would be the new concentrations at equilibrium ?

52. At 473 K, partially dissociated vapours of PCl_5 are 62 times as heavy as H_2. Calculate degree of dissociation of PCl_5.

53. One mole of N_2 and 3 mole of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate degree of dissociation of PCl_5 and K_P of the reaction :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

54. One mole of N_2 is mixed with three mole of H_2 in a 4 litre vessel. If 0.25% N_2 is converted into NH_3 by the reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

calculate K_C. Also report K_C for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$.

55. NH_3 is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium of the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$. Calculate % of mole of NH_3 actually decomposed.

56. In a mixture of N_2 and H_2 in the ratio 1 : 3 at 30 atm and 300°C, the % of NH_3 at equilibrium is 17.8. Calculate K_P for $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

57. A reaction carried out by 1 mole of N_2 and 3 mole of H_2 shows at equilibrium, the mole fraction of NH_3 as 0.012 at 500°C and 10 atm pressure. Calculate K_P. Also report the pressure at which mole % of NH_3 in equilibrium mixture is increased to 10.4.

58. At 450°C, the equilibrium constant K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ was found to be 1.6×10^{-5} at a pressure of 200 atm. If N_2 and H_2 are taken in 1 : 3 ratio, what is the % of NH_3 formed at this temperature ?

59. Calculate K_C for the reaction :

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$$

If 1.58 mole of H_2S, 1.27 mole of H_2 and 2.78×10^{-6} mole of S_2 are in equilibrium in a flask of capacity 180 litre at 750°C.

60. What is the % dissociation of H_2S, if 1 mole of H_2S is introduced into a 1.10 litre vessel at 1000 K ? K_C for the reaction :

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g) \text{ is } 1 \times 10^{-6}.$$

61. At 90°C, the equilibrium, $H_2(g) + S(g) \rightleftharpoons H_2S(s)$ was established having $K = 6.8 \times 10^{-2}$. If 0.20 mole of hydrogen and 1.0 mole of sulphur are heated to 90°C in one litre vessel, what will be the partial pressure of H_2S at equilibrium ?

62. Calculate the per cent dissociation of $H_2S(g)$, if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K. For the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ the value of K_C is 1.0×10^{-6}. **(Roorkee 1994)**

63. K_P for the reaction $2O_3(g) \rightleftharpoons 3O_2(g)$; is 1.3×10^{57} atm. How many O_3 molecules are present in equilibrium in 10 million cubic metres of air at 25°C and 720 mm Hg pressure ?

64. At 1000 K, the pressure of iodine gas is found to be 0.112 atm due to partial dissociation. Had there been no dissociation the pressure would have been 0.074 atm? Calculate K_P for the reaction, $I_2(g) \rightleftharpoons 2I(g)$.

65. When S in the form of S_8 is heated at 900 K, the initial pressure of 1 atmosphere falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the K_P for reaction. **(Roorkee 1990)**

66. For the reaction, $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; H_2 is introduced into a five litre flask at 327°C, containing 0.2 mole of $CO(g)$ and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate K_C and K_P. **(IIT 1990)**

67. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 750 K alongwith a catalyst so that the following reaction can take place.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate :

(i) K_P and K_C

(ii) The final pressure, if the same mole of CO and H_2 as before are used but without catalyst so that the reaction does not take place. **(IIT 1993)**

68. The value of K_P is 1×10^{-3} atm^{-1} at 25°C for the reaction: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$. A flask contains NO at 0.02 atm and at 25°C. Calculate the mol of Cl_2 that must be added, if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mol of gas produce 1 atm pressure at 25°C. (Ignore probable association of NO to N_2O_2) **(Roorkee 2001)**

69. A graph plotted between $\log_{10} K_C$ and $1/T$ is straight line with intercept 10 and slope equal to 0.5. Calculate:

(i) pre-exponential factor A.

(ii) heat of reaction at 298 K.

(iii) equilibrium constant at 298 K.

(iv) equilibrium constant at 800 K assuming ΔH remains constant in between 298 K and 800 K.

70. K_P for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.6×10^{-4} atm^{-2} at 400°C. What will be K_P at 500°C? Heat of reaction in this temperature range is –25.14 kcal.

71. K_C for $\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftharpoons NH_3$ are 0.0266 and 0.0129 atm^{-1} respectively at 350°C and 400°C. Calculate heat of formation of NH_3.

72. Equilibrium constant K_P for

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

is 0.0118 atm at 1065°C and heat of dissociation is 42.4 kcal. Find equilibrium constant at 1132°C.

73. K_P for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 1.64×10^{-4}. Find K_C. Also find $\Delta G°$ using K_P and K_C values and interpret the difference.

74. Calculate the value of $\log K_P$ for the reactions,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at 25°C. The standard enthalpy of formation of $NH_3(g)$ is –46 kJ and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130 and 192 JK^{-1} mol^{-1} respectively. ($R = 8.3$ $JK^{-1}mol^{-1}$) **(Roorkee 1999)**

75. $\Delta G°$ for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ is -16.5 KJ mol^{-1}. Find out K_P for the reaction. Also report K_P and $\Delta G°$ for,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \text{ at } 25°C.$$

76. The plot of $\log_{10} K_P$ against $\frac{1}{T}$ for the reaction :

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

is a straight line with slope = 4.95×10^3. Calculate K_P at 25°C if standard entropies for $SO_2(g)$, $O_2(g)$ and $SO_3(g)$ are 248.2, 205.1 and 256.8 JK^{-1} mol^{-1} at 25°C respectively.

77. Show that $2.303 \log_{10} K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$; where K is equilibrium constant and $\Delta H°$ and $\Delta S°$ are standard enthalpy and standard entropy change at temperature T.

78. The heat enthalpy and standard free energy change for the equilibrium :

$$Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$$

are 224 KJ mol^{-1} and 33 KJ mol^{-1} respectively at the temperature 920 K. Calculate the temperature at which equilibrium constant becomes greater than 1. Assume $\Delta G°$ and ΔH remains constant.

79. Calculate the composition of A and B in an equilibrium mixture following the reaction :

	$A \rightleftharpoons B$		(100 mole of equilibrium mixture is present at 300 K)
$\Delta H°$ (in kJ)	24.27	25.44	
$\Delta S°$ (in J)	246.4	253.3	

80. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate $\Delta G°$ for the following equilibria :

$$B = A \quad ; \quad \Delta G_1^0 = ?$$

$$B = C \quad ; \quad \Delta G_2^0 = ?$$

From the calculated value of ΔG_1^0 and ΔG_2^0 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

81. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$

$(G^0_{N_2O_4})_{298K} = 100\ kJ\ mol^{-1}$ and $(G^0_{NO_2})_{298} = 50\ kJ\ mol^{-1}$

(i) When 5 mole/litre of each is taken, calculate the value of ΔG for the reaction at 298 K.

(ii) Find the direction of reaction and concentration at equilibrium **(IIT 2004)**

82. Consider the reaction $A \rightleftharpoons B$. The ΔH_f^0 for A and B are −24.27 and −25.44 kJ/mol respectively. $S°$ for A and B are 246.4 and 252.3 $JK^{-1}\ mol^{-1}$ respectively. What is the composition of equilibrium mixture at 298 K ?

83. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/litre at 288 K and 1.84 g/litre at 348 K. Calculate the enthalpy of reaction : $N_2O_4 \rightleftharpoons 2NO_2$. Also calculate the entropy change during the reaction at 348 K.

84. Calculate the equilibrium concentration ratio of C to A, if 2.0 mol each of A and B were allowed to come to equilibrium $A + B \rightleftharpoons C + D$ at 300 K. The $\Delta G°$ for the change is 460 cal.

85. $\Delta G° = 77.77\ kJ\ mol^{-1}$ at 1000 K for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$. What is the partial pressure of NO under equilibrium at 1000 K for air at 1 atm pressure containing 80% N_2 and 20% O_2 by volume ?

86. 88 g chunk of dry ice and 30 g graphite were placed in a 5 litre container and the mixture was heated to achieve the equilibrium :

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Calculate the value of K_P at 1000 K if the density of gas mixture is 18.3 g/litre. What is the value of K_p at 1100 K if density of gas mixture is 18.9 g/litre. Also calculate the enthalpy of reaction.

87. Following data are given for the reaction :

$$H_2(g) + \frac{1}{2}S_2(g) \rightleftharpoons H_2S(g)$$

T(K)	1023	1218	1362	1473	1667
$\log_{10} K_P$	2.025	1.305	0.902	0.643	0.257

Assuming $\Delta H°$ and $\Delta S°$ constant for the given range, calculate $\Delta H°$ for the reaction in the range 1000 to 1218 K. Calculate $\Delta G°$ and $\Delta S°$ at 1023 K.

88. Consider the equilibrium $A(g) \rightleftharpoons 2B(g) + 3C(g)$ at 25°C. When A is loaded into a cylinder at 10.0 atm and the system is allowed to come an equilibrium, the final pressure is found to be 15.76 atm. What is standard Gibb's energy change for the reaction ?

89. Given below are the values of $\Delta H°$ and $\Delta S°$ for the reaction at 27°C.

$$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

$\Delta H° = -98.32\ kJ\ mol^{-1}$ and $\Delta S° = -95\ JK^{-1}\ mol^{-1}$. Find K_P for the reaction.

90. For $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, the observed pressure for reaction mixture in equilibrium is 1.12 atm at 106°C. What is the value of K_P for the reaction ?

91. Some solid NH_4HS is placed in flask containing 0.5 atm of NH_3. What would be pressures of NH_3 and H_2S when equilibrium is reached ?

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$; $\quad K_P = 0.11$

92. The equilibrium pressure of

$NH_4CN(s) \rightleftharpoons NH_3(g) + HCN(g)$ is 0.298 atm.

Calculate K_P. If $NH_4CN(s)$ is allowed to decompose in presence of NH_3 at 0.25 atm, calculate partial pressure of HCN at equilibrium.

93. When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_C and K_P for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ?

(IIT 1999)

94. Ammonium carbonate dissociates as

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original pressure.

95. What concentration of CO_2 be in equilibrium with 2.5×10^{-2} mol litre^{-1} of CO at 100°C for the reaction ?
$FeO(s)+CO(g)\rightleftharpoons Fe(s)+CO_2(g)$; $K_C=5.0$

96. In the reaction, $C(s)+CO_2(g)\rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_P.

97. The amount of CO_2 in a gaseous mixture of CO_2 and CO is determined by passing the mixture into an aqueous solution that contains excess of $Ba(OH)_2$. The CO_2 reacts yielding a precipitate of $BaCO_3$ but CO does not react. This method is used to analyse the equilibrium composition of gas when 1.77 g CO_2 reacted with 2.0 g graphite in a 1.0 litre container at 1100 K. The analysis yielded 3.41 g of $BaCO_3$. Use this data to calculate K_P at 1100 K for the reaction.

$$CO_2(g)+C(s)\rightleftharpoons 2CO$$

98. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm Some of the CO_2 is converted into CO on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.8 atm. **(Roorkee 1993)**

99. At 817°C, K_P for the reaction between $CO_2(g)$ and excess hot graphite (s) is 10 atm.

(a) What are the equilibrium concentration of the gases at 817°C and a total pressure of 5 atm ?

(b) At what total pressure, the gas contains 5% CO_2 by volume ? **(Roorkee 2000)**

100. The equilibrium attained in a closed container is $H_2O(l)\rightleftharpoons H_2O(v)$ at 40°C. The aqueous tension of water in container is 23 mm at 40°C. What is its K_P?

101. When 20 g of $CaCO_3$ were put into 10 litre flask and heated to 800°C, 35% of $CaCO_3$ remained unreacted at equilibrium. Calculate K_P for decomposition of $CaCO_3$.

102. At a certain temperature, K_P for dissociation of solid $CaCO_3$ is 4×10^{-2} atm and for the reaction, $C(s)+CO_2\rightleftharpoons 2CO$ is 2.0 atm respectively. Calculate the pressure of CO at this temperature when solid C, CaO, $CaCO_3$ are mixed and allowed to attain equilibrium.

103. Would 1% CO_2 in air be sufficient to prevent any loss in weight when M_2CO_3 is heated at 120° C?

$$M_2CO_3(s)\rightleftharpoons M_2O(s)+CO_2(g)$$

$K_P=0.0095$ atm at 120°C. How long would the partial pressure of CO_2 have to be to promote this reaction at 120°C?

104. In the preparation of quick lime from limestone, the reaction is,

$$CaCO_3\rightleftharpoons CaO(s)+CO_2(g)$$

Experiments carried out between 850°C and 950°C led to set of K_P values fitting in empirical equation $\ln K_P=7.282-\frac{8500}{T}$ where T is absolute temperature.

If the reaction is carried out in quiet air, what minimum temperature would be predicted from this equation for almost complete decomposition of lime ?

105. Under what pressure conditions $CuSO_4\cdot5H_2O$ be efflorescent at 25°C? How good a drying agent is $CuSO_4\cdot3H_2O$ at the same temperature ? Given

$$CuSO_4\cdot5H_2O(s)\rightleftharpoons CuSO_4\cdot3H_2O(s)+2H_2O(v)$$

$K_P=1.086\times10^{-4}$ atm^2 at 25°C. Vapour pressure of water at 25°C is 23.8 mm of Hg.

106. From the data given below derive which of the following reactant is most effective drying agent at 0°C. Given $P^\circ_{H_2O}=4.58$ mm at 0°C.

(i) $SrCl_2\cdot6H_2O(s)\rightleftharpoons SrCl_2\cdot2H_2O(s)+4H_2O(g)$;
$K_P=6.9\times10^{-12}$ atm^4

(ii) $Na_2SO_4\cdot10H_2O(s)\rightleftharpoons Na_2SO_4(s)+10H_2O(g)$;
$K_P=4.08\times10^{-25}$ atm^{10}

(iii) $Na_2HPO_4\cdot12H_2O(s)\rightleftharpoons Na_2HPO_4\cdot7H_2O(s)+5H_2O(g)$;
$K_P=5.25\times10^{-13}$ atm^5

107. For the reaction,

$$SnO_2(s)+2H_2(g)\rightleftharpoons Sn(l)+2H_2O(g)$$

the equilibrium mixture of steam and hydrogen contained 45% and 24% H_2 at 900 K and 1100 K respectively. Calculate K_P at both the temperatures. Generally should it be higher or lower temperatures for better reduction of SnO_2 ?

108. For the equilibrium :

$LiCl\cdot3NH_3(s)\rightleftharpoons LiCl\cdot NH_3(s)+2NH_3$, $K_P=9$ atm^2 at 40°C. A 5 litre vessel contains 0.1 mole of $LiCl\cdot NH_3$. How many mole of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion ?

109. The equilibrium : $2Na(g)\rightleftharpoons Na_2(g)$ was attained at 1.013 M Pa and 1500 K. The mass % of $Na(g)$ at equilibrium was found to be 71.0. Calculate K_P of reaction.

110. A small thermometer is broken in a closed room of dimensions $6\times5\times3\,m^3$ and the mercury shows the equilibrium : $Hg(l)\rightleftharpoons Hg(v)$ at 27°C. The atomic mass of Hg is 200.5 and vapour pressure of Hg at 27°C is 0.002 mm. Is it dangerous to enter the room if safety limit to $Hg(v)$ is 0.05 mg/m^3 ?

111. In an experiment starting with 1 mole C_2H_5OH, 1 mole CH_3COOH and 1 mole of water, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Calculate K_C.

112. When C_2H_5OH and CH_3COOH are mixed in equivalent proportion, equilibrium is reached when 2/3 of acid and alcohol are used. How much ester will be present when 2 g molecule of acid were to react with 2 g molecule of alcohol?

113. When α – D glucose is dissolved in water, it undergoes a partial conversion to β – D glucose to exhibit mutarotation. This conversion stops when 63.6% of glucose is in β form. Assuming that equilibrium has been attained, calculate K_C for mutarotation.

114. Calculate K_C for the reaction, $KI + I_2 \rightleftharpoons KI_3$. Given that initial mass of KI is 1.326 g. Mass of KI_3 is 0.105 g and no. of mole of free I_2 is 0.0025 at equilibrium and the volume of solution is one litre. The solubility of I_2 in water is 0.0013 M.

115. Sulphide ions in alkaline solution react with solid sulphur to form polyvalent sulphide ions. The equilibrium constant for the formation of S_2^{2-} and S_3^{2-} from S and S^{2-} ions are 1.7 and 5.3 respectively. Calculate equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S.

116. To 500 mL of 0.150 M $AgNO_3$ solution were added 500 mL of 1.09 M Fe^{2+} solution and the reaction is allowed to reach an equilibrium at 25°C.

$$Ag^+(aq.) + Fe^{2+}(aq.) \rightleftharpoons Fe^{3+}(aq.) + Ag(s)$$

For 25 mL of the solution, 30 mL of 0.0832 M $KMnO_4$ were required for oxidation. Calculate equilibrium constant for the reaction at 25°C.

117. For the reaction,

$$2Fe^{3+}(aq.) + (Hg_2)^{2+}(aq.) \rightleftharpoons 2Fe^{2+}(aq.) + 2Hg^{2+}(aq.)$$

$K_C = 9.14 \times 10^{-6}$ at 25°C. If the initial concentration of the ions are $Fe^{3+} = 0.5\,M$, $(Hg_2)^{2+} = 0.5\,M$, $Fe^{2+} = 0.03\,M$ and $Hg^{2+} = 0.03\,M$. What will be the concentrations of ions at equilibrium ?

118. 0.1 mole each of ethyl alcohol and acetic acid are allowed to react and at equilibrium, the acid was exactly neutralized by 100 mL of 0.85 N NaOH. If no hydrolysis of ester is supposed to have undergo, find K_C.

119. The rate of formation of the complex $[Fe(dipy)_3]^{2+}$ at 25°C following the reaction :

$$Fe^{2+} + 3\,dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$$

is given as : $\text{rate} = 1.45 \times 10^{13}[Fe^{2+}][dipy]^3$

The rate of disappearance of complex is given as :

$$\text{rate} = 1.22 \times 10^{-4}\,[Fe(dipy)_3]^{2+}$$

Calculate the stability constant of complex. *dipy* is abbreviated for dipyridyl a chelating agent.

120. For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$, the K_C at 25°C is 4×10^{-19}. Calculate $[Ag^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

(IIT 1994)

121. The equilibrium constant for the reaction :

H_3BO_3 + glycerine $\rightleftharpoons$ (H_3BO_3 + glycerine complex)

is 0.90. How much glycerine should be added to one litre of 0.10 M H_3BO_3 solution, so that 60% of the H_3BO_3 is converted to boric acid-glycerine complex?

122. For gaseous reaction $A + B \rightleftharpoons C$, the equilibrium concentration of A and B at a temperature are 15 mol litre^{-1}. When volume is doubled the reaction had equilibrium concentration of A as 10 mol litre^{-1}. Calculate :

(a) K_C

(b) concentration of C in original equilibrium.

123. When NO and NO_2 are mixed, the following equilibria are readily obtained;

$$2NO_2 \rightleftharpoons N_2O_4 \qquad K_P = 6.8\ \text{atm}^{-1}$$

and $\quad NO + NO_2 \rightleftharpoons N_2O_3$

In an experiment when NO and NO_2 are mixed in the ratio of 1 : 2, the final total pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate :

(a) the equilibrium partial pressure of NO.

(b) K_P for $NO + NO_2 \rightleftharpoons N_2O_3$.

124. Following two equilibria are established on mixing two gases A_2 and C.

(i) $3A_2(g) \rightleftharpoons A_6(g) \qquad K_P = 1.6\ \text{atm}^{-2}$

(ii) $A_2(g) + C(g) \rightleftharpoons A_2C(g)$

If A_2 and C are mixed in 2 : 1 molar ratio, calculate the equilibrium partial pressure of A_2, C, A_2C and K_P for the reaction (ii). Given that the total pressure to be 1.4 atm and partial pressure of A_6 to be 0.2 atm at equilibrium.

125. 1 mole of A in 1 litre vessel maintained at constant T shows the equilibrium :

$$A(g) \rightleftharpoons B(g) + 2C(g) \qquad K_{C_1}$$

$$C(g) \rightleftharpoons 2D(g) + 3B(g) \qquad K_{C_2}$$

If the equilibrium pressure is $\frac{13}{6}$ times of initial pressure and $[C]_{eq.} = \frac{4}{9}[A]_{eq.}$, calculate K_{C_1} and K_{C_2}.

126. Solid NH_4I on rapid heating in a closed vessel at 357°C develops a constant pressure of 275 mm Hg owing to

partial decomposition of NH_4I into NH_3 and HI, but the pressure gradually increases further (when the excess solid residue remains in the vessel) owing to dissociation of HI. Calculate the final pressure developed at equilibrium K_P for dissociation of HI is 0.015 at 357°C.

127. N_2 and O_2 combine at a given temperature to produce NO. At equilibrium the yield of NO is 'x' per cent by volume. If $x=\sqrt{K.a.b}-\frac{K(a+b)}{4}$ where K is the equilibrium constant of the given reaction at the given temperature and a and b are the volume percentage of N_2 and O_2 respectively in the initial pure mixture, what should be the initial composition of the reacting mixture in order that maximum yield of NO is ensured? Also report the maximum value of K at which 'x' is maximum.

128. The standard Gibb's energy change for the reaction :

$$2AB \rightleftharpoons A_2 + B_2$$

is 11.8 kJ at 230 K and 1 atm. Calculate degree of dissociation of AB at 230 K.

129. In a reaction at equilibrium 'X' mole of the reactant A decompose to give 1 mole each of C and D. It has been found that the fraction of A decomposed at equilibrium is independent of initial concentration of A. Calculate X.

130. The heat of reaction at constant volume for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300 K. Calculate the ratio of equilibrium constants K_P and K_C.

131. A vessel of 2.50 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at 440°C as :

$$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$$

After equilibrium the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 1.029 g of PbS as precipitate. What is value of K_C of the reaction at 440°C ? (Atomic mass of Pb = 206)

132. Gas A (mol. mass 16) and gas B (mol. mass 4) are confined into a vessel at partial pressure of 2 atm each at 27°C. The gases are then allowed to effuse out at 27°C through a value till the pressure inside the vessel becomes 2 atm after which the valve is closed and the gases are heated to 127°C and allowed to react as $A + B \rightleftharpoons C$ $K_P = 0.1\ atm^{-1}$. Calculate the partial pressure of C at equilibrium assuming C is not formed till the effusing process is completed at 27°C.

133. A gas mixture of volumetric composition 45% CO, 50% CO_2 and 5% N_2 was passed at 1380 K over a briquet of ZnO, so that Zn vapours was produced according to the reaction: $ZnO(s) + CO(g) \rightleftharpoons Zn(g) + CO_2(g)$. Under steady condition, the rate of input gas flow at STP is 0.224 $dm^3\ min^{-1}$. The rate of loss of mass of ZnO is 5×10^{-4} mol min^{-1}. $P = 770$ torr. Find K_P at 1380 K assuming ideal gas behaviour.

134. A certain gas A polymerises to a small extent at a given temperature and pressure : $nA \rightleftharpoons (A)_n$. Show that the gas obeys the approximate equation :

$$\frac{PV}{RT} = \left[1 - \frac{(n-1)K_C}{V^{n-1}}\right]$$

where $K_C = \frac{[A_n]}{[A]^n}$

and V is the volume of the container. Assume initially one mole of A was taken in the container.

135. Steam is passed over hot carbon to attain the following equilibrium at 400 K.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g).$$

The equilibrium constant $K = 1.34$ (dimension less) and the total pressure of the equilibrium mixture is 200 kPa. What are the mole fractions of all substances in equilibrium mixture ?

136. If equilibrium constant K_C of the reaction :

$$2Ag(s) + 2I^- + 2H_2O \rightleftharpoons 2AgI(s) + H_2(g) + 2OH^-$$

is 1.2×10^{-23} (dimension less) at 25°. If concentrations of I^- at equilibrium is 0.10 and pressure of H_2 gas at equilibrium is 60 kPa, calculate the pH of solution at equilibrium.

137. A gaseous substance $AB_2(g)$ reacts with solid A to form $AB(g)$ and the reaction attains equilibrium :

$$AB_2(g) + A(s) \rightleftharpoons 2AB(g)$$

The initial and final pressure are 0.7 and 0.95 bar. Calculate K_P. Also if the equilibrium mixture is expanded reversibly and isothermally till the equilibrium pressure falls to 0.4 bar, calculate the volume percentage of $AB(g)$ and $AB_2(g)$ at final equilibrium.

138. For the reaction :

$$CH_3COCH_3(g) \rightleftharpoons C_2H_6(g) + CO(g)$$

initial pressure of CH_3COCH_3 is 100 mm. The mole fraction of CO(g) is 1/3 at equilibrium. What is K_C?

SOLUTIONS (Numerical Problems)

1. (1) A system is said to be homogeneous if phase (P) =1.
A system with $P \geq 2$ is heterogeneous.

(2) To determine phase follow the rules given below.

System	Phase	Explanation
$S+S$	$=2$	No. of solid in mixture give number of P, *i.e.*, $P=2$
$S+L$	$=1$	Soluble systems lead to $P=1$
$S+L$	$=2$	Insoluble system lead to $P=2$
$L+L$	$=2$	Immiscible liquids lead to $P=2$
$L+L$	$=1$	Miscible liquids lead to $P=1$
$G+G$	$=1$	All gases in a mixture give P = 1

Given Systems	a	b	c	d	e	f	g
No. of phase	2	2	2	2	1	2	3

$\therefore$ Homogeneous system is : **e**

Heterogeneous systems are : **a, b, c, d, f, g**

2. **Note :** 1. Write K_P for heterogeneous systems if gaseous phase is present.
2. Write K_C for homogeneous solution phase.
3. Write K_P or K_C for homogeneous gaseous phase.

(a) $K_P = [P'_{O_2}]^{3/2}$

(b) $K_P = [P'_{H_2O}]/P'_{H_2} = \frac{n_{H_2O}}{n_{H_2}} \times [P/\Sigma N]^0$

(c) $K_P = [P'_{CO_2}]^2/[P'_{O_2}]^5 = \frac{[n_{CO_2}]^2}{[n_{O_2}]^5} \cdot \left[\frac{P}{\Sigma N}\right]^{-3}$

(d) $K_P = \frac{[P'_{HI}]^2}{P'_{H_2} \times P'_{I_2}}$ or $K_C = \frac{[HI]^2}{[H_2][I_2]}$

(e) $K_P = \frac{[P'_{NH_3}]^2}{[P'_{N_2}][P'_{H_2}]^3}$ or $K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(f) $K_C = \frac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

3.

	N_2	+ $3H_2$	$\rightleftharpoons$	$2NH_3$	
Initial mole	1	3		0	
Final mole	0	0		2	($\because$ complete conversion)

$\therefore$ Ratio of initial and final volumes $= \frac{\text{Initial mole}}{\text{Final mole}}$

($\because V \propto n$ if P and T are constant) $= \frac{4}{2} = 2$

4. For $2H_2O \rightleftharpoons 2H_2 + O_2$ $K_1 = \frac{[H_2]^2[O_2]}{[H_2O]^2}$ ...(1)

For $2CO_2 \rightleftharpoons 2CO + O_2$ $K_2 = \frac{[CO]^2[O_2]}{[CO_2]^2}$ ...(2)

For $CO_2 + H_2 \rightleftharpoons H_2O + CO$ $K = \frac{[H_2O][CO]}{[CO_2][H_2]}$ ...(3)

Thus, by Eqs. $\frac{(2)}{(1)}$, $\frac{K_2}{K_1} = \frac{[CO]^2[O_2]}{[CO_2]^2} \times \frac{[H_2O]^2}{[H_2]^2[O_2]}$

$\frac{K_2}{K_1} = \frac{[CO]^2[H_2O]^2}{[CO_2]^2[H_2]^2} = K^2$ By Eq. (3)

or $K = \sqrt{\left(\frac{K_2}{K_1}\right)} = \sqrt{\left(\frac{1.4\times10^{-12}}{2.1\times10^{-13}}\right)} = \mathbf{2.58}$

5. For $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2$

$K_{C_1} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 0.15$ ...(1)

For $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ ...(2)

By reversing Eq. (1), $\frac{1}{K_{C_1}} = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$

On making square, $\left(\frac{1}{K_{C_1}}\right)^2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_C$

By Eq. (2)

$K_C = \left[\frac{1}{0.15}\right]^2 = \mathbf{44.44\ mol^{-1}\ litre^1}$

6. For $2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} I$

$K_{C_1} = \frac{K_1}{K_2} = \frac{[I]}{[A]^2}$ ...(1)

For $I \rightleftharpoons B + C$

$K_{C_2} = \frac{K_3}{K_4} = \frac{[B][C]}{[I]}$ ...(2)

For $2A \rightleftharpoons B + C$

$K_C = \frac{[B][C]}{[A]^2}$

By Eqs. (1) $\times$ (2), $K_C = K_{C_1} \times K_{C_2} = \frac{K_1}{K_2} \times \frac{K_3}{K_4}$

7. $K_P = K_C(RT)^{\Delta n}$

$K_P = 0.5 \times (0.082 \times 400)^{-2}$

$K_P = \mathbf{4.648 \times 10^{-4}\ (atm)^{-2}}$

8. $A + B \rightleftharpoons 3C$

Before reaction, $[A] = 1/3$, $[B] = 2/3$, $[C] = 4/3$

Thus, $Q = \frac{[C]^3}{[A][B]} = \frac{4^3 \times 3 \times 3}{3^3 \times 1 \times 2} = \frac{64}{6} = 10.66$

(a) Since $K_C = 10$, thus Q must decrease to attain K_C value and thus, $[C]$ must decrease or $[A]$ and $[B]$ should

increase. Thus, reaction will occur in backward direction.

(b) Since $K_C = 15$, thus Q must increase to attain K_C value and thus, $[C]$ must increase or $[A]$ and $[B]$ should decrease. Thus, reaction will occur in forward direction.

(c) $Q = K_C$; thus, reaction is in equilibrium.

9.

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

Mole before dissociation	1	0	0
Mole after dissociation	$(1-x)$	x	$\frac{x}{2}$

Total mole at equilibrium $(\Sigma n) = 1 - x + x + \frac{x}{2} = 1 + \frac{x}{2}$

Now, $K_P = \frac{{}^nB_2 \times ({}^nAB)^2}{(n_{AB_2})^2} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n}$

$$K_P = \frac{\frac{x}{2}\cdot(x)^2}{(1-x)^2} \times \left[\frac{P}{1+\frac{x}{2}}\right]^1$$

$$K_P = \frac{x^3 P}{2} \left[\because x \text{ is small, } \therefore 1-x \approx 1 \text{ and } 1+\frac{x}{2} \approx 1\right]$$

or $$x = \sqrt[3]{\frac{2K_P}{P}}$$

10. The ratio $\frac{[\text{Product}]}{[\text{Rectant}]}$ is maximum when $K = 10^{10}$ and thus, reaction goes farthest to completion when $K = 10^{10}$.

11. For $A(g) \rightleftharpoons B(g)$; $K_C = \frac{[B]}{[A]} = 1.1 \Rightarrow [B] > [A]$

If $[B] = 1$; $[A] = 0.91$

Case I $0.91 < [A] \le 1$ Only $[B] > 1$

Case II $[A] > 1$ Both $[A]$ and $[B] > 1$

12.

$$C_6H_{12}O_6 \rightleftharpoons 6HCHO \qquad K_C = \frac{1}{6\times10^{22}}$$

Initial conc.	1	0
Conc. at eq.	$(1-\alpha)$	6α

$$\therefore K_C = \frac{1}{6\times10^{22}} = \frac{(6\alpha)^6}{(1-\alpha)} \quad [1-\alpha = 1 \text{ since } K_C \text{ is very small}]$$

or $$(6\alpha)^6 = 1.67\times10^{-23} \text{ or } 6 \log 6\alpha = -22.78$$

or $$\log 6\alpha = -3.796$$

or $$\alpha = \frac{1.59\times10^{-4}}{6} = \mathbf{2.65\times10^{-5}\,M}$$

$\therefore$ $$[HCHO] = 6\alpha = \mathbf{1.59\times10^{-4}\,M}$$

13.

$$A + B \rightleftharpoons C + D$$

Initial concentration	2a	a	0	0
Concentration at equilibrium	$(2a-x)$	$(a-x)$	x	x

Given, initially $[A] = 2[B] = 2a$

Let concentration of B initially be a mol/litre.

$\therefore$ $$K_C = \frac{x\cdot x}{(2a-x)(a-x)} \quad ...(1)$$

Given at equilibrium, $[C] = 3[B]$ $\therefore$ $x = 3(a-x)$

$$x = \frac{3a}{4} \quad ...(2)$$

$\therefore$ By Eqs. (1) and (2), $$K_C = \frac{\frac{3a}{4}\times\frac{3a}{4}}{\left(2a-\frac{3a}{4}\right)\left(a-\frac{3a}{4}\right)} = \mathbf{1.8}$$

14.

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

Initial mole	1	2	0
Final mole at equilibrium	$(1-x)$	$(2-x)$	$2x$

Total volume of both containers on joining becomes 3 litre.

$\therefore$ At equilibrium, $[A_2] = \frac{1-x}{3}$; $[B_2] = \frac{2-x}{3}$; $[AB] = \frac{2x}{3}$

$$\therefore K_C = \frac{[AB]^2}{[A_2][B_2]} = \frac{4x^2}{9\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = \frac{4x^2}{(2-3x+x^2)} = 50$$

$\therefore$ $4x^2 = 100 - 150x + 50x^2$ or $46x^2 - 150x + 100 = 0$

$x = 0.93$ and 2.326 which is not valid since $x \ngeq 2$

$\therefore$ Mole of AB $= 2x = 2(0.93) = \mathbf{1.86}$

15.

$$A + 2B \rightleftharpoons AB_2$$

Initial mole	1	2	0
Mole at equilibrium	$(1-x)$	$(2-2x)$	x

Total mole at equilibrium $= 1 - x + 2 - 2x + x = 3 - 2x$

Let pressure at equilibrium be P;

$\because$ $$K_P = \frac{n_{AB_2}}{n_A \times (n_B)^2} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

$\therefore$ $$K_P = \frac{x}{(1-x)(2-2x)^2} \times \left[\frac{P}{(3-2x)}\right]^{-2}$$

$$= \frac{x(3-2x)^2}{(1-x)(2-2x)^2 \cdot P^2} \quad ...(1)$$

Given that, $x = 0.6$ and $\Delta n = -2$

$\therefore$ $$K_P = K_C(RT)^{\Delta n} = 0.3475\times(0.0821\times473)^{-2} \quad ...(2)$$

By Eqs. (1) and (2),

$\therefore$ $$0.3475\times(0.0821\times473)^{-2} = \frac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2}$$

$$= \frac{0.6\times(1.8)^2}{P^2(0.4)(0.8)^2}$$

$$P = \mathbf{181.5\ atm}$$

16.

$$2HI \rightleftharpoons H_2 + I_2$$

Mole at equilibrium	$\frac{1638.4}{128}$	$\frac{7.8}{2}$	$\frac{203.2}{254}$
	$= 12.8$	3.9	0.8

Let volume of container be V litre

$$[H_2] = \frac{3.9}{V}; [HI] = \frac{12.8}{V}; [I_2] = \frac{0.8}{V}$$

$\therefore$ $$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{3.9\times0.8}{V\times V\times\left(\frac{12.8}{V}\right)^2} = 0.019$$

$\therefore$ $$K_C = \mathbf{0.019}$$

For the given reaction $\Delta n = 0$ and thus there will be no effect on equilibrium concentration of reactants and products if the matter is transferred to attain equilibrium in 2 litre vessel.

17.

	H_2	+ I_2	$\rightleftharpoons$ 2HI	Given,
Volume at $t=0$	60	42	0	$\because 2x=28$
Volume at equilibrium	$(60-x)$	$(42-x)$	$2x$	$\therefore x=14$
	$(60-14)$	$(42-14)$	28	

Since at constant P and T, mole $\propto$ volume of gas (By $PV=nRT$). Thus, volume of gases given can be directly used as concentration. This can be done only for reactions having $\Delta n = 0$.

$$\therefore \quad K_C = \frac{28\times 28}{46\times 28} = \frac{28}{46}$$

Now for dissociation of HI; $2HI \rightleftharpoons H_2 + I_2$

Mole at $t=0$	1	0	0
Mole at equilibrium	$(1-\alpha)$	$\alpha/2$	$\alpha/2$

where α is degree of dissociation

$$K_{C_1} = \frac{\alpha^2}{4(1-\alpha)^2} = \frac{1}{K_C}$$

$$\therefore \quad \frac{\alpha}{2(1-\alpha)} = \sqrt{\left(\frac{46}{28}\right)}$$

$$\therefore \quad \alpha = \mathbf{0.719} \text{ or } \mathbf{71.9\%}$$

18.

$$HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$$

Initial Mole	1	0	0
Mole at equilibrium	$(1-\alpha)$	$\alpha/2$	$\alpha/2$

Where α is degree of dissociation and volume of container is V litre.

$$K_P = K_C = \frac{\left(\frac{\alpha}{2V}\right)^{1/2}\left(\frac{\alpha}{2V}\right)^{1/2}}{\frac{(1-\alpha)}{V}} = \frac{\alpha}{2(1-\alpha)}$$

$$\therefore \quad K_P = K_C = \frac{0.2}{2(1-0.2)} \qquad (\because \alpha = 0.2)$$

$$K_P = K_C = \mathbf{0.125}$$

19. Given, $K_P = 1.84\times 10^{-2}$

$\because \Delta n = 0 \quad \therefore \quad K_P = K_C = 1.84\times 10^{-2}$

$$2HI \rightleftharpoons H_2 + I_2$$

Concentration at equilibrium	a	0.4789	0.4789

Since, given $[H_2] = 0.4789 \quad \therefore \quad [I_2] = 0.4789$ mole litre^{-1}

Conc. of HI at equilibrium is a mol litre^{-1}

$$\therefore \quad K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.4789\times 0.4789}{a^2}$$

$$\therefore \quad a^2 = \frac{0.4789\times 0.4789}{1.84\times 10^{-2}} \qquad (\because K_C = 1.84\times 10^{-2})$$

$$\therefore \quad a = 3.53$$

or [HI] at equilibrium = **3.53 mole litre^{-1}**

20.

	H_2	+ I_2	$\rightleftharpoons$ 2HI
Initial pressure	0.5	0.5	0
At. eq.	$(0.5-x)$	$(0.5-x)$	$2x$

$$\therefore \quad K_P = \frac{(2x)^2}{(0.5-x)^2} = 49$$

$$\text{or} \quad \frac{2x}{(0.5-x)} = 7 \text{ or } 2x = 3.5-7x \text{ or } 9x = 3.5$$

$$x = \frac{3.5}{9} = 0.389$$

At equilibrium : $P'_{H_2} = 0.5-0.389 = \mathbf{0.111}$ **atm**

$$P'_{I_2} = 0.5-0.389 = \mathbf{0.111} \text{ atm}$$

$$P'_{HI} = 0.389\times 2 = \mathbf{0.778} \text{ atm}$$

21.

	H_2	+ I_2	$\rightleftharpoons$ 2HI
Initial mole	1	2	3
Mole at equilibrium	$(1-x)$	$(2-x)$	$(3+2x)$

Let volume of container be V litre.

$$\therefore \quad K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\frac{3+2x}{V}\right]^2}{\left[\frac{1-x}{V}\right]\left[\frac{2-x}{V}\right]}$$

$$45.9 = \frac{(3+2x)^2}{(1-x)(2-x)} \qquad (\because K_C = 45.9)$$

$$45.9 = \frac{9+4x^2+12x}{2-3x+x^2}$$

$$\therefore \quad x = 0.684$$

$$\therefore \quad [H_2] = 1-0.684 = \mathbf{0.316} \text{ mol litre}^{-1} \qquad (\because V = 1 \text{ litre})$$

$$[I_2] = 2-0.684 = \mathbf{1.316} \text{ mol litre}^{-1}$$

$$[HI] = 3+2(0.684) = \mathbf{4.368} \text{ mol litre}^{-1}$$

22.

	2HI	$\rightleftharpoons$ H_2	+ I_2
Mole at $t=0$	$\frac{0.96}{128}$	0	0
or	7.5×10^{-3}	0	0
Mole at equilibrium	$(7.5\times 10^{-3}-x)$	$\frac{x}{2}$	$\frac{x}{2}$

Meq. of I_2 formed at equilibrium = Meq. of hypo used for reaction mixture

$$\frac{w_{I_2}}{E}\times 1000 = 15.7\times\frac{1}{10} \quad \therefore \quad \left(\frac{w}{E}\right)\text{of } I_2 = 1.57\times 10^{-3}$$

$$\therefore \quad \text{Mole of } I_2 \text{ formed} = \frac{1.57\times 10^{-3}}{2} = 0.785\times 10^{-3}$$

$$\frac{x}{2} = 0.785\times 10^{-3}$$

$$x = 1.57\times 10^{-3}$$

$\therefore$ Degree of dissociation of HI

$$(\text{or } \alpha_{HI}) = \frac{\text{Mole dissociated}}{\text{Mole taken}}$$

$$= \frac{1.57\times 10^{-3}}{7.5\times 10^{-3}}$$

$$\alpha_{HI} = \mathbf{0.209} \text{ or } \mathbf{20.9\%}$$

23. Given α for HI = 0.8

$$2HI \rightleftharpoons H_2 + I_2$$

Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	$\frac{\alpha}{2}$	$\frac{\alpha}{2}$

$$\therefore \quad K_C = \frac{\alpha^2}{4(1-\alpha)^2} = \frac{(0.8)^2}{4(1-0.8)^2} = 4$$

Now, $H_2 + I_2 \rightleftharpoons 2HI$

Initial mole	2	2	0
Mole after reaction	$(2-x)$	$(2-x)$	$2x$

$$\therefore \quad K_C' = \frac{1}{K_C} = \frac{4x^2}{(2-x)^2}$$

or $$\frac{4x^2}{(2-x)^2} = \frac{1}{4} \text{ or } \frac{2x}{2-x} = \frac{1}{2} \text{ or } x = \frac{2}{5}$$

Thus, I_2 left $= 2 - \frac{2}{5} = \frac{8}{5}$ mole $= \frac{8}{5} \times 2$ equivalent

or $Na_2S_2O_3$ required can be calculated by

Meq. of $Na_2S_2O_3$ = Meq. of I_2 left

$$2 \times V = \frac{8}{5} \times 2 \times 1000$$

$$\therefore \quad V = 1600\,\text{mL} = \mathbf{1.6\ litre}$$

24. The lowering of activation energy by a catalyst occurs for forward reaction as well as for backward reaction.

Thus, in presence of catalyst,

Energy of activation for forward reaction

$$(E_{a_1}) = 167 - 80 = 87\ \text{kJ mol}^{-1}$$

Energy of activation for backward reaction

$$(E_{a_2}) = 180 - 80 = 100\ \text{kJ mol}^{-1}$$

$\therefore$ For forward reaction $K_1 = A_1 e^{-E_{a_1}/RT}$

For backward reaction $K_2 = A_2 e^{-E_{a_2}/RT}$

where A_1 and A_2 are frequency factors and E_{a_1} and E_{a_2} are energies of activation.

$$\therefore \quad K_C = \frac{K_1}{K_2} = \frac{A_1}{A_2} \cdot e^{[(-E_{a_1}/RT) + E_{a_2}/RT)]}$$

$$= \frac{4 \times 10^{-4}}{2 \times 10^{-3}} \times e^{[(-87+100)/(8.314 \times 10^{-3} \times 300)]}$$

$$K_C = 2 \times 10^{-1} e^{+13/(8.314 \times 300 \times 10^{-3})}$$

$$K_C = \mathbf{36.8}$$

25. $H_2 + I_2 \rightleftharpoons 2HI$

Eq. conc.	0.5	0.5	1.23

$$\therefore \quad K_C = \frac{[1.23]^2}{0.5 \times 0.5} = 6.05$$

On removing 0.60 mole of HI the reaction will proceed in forward direction

$H_2 + I_2 \rightleftharpoons 2HI$

New conc.	0.5	0.5	0.63
Eq. conc.	$(0.5-X)$	$(0.5-X)$	$(0.63+2X)$

$$\therefore \quad 6.05 = \frac{(0.63+2X)^2}{(0.5-X)(0.5-X)} \text{ or } X = 0.134$$

$$\therefore \quad [I_2] = [H_2] = 0.5 - 0.134 = \mathbf{0.366}$$

$$[HI] = 0.63 + (2 \times 0.134) = \mathbf{0.898}$$

26. For the given reaction of H_2 and Br_2 to give HBr, the value of equilibrium constant $K_C = 5 \times 10^8$ and thus, exceptionally higher value of K_C suggests that reaction goes almost to completion, *i.e.*,

$H_2 + Br_2 \rightleftharpoons 2HBr$

Before reaction	0.6	0.2	0
At equilibrium	0.4	0	0.4

Thus, $HBr = \mathbf{0.4\ mol}$

$H_2 = \mathbf{0.4\ mol}$

$Br_2 = \mathbf{0.0}$

Note : However if as all the concentrations of Br_2 is needed at equilibrium, it may be calculated as follows. Notice that $[Br_2]$ is in significant.

$2HBr \rightleftharpoons H_2 + Br_2$

0.4	0.4	0
$(0.4-2x)$	$(0.4+x)$	x

$$\therefore \quad K_C = \frac{1}{5 \times 10^8} = \frac{(0.4+x)x}{(0.4+2x)^2} = \frac{0.4 \times x}{(0.4)^2}$$

$$\therefore \quad x = \mathbf{8 \times 10^{-10}\ mol}$$

27. $N_2 + O_2 \rightleftharpoons 2NO$

Initial	a	$(100-a)$	0
Final	$(a-x)$	$(100-a-x)$	$2x$

Given, $$\frac{2x}{100} = \frac{1.8}{100} \quad \therefore \ x = 0.9$$

Also, $$K_P = K_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(2x)^2}{(a-x)(100-a-x)} = 2.1 \times 10^{-3}$$

$$\therefore \quad a = 79\%;\ 100 - a = \mathbf{21\%}$$

Note : Two values of 'a' are obtained as $a = 79\%$ and $a = 21\%$. Note that air contains more N_2 than O_2 ; thus $a = 79\%$.

28. (i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Initial mole	3	1	0	0
Mole at equilibrium	$(3-x)$	$(1-x)$	x	x

Total mole at equilibrium $= 3 - x + 1 - x + x + x = 4$

Now, $$K_C = \frac{x^2}{(3-x)(1-x)}$$

$$\therefore \quad \frac{x^2}{3 + x^2 - 4x} = 0.63 \qquad (\because K_C = 0.63)$$

$$\therefore \quad x = 0.681$$

$\therefore$ Mole of H_2 formed $= \mathbf{0.681}$

(ii) Total pressure at equilibrium $= 2$ atm

Total mole at equilibrium $= 4$

$P_g' = P_M \times$ mole fraction of that gas

$$\therefore \quad P'_{CO_2} = P_{H_2} = \frac{x \cdot P}{4} = \frac{0.681 \times 2}{4} = \mathbf{0.34\ atm}$$

$$P'_{CO} = \frac{(3-x) \cdot P}{4} = \mathbf{1.16\ atm}$$

$$P'_{H_2O} = \frac{(1-x) \cdot P}{4} = \mathbf{0.16\ atm}$$

29. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Mole at equilibrium	0.4	0.3	0.2	0.6

(a) $$\therefore \quad K_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{0.2 \times 0.6}{0.4 \times 0.3} = \mathbf{1}$$

($\because \Delta n = 0$, $\therefore$ Volume terms are not needed.)

(b) Now it is desired to increase the conc. of CO by 0.2 at equilibrium by forcing CO_2 into equilibrium mixture. Suppose a mole of CO_2 are forced in vessel at equilibrium; by doing so reaction proceeds in backward direction, *i.e.*,

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Addition at initial equilibrium	(0.2+a)	0.6	0.4	0.3
Mole at new equilibrium	(0.2+a − 0.2)	(0.6 − 0.2)	(0.4 + 0.2)	(0.3 + 0.2)
	a	0.4	0.6	0.5

$$\therefore \quad \frac{1}{K_C} = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{0.6\times 0.5}{a\times 0.4}$$

$$\therefore \quad a = \mathbf{0.75\ mol}$$

30.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Mole at $t=0$	1	1	0	0
Mole at equilibrium	$(1-x)$	$(1-x)$	x	x

Given that Vol. % of CO = 0.16

$\because$ Mole of CO = x

Total mole at equilibrium = $1-x+1-x+x+x=2$

$$\therefore \quad \frac{x}{2} = \frac{0.16}{100} \quad \therefore \quad x = 0.0032$$

Now, $$K_C = K_P = \frac{x^2}{(1-x^2)}$$

($\because \Delta n = 0$, volume terms are not needed)

$$K_P = \frac{(0.0032)^2}{(1-0.0032)^2} = \mathbf{1.03\times 10^{-5}}$$

31. (a)

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (\because K_C = 0.11)$$

Mole at $t=0$	0.45	0.45	0	0
Mole at equilibrium	(0.45 − x)	(0.45 − x)	x	x

$$\therefore \quad K_C = 0.11 = \frac{x\cdot x}{(0.45-x)^2}$$

($\because \Delta n = 0$, $\therefore$ volume terms are not needed)

or $$\frac{x}{(0.45-x)} = 0.3317 \ \therefore\ x = 0.112$$

$\therefore$ Mole of CO_2 = Mole of H_2 = $0.45-0.112 = \mathbf{0.338\ mol}$

Mole of CO = Mole of H_2O = **0.112 mol**

(b)

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Initial mole	0.45	0.45	0	0
Mole further added	(0.45 + 0.34)	(0.45 + 0.34)	0	0
Mole at new equilibrium	(0.79 − x)	(0.79 − x)	(1 + x)	(1 + x)

$$\therefore \quad K_C = \frac{x^2}{(0.79-x)^2} = 0.11 \ \therefore\ x = 0.197$$

$\therefore$ Mole of CO_2 = Mole of H_2 = $0.79-0.197 = \mathbf{0.593\ mol}$

Mole of CO = Mole of H_2O = **0.197 mol**

32.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

Mole at $t=0$	1	1	1	1
Mole at equilibrium	$(1-x)$	$(1-x)$	x	x

$$\therefore \quad K_C = \frac{\left(\frac{1+x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{(1+x)^2}{(1-x)^2}$$

$$\therefore \quad \frac{(1+x)^2}{(1-x)^2} = 16 \qquad (\because K_C = 16)$$

$$\therefore \quad \frac{(1+x)}{(1-x)} = 4 \text{ or } x = \frac{3}{5} = 0.6$$

$\because$ Volume = 1 litre

$$\therefore \quad [SO_2] = [NO_2] = 1-x = 1-0.6 = \mathbf{0.4\ mol\ litre^{-1}}$$

$$[SO_3] = [NO] = 1+x = 1+0.6 = \mathbf{1.6\ mol\ litre^{-1}}$$

33.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_C = 100 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad ...(1)$$

(a) $\because$ $[SO_3] = [SO_2]$

By Eq. (1), $$100 = \frac{1}{[O_2]} \text{ or } [O_2] = \frac{1}{100}$$

or $$\frac{\text{mole of } O_2}{\text{volume}} = \frac{1}{100} \qquad (\because V = 10 \text{ litre})$$

$$\therefore \quad \text{Mole of } O_2 = \frac{1}{100}\times 10 = \mathbf{0.1}$$

(b) $$[SO_3] = 2[SO_2]$$

By Eq. (1), $$100 = \frac{4}{[O_2]} \text{ or } [O_2] = \frac{4}{100}$$

$$\therefore \quad \text{Mole of } O_2 = \frac{4}{100}\times 10 = \mathbf{0.4}$$

34. For equilibrium mixture, $PV = \frac{w}{m}RT$

$$\therefore \quad \text{Molar mass}_{\text{mixture}} = \frac{wRT}{VP}$$

$\because$ $\frac{w}{V} = 0.925\ g/L$, $T = 900$ K, $P = 1$ atm, $R = 0.0821$

$$\text{Molar mass}_{\text{mixture}} = \frac{0.925\times 0.0821\times 900}{1} = 68.35$$

Experimental molar mass of SO_3 = 68.35

Normal molar mass of SO_3 = 80

$\because$

$$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$$

Mole before equilibrium	1	0	0
Mole at equilibrium	$(1-\alpha)$	α	$\alpha/2$

where α is degree of dissociation.

$$\frac{1}{\text{Normal molar mass}} \propto$$

No. of particles before dissociation, *i.e.*, 1

$$\frac{1}{\text{Apparent molar mass}} \propto$$

No. of particles after dissociation, *i.e.*, $1+(\alpha/2)$

$$\therefore \quad \frac{\text{Normal molar mass}}{\text{Apparent molar mass}} = 1+\frac{\alpha}{2} \ \therefore\ 1+\frac{\alpha}{2} = \frac{80}{68.35}$$

$$\alpha = \mathbf{0.3408} \quad \text{or} \quad \mathbf{34.08\%}$$

35. Consider the reaction,

$$2SO_3 \rightleftharpoons 2SO_2 + O_2; \quad K_P = \frac{1}{900}\text{atm}$$

Initial pressure	1	0	2
Pressures left at equilibrium	$(1-x)$	x	$2+\frac{x}{2}$

$$\therefore \quad K_P = \frac{(P'_{SO_2})^2(P'_{O_2})}{(P'_{SO_3})^2}$$

$$\frac{1}{900}=\frac{x^2\left(2+\frac{x}{2}\right)}{(1-x)^2}$$

$\therefore$ Since, K_P of this reaction is small and thus, $x<<<1$,

$\therefore$ x^3 is negligible

$$\therefore \quad \frac{1}{900}=\frac{x^2(2)}{(1-x)^2}=\frac{2x^2}{(1-x)^2} \quad \therefore \quad \frac{1}{30}=\frac{\sqrt{2x}}{(1-x)} \quad \therefore \quad x=0.0236$$

At equilibrium $\therefore$ $P'_{SO_3}=1-x=1-0.0236=\mathbf{0.9764\ atm}$

$$P'_{SO_2}=x=\mathbf{0.0236\ atm}$$

$$P'_{O_2}=2+\frac{x}{2}=\mathbf{2.0118\ atm}$$

36.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_2(g)$$

Mole at equilibrium: 0.5 | 0.12 | 5.0

Volume = 1 litre

(a) $$K_C=\frac{[SO_3]^2}{[SO_2]^2[O_2]}=\frac{(5)^2}{(0.5)^2(0.12)}$$

$$K_C=\mathbf{833.33\ mol\ litre^1}$$

(b) $$K_P=K_C\ (RT)^{\Delta n}=833.33\times(0.0821\times 873)^{-1}$$

$$=\mathbf{11.62\ (atm)^{-1}}$$

(c) Now O_2 is forced into the vessel in order to increase the concentration of SO_3 to 5.2 mole litre^{-1}.

Let a mole of O_2 be introduced in it to increase SO_3 to 5.2 mole. Thus, 0.2 mole of SO_2 and 0.1 mole of O_2 will be consumed to show forward reaction.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

At 1 equilibrium: 0.5 | 0.12 | 5

New equilibrium: $(0.5-0.2)$ | $(0.12+a-0.1)$ | 5.2

$$\therefore \quad 833.33=\frac{(5.2)^2}{(0.02+a)(0.3)^2} \quad \therefore \quad a=\mathbf{0.34\ mol}$$

37.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Mole before equilibrium: a | 0

Mole at equilibrium: $(a-x)$ | $2x$

Given that original volume $=\frac{75}{100}\times$ existing volume at equilibrium

Since, mole $\propto$ volume (at constant P and T)

$\therefore$ Initial mole $=\frac{75}{100}\times$ mole at equilibrium

$$a=\frac{75}{100}(a+x)$$

$\therefore$ $$x=\frac{25}{75}a=0.33a$$

Now, % decomposition $(\alpha)=\frac{x}{a}=\frac{0.33a}{a}=\mathbf{0.33\ or\ 33\%}$

38.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Mole before equilibrium: 1 | 0

Mole at equilibrium: $(1-x)$ | $2x$

$$K_P=\frac{4x^2}{(1-x)}\times\left[\frac{P}{\Sigma n}\right]^{\Delta n}$$

$$640=\frac{4x^2}{(1-x)}\frac{160}{(1+x)}$$

$$4=\frac{4x^2}{1-x^2} \quad \text{or} \quad 1-x^2=x^2 \quad \text{or} \quad 2x^2=1$$

$\therefore$ $x^2=1/2$ or $x=0.707=70.7\%$

Also, $$640=\frac{4\times(0.5)^2}{0.5}\times\frac{P}{1.5} \qquad (\text{if } x=0.5)$$

$$P=\mathbf{480\ mm}$$

39.

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \left[\because P\propto 0.1 \quad \therefore 1\propto 0.1\right]$$

0.1 | 0

$(0.1-\alpha)$ | 2α

$$\left[\begin{matrix}\text{If } V \text{ and } T\\ \text{are constant}\end{matrix}\right) \quad P\propto 0.1+\alpha \quad P=[(0.1+\alpha)/0.1]\Bigg]$$

$$K_P=\frac{(2\alpha)^2}{(0.1-\alpha)}\times\left[\frac{P}{0.1+a}\right]^1 \quad \text{or} \quad K_P=\frac{40\alpha^2}{(0.1-\alpha)}$$

or $$\frac{40\alpha^2}{(0.1-\alpha)}=0.14$$

$\therefore$ $$\alpha=0.017$$

$\therefore$ $$NO_2=0.017\times 2=\mathbf{0.034\ mol}$$

40.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial mole: 1 | 0

Mole at equilibrium: $(1-0.310)=0.69$ | $(2\times 0.310)=0.62$ (Given $\alpha=0.31$)

$\therefore$ Total mole at equilibrium $= 0.69 + 0.62 = 1.31$

$$\because \quad K_P=\frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n}=\frac{(0.62)^2}{(0.69)}\times\left(\frac{1}{1.31}\right)^1$$

$(\because \Delta n=1,\ P=1\text{ atm})$

$=0.425$atm

For dissociation at 10 atm pressure at 40°C

$$N_2O_4 \rightleftharpoons 2NO_2$$

1 | 0

$(1-\alpha)$ | 2α (α is degree of dissociation)

$$K_P=\frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n}=\frac{4\alpha^2}{(1-\alpha)}\left(\frac{10}{1+\alpha}\right)$$

or $$0.425=\frac{4\alpha^2\times 10}{(1-\alpha^2)}$$

$$\alpha=\mathbf{10.25\%}$$

41.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Mole before equilibrium: 1 | 0 (Let α be degree of dissociation)

Mole after equilibrium: $(1-\alpha)$ | 2α

$\therefore$ Total mole at equilibrium $= 1+\alpha = 1+0.66 = 1.66$

$(\because \alpha = 0.66)$

1 mole of N_2O_4 is taken, mole at equilibrium = 1.66

$\frac{10}{92}$ mole of N_2O_4 is taken, mole at equilibrium

$$=\frac{1.66\times 10}{92}=0.18$$

$\because$ $$PV=\frac{w}{m}RT$$

$$1\times V=0.18\times 0.0821\times 340$$

$\therefore$ $$V=5.02\text{ litre}$$

Thus, volume of 10 g N_2O_4 under above condition is **5.02 litre.**

42.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Mole before equilibrium: 1, 0
Mole at equilibrium: $1-\alpha$, 2α
where α is degree of dissociation = 0.503

$$K_P = \frac{(n_{NO_2})^2}{(n_{N_2O_4})} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n} = \frac{(2\alpha)^2}{(1-\alpha)}\left(\frac{P}{(1+\alpha)}\right)^1$$

$$K_P = \frac{4\alpha^2 P}{1-\alpha^2} = \frac{4\times(0.503)^2\times 1}{1-(0.503)^2} = 1.355$$

Now, $N_2O_4 \rightleftharpoons 2NO_2$ (at pressure P)

$1 \quad 0$

$(1-x) \quad 2x$

Given, $\frac{N_2O_4}{NO_2} = \frac{1-x}{2x} = \frac{1}{8}$ $\left(\therefore x = \frac{8}{10} = 0.8\right)$

Using again at pressure P

$$\therefore \quad K_P = \frac{4x^2\times P}{1-x^2}$$

$$1.355 = \frac{4\times(0.8)^2\times P}{1-(0.8)^2}$$

$$P = \mathbf{0.19\ atm}$$

43.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Pressure at equilibrium: 0.28, 1.1

$$\therefore \quad K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.1)^2}{0.28} = 4.32\text{atm}$$

Now if volume of container is doubled, *i.e.*, pressure decreases and will become half, the reaction will proceed in the direction where the reaction shows an increase in mole, *i.e.*, decomposition of N_2O_4 is favoured.

$$N_2O_4 \rightleftharpoons 2NO_2$$

New pressure at equilibrium: $\left(\frac{0.28}{2}-P\right)$, $\left(\frac{1.1}{2}+2P\right)$

where reactant N_2O_4 equivalent to pressure P is used up in doing so.

Again, $$K_P = \frac{\left[\frac{1.1}{2}+2P\right]^2}{\left[\frac{0.28}{2}-P\right]} = \frac{[0.55+2P]^2}{[0.14-P]} = 4.32$$

$$P = \mathbf{0.045}$$

$\therefore$ Now, $P_{N_2O_4} = 0.14-0.045 = \mathbf{0.095\ atm}$

P_{NO_2} at new eq. $= 0.55+2\times 0.045$

$$P_{NO_2} = \mathbf{0.64\ atm}$$

44.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Pressure at equilibrium: 0.7, 0.3

$$\therefore \quad K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{0.3\times 0.3}{0.7} = 0.1286\ \text{atm}$$

Now assume decomposition at 10 atm pressure

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial mole: 1, 0
Mole at equilibrium: $(1-x)$, $2x$

$$K_P = \frac{(n_{NO_2})^2}{n_{N_2O_4}} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n} = \frac{(2x)^2}{(1-x)} \times \left[\frac{10}{(1+x)}\right]^1$$

or $$0.1286 = \frac{4x^2\times 10}{(1-x^2)}$$

$$\therefore \quad x = 0.0565$$

$$\therefore \quad P'_{NO_2} = \frac{2x}{(1+x)} \times P = \frac{2\times 0.0565\times 10}{(1+0.0565)} = \mathbf{1.07\ atm}$$

$$P'_{N_2O_4} = \left[\frac{1-0.0565}{1+0.0565}\right]\times 10 = \mathbf{8.93\ atm}$$

45.

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.06)^2}{0.750\times 0.98} = 4.90\times 10^{-3}$$

if $V = 0.750+2.250 = 3$ litre, *i.e.*, volume increases and the reaction will proceed in forward reaction, *i.e.*,

$$N_2O_4 \rightleftharpoons 2NO_2$$

$(0.98-x) \quad (0.06+2x)$

$$\therefore \quad 4.90\times 10^{-3} = \frac{(0.06+2x)^2}{3\times(0.98-x)} \quad \text{or} \quad x = 0.029$$

$$\therefore \quad [N_2O_4] = \frac{0.98-0.029}{3} = \mathbf{0.317\ mol\ litre^{-1}}$$

$$[NO_2] = \frac{0.06+0.029\times 2}{3} = \mathbf{0.039\ mol\ litre^{-1}}$$

46.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial mole: 1, 0, 0
Mole at equilibrium: $1-\alpha$, α, α
where α is degree of dissociation

$$\therefore \quad P'_{Cl_2} = \left[\frac{\alpha}{1+\alpha}\right]\times P; \quad P'_{PCl_3} = \left[\frac{\alpha}{1+\alpha}\right]\times P;$$

$$P'_{PCl_5} = \left[\frac{1-\alpha}{1+\alpha}\right]\times P$$

$$\therefore \quad K_P = \frac{P'_{PCl_3}\times P'_{Cl_2}}{P'_{PCl_5}} = \frac{\left[\frac{\alpha\times P}{1+\alpha}\right]\left[\frac{\alpha\times P}{1+\alpha}\right]}{\left[\frac{1-\alpha}{1+\alpha}\right]\times P}$$

$$K_P = \frac{\alpha^2 P}{1-\alpha^2}$$

$$\therefore \quad \alpha = \sqrt{\left(\frac{K_P}{P+K_P}\right)} \qquad \textbf{Hence proved.}$$

47.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial mole: a, 0, 0
Mole at equilibrium: $(a-0.1)$, 0.1, 0.1

$$\therefore \quad K_C = \frac{\frac{0.1}{1}\times\frac{0.1}{1}}{\frac{a-0.1}{1}} \qquad (\because \text{volume is 1 litre})$$

or $$0.0414 = \frac{0.01}{(a-0.1)}$$

$$\therefore \quad a = \mathbf{0.3415\ mol}$$

48.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Mole before dissociation: 0.1, 0, 0
Mole after dissociation: $(0.1-x)$, x, x

Given, volume of container = 8 litre

Now, $$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{8}\cdot\frac{x}{8}}{\frac{(0.1-x)}{8}} = \frac{x^2}{8(0.1-x)} \quad \ldots(1)$$

Also, $PV = nRT$ for the equilibrium mixture at 540 K.

$$1\times 8 = (0.1+x)\times 0.082\times 540$$

$$\therefore \quad x = 0.08$$

Thus, from Eqs. (1) and (2), ...(2)

$$K_C = \frac{0.08\times 0.08}{8(0.1-0.08)} = 4\times 10^{-2} \text{ mol litre}^{-1}$$

Also, $K_P = K_C (RT)^{\Delta n}$; $\Delta n = +1$

$$= 4\times 10^{-2}(0.082\times 540) = \mathbf{1.77 \text{ atm}}$$

49.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Mole before dissociation	1	0	0
Mole after dissociation	$1-\alpha$	α	α

Given, $\alpha = 0.1$ at 4 atm pressure

$$\therefore \quad K_P = \frac{n_{PCl_3}\times n_{Cl_2}}{n_{PCl_5}} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n}$$

$$= \frac{\alpha\cdot\alpha}{(1-\alpha)}\left[\frac{P}{1+\alpha}\right]^1 = \frac{P\alpha^2}{1-\alpha^2} = \frac{4\times(0.1)^2}{1-(0.1)^2}$$

$$K_P = 0.040 \text{ atm}$$

Again when α is desired at 0.2, K_P remains constant and thus,

$$K_P = \frac{P\alpha^2}{1-\alpha^2}$$

$$0.040 = \frac{P\times(0.2)^2}{1-(0.2)^2}$$

$$\therefore \quad \mathbf{P = 0.96 \text{ atm}}$$

50.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial mole	1	0	0
Mole at equilibrium	(1 – 0.4)	0.4	0.4

Total mole at equilibrium $= 1 - 0.4 + 0.4 + 0.4 = 1.4$

$$\frac{\text{Normal } m_{PCl_5}}{\text{Observed } m_{PCl_5}} = 1+\alpha = 1.4$$

$$\therefore \quad \text{Observed } m_{PCl_5} = \frac{208.5}{1.4}$$

From $PV = \frac{w}{m}RT$ at equilibrium

$$\frac{w}{V} = \frac{Pm}{RT} = \frac{1\times 208.5}{1.4\times 0.0821\times 400} = \mathbf{4.53 \text{ g/litre}}$$

51.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5$$

Initially $\quad 2\,M \quad 1\,M \quad 4\,M$

$$\therefore \quad K_C = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{4}{2\times 1} = 2$$

Now 2 mole of Cl_2 in 2 litre container are added, *i.e.*, $[Cl_2]$ is increased by 1 M, which will direct the reaction is forward. Thus,

$$\underset{2\,M}{PCl_3} + \underset{1\,M+1\,M}{Cl_2} \rightleftharpoons \underset{4\,M}{PCl_5}$$

$$\underset{(2-a)}{} \qquad \underset{(2-a)}{} \qquad \underset{(4+a)}{}$$

or $$K_C = \frac{(4+a)}{(2-a)^2}$$

or $$2 = \frac{4+a}{(2-a)^2} \quad \therefore \ a = 0.5$$

Thus, new concentrations of reactants and products at equilibrium are

$$[PCl_3] = \mathbf{1.5\,M}; \quad [Cl_2] = \mathbf{1.5\,M}; \quad [PCl_5] = \mathbf{4.5\,M}$$

(ii) If the initial equilibrium mixture is transferred in 4 litre vessel then,

$$PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$$

Conc. in 2 litre vessel	2	1	4
Conc. in 4 litre vessel	$\frac{2}{2}$	$\frac{1}{2}$	$\frac{4}{2}$ (Initial volume is doubled)
	=1	$\frac{1}{2}$	2

This will cause an decrease in pressure and thus, equilibrium will shift in backward direction, *i.e.*, new equilibrium conc.

$$\underset{(1+x)}{} \qquad \underset{\left(\frac{1}{2}+x\right)}{} \qquad \underset{(2-x)}{}$$

$$\therefore \quad K_C = 2 = \frac{2-x}{(1+x)\left(\frac{1}{2}+x\right)}$$

or $$2\left(\frac{1}{2}+x^2+\frac{3}{2}x\right) = 2-x \quad \text{or} \quad 2x^2+4x-1=0$$

$$\therefore \quad x = \frac{-4\pm\sqrt{16-4\times(2)\times(-1)}}{2\times 2}$$

$$\therefore \quad x = 0.225\,M$$

$$\therefore \quad [PCl_5] = 2-0.225 = \mathbf{1.775\,M}$$

$$[Cl_2] = 0.5+0.225 = \mathbf{0.725\,M}$$

$$[PCl_3] = 1+0.225 = \mathbf{1.225\,M}$$

52.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Mole before dissociation	1	0	0
Mole after dissociation	$1-\alpha$	α	α

Since, $\frac{1}{\text{Normal molar mass}} \propto$ Particles before dissociation

$$\frac{1}{\text{Exp. molar mass}} \propto \text{Particles after dissociation}$$

$$\therefore \quad \frac{\text{Normal molar mass}}{\text{Exp. molar mass}} = \frac{\text{Particles after dissociation}}{\text{Particles before dissociation}}$$

$$= 1+\alpha$$

$\because$ Exp. molar mass = 62 × molar mass of H_2 = 62 × 2

$$\frac{208.5}{62\times 2} = 1+\alpha \quad \therefore \quad \alpha = \mathbf{0.6815 \text{ or } 68.15\%}$$

53.

$$N_2 + \left[PCl_5 \rightleftharpoons PCl_3 + Cl_2\right]$$

Mole at $t = 0$	1	3	0	0
Mole at equilibrium	1	$(3-x)$	x	x

$\therefore$ Total mole present at equilibrium $= 4+x$

Given, total pressure at equilibrium = 2.05

Now, $PV = nRT$ (at equilibrium)

$$2.05\times 100 = (4+x)\times 0.0821\times 500$$

$$\therefore \quad x = 0.9939$$

Now degree of dissociation for $PCl_5 = \frac{\text{Mole dissociated}}{\text{Total mole}}$

$$= \frac{0.9939}{3} = \mathbf{0.3313} \text{ or } \mathbf{33.13\%}$$

$$\therefore \quad K_P = \left[\frac{n_{PCl_3}\times n_{Cl_2}}{n_{PCl_5}}\right]\times\left[\frac{P}{\Sigma n}\right]^{+1} = \frac{x^2}{(3-x)}\times\left[\frac{2.05}{4+x}\right]$$

$$= \frac{(0.9939)^2}{(3-0.9939)}\times\left[\frac{2.05}{4+0.9939}\right]$$

$$K_P = \mathbf{0.20}$$

54. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Mole at $t=0$	1	3	0
Mole at equilibrium	$(1-x)$	$(3-3x)$	$2x$

$$\therefore \quad K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3} = \frac{4x^2V^2}{(1-x)(3-3x)^3} \quad ...(1)$$

Now, given $x = \frac{0.25}{100}$ and $V = 4$ litre

$\therefore$ By Eq. (1), $K_C = \mathbf{1.49\times10^{-5}\ litre^2\ mol^{-2}}$

Now for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$; $K_{C_1} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

$\therefore$ $K_{C_1} = \sqrt{(K_C)} = \mathbf{3.86\times10^{-3}\ litre\ mol^{-1}}$

55. $2NH_3 \rightleftharpoons N_2 + 3H_2$

Initial Mole	a	0	0
Mole at equilibrium	$(a-2x)$	x	$3x$

Initial pressure of NH_3 of a mole = 15 atm at 27°C

The pressure of a mole of NH_3 = P atm at 347°C

$$\therefore \quad \frac{15}{300} = \frac{P}{620} \quad \therefore \quad P = 31 \text{ atm}$$

At constant volume and at 347°C mole $\propto$ pressure

$a \propto 31$ (Before equilibrium)

$a + 2x \propto 50$ (After equilibrium)

$$\therefore \quad \frac{a+2x}{a} = \frac{50}{31} \quad \therefore \quad x = \frac{19}{62}a$$

$\therefore$ % of NH_3 decomposed $= \frac{2x}{a}\times100$

$$= \frac{2\times19a}{62\times a}\times100 = \mathbf{61.3\%}$$

56. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Mole before dissociation	1	3	0
Mole at equilibrium	$(1-x)$	$(3-3x)$	$2x$

$\therefore$ Total mole at equilibrium $= 4-2x$

and mole of NH_3 at equilibrium $= 2x$

$\because$ % of NH_3 in mixture = 17.8

$$\therefore \quad \frac{2x}{4-2x} = \frac{17.8}{100} \quad \therefore \quad x = 0.302$$

Now, $K_P = \frac{(n_{NH_3})^2}{n_{N_2}\times(n_{H_2})^3}\times\left(\frac{P}{\Sigma n}\right)^{\Delta n}$

$$= \frac{4x^2}{(1-x)(3-3x)^3}\times\left(\frac{P}{4-2x}\right)^{-2} = \frac{4x^2(4-2x)^2}{P^2(1-x)(3-3x)^3}$$

Now, $P = 30$ atm and $x = 0.302$

$\therefore$ $K_P = \mathbf{7.29\times10^{-4}\ atm^{-2}}$

57. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Mole before reaction	1	3	0
Mole at equilibrium	$1-x$	$(3-3x)$	$2x$

Given, mole fraction of NH_3 = 0.012 at P = 10atm

$$\therefore \quad \frac{2x}{(4-2x)} = 0.012$$

$$\therefore \quad x = 0.0237$$

$$\therefore \quad K_P = \frac{(P'_{NH_3})}{(P'_{N_2})\times(P'_{H_2})^3} = \frac{\left[\frac{2x\cdot P}{(4-2x)}\right]^2}{\frac{(1-x)\cdot P}{(4-2x)}\left[\frac{(3-3x)P}{(4-2x)}\right]^3}$$

$$K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3P^2} \quad ...(1)$$

$$= \frac{4(0.0237)^2[4-2(0.0237)]^2}{(1-0.0237)[3-3(0.0237)]^3\times100}$$

$$K_P = \mathbf{1.431\times10^{-5}\ atm^{-2}}$$

Let mole % of NH_3 in equilibrium mixture be increased to 10.4 at pressure P.

$$\therefore \quad \frac{2x}{4-2x} = \frac{10.4}{100} \quad \text{or} \quad x = 0.1884$$

Now again using Eq. (1), $K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3\cdot P^2}$

$$1.431\times10^{-5} = \frac{[4\times(0.1884)^2][4-2(0.1884)]^2}{[1-0.1884][3-3(0.1884)]^3\times P^2}$$

$$P = \mathbf{105.41\ atm}$$

58. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Mole before equilibrium	1	3	0
Mole after equilibrium	$(1-x)$	$3(1-x)$	$2x$

$$\therefore \quad K_P = \frac{(2x)^2(4-2x)^2}{(1-x)[3(1-x)]^3\times P^2}$$

$$K_P = \frac{16\times x^2\times(2-x)^2}{27(1-x)^4\times P^2}$$

$$\text{or} \quad 1.6\times10^{-5} = \frac{16x^2(2-x)^2}{27(1-x)^4\times(200)^2}$$

$$\therefore \quad \frac{x^2(2-x)^2}{(1-x)^4} = \frac{1.6\times10^{-5}\times27\times(200)^2}{16}$$

$$= \frac{16\times10^{-6}\times27\times(200)^2}{16}$$

$$\therefore \quad \frac{x(2-x)}{(1-x)^2} = 200\times10^{-3}\times\sqrt{27} = 1.039$$

$$\therefore \quad x = 0.301$$

$\therefore$ Mole of NH_3 formed $= 2\times0.301 = 0.602$

Total mole at equilibrium $= 4-2\times0.301 = 3.398$

% of NH_3 at equilibrium $= \frac{0.602}{3.398}\times100 = \mathbf{17.76\%}$

59. $2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$

Mole at equilibrium	1.27	2.78×10^{-6}	1.58

Volume of container = 180 litre

$$K_C = \frac{[H_2S]^2}{[H_2]^2[S_2]} = \frac{\left(\frac{1.58}{180}\right)^2}{\left(\frac{1.27}{180}\right)^2\left(\frac{2.78\times10^{-6}}{180}\right)}$$

$$= \frac{(1.58)^2 \times 180}{(1.27)^2 \times (2.78\times10^{-6})}$$

$$K_C = \mathbf{1.002\times10^8\ litre\ mol^{-1}}$$

60.

	$2H_2S(g)$	$\rightleftharpoons 2H_2(g)$	$+ S_2(g)$
Mole before dissociation	1	0	0
Mole after dissociation	$(1-\alpha)$	α	$\frac{\alpha}{2}$

Where α is degree of dissociation of H_2S

Volume of container = 1.10 litre

$$\therefore \quad K_C = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left[\frac{\alpha}{1.1}\right]^2\left[\frac{\alpha}{2\times1.1}\right]}{\left[\frac{1-\alpha}{1.1}\right]^2} = 1\times10^{-6}$$

Assuming $1-\alpha \approx 1$ since α is small because $K_C \approx 10^{-6}$

$$\therefore \quad \frac{\alpha^3}{2(1.1)} = 10^{-6}$$

$$\alpha = 1.3\times10^{-2} = \mathbf{1.3\%}$$

61.

	$H_2(g)$	$+ S(s)$	$\rightleftharpoons H_2S(g)$
Mole before reaction	0.2	1.0	0
Mole at equilibrium	$(0.2-x)$	$(1-x)$	x

Thus, $K = \frac{[H_2S]}{[H_2]}$ or $6.8\times10^{-2} = \frac{x}{(0.2-x)}$

$$\therefore \quad x = 0.013$$

Now, $P_{H_2S} = \frac{0.013\times0.0821\times363}{1}$ $\left[\text{from } P = \frac{nRT}{V}\right]$

$$P_{H_2S} = \mathbf{0.387\ atm}$$

62. **2%**

63. Volume of air $= 10\times10^6\ m^3 = 10\times10^6\times10^3$ litre $= 10^{10}$ litre

Volume of $O_2 = 20\%$ air $= \frac{20\times10^{10}}{100} = 20\times10^8$ litre

$$\therefore \quad n_{O_2} = \frac{PV}{RT} = \frac{720}{760}\times\frac{20\times10^8}{0.0821\times298} = 7.74\times10^7$$

Now, $K_P = \frac{(n_{O_2})^3}{(n_{O_3})^2}\times\frac{P}{\Sigma n}$

$$\because \quad n_{O_2} >> n_{O_3} : K_P = 1.3\times10^{57}$$

$$\therefore \quad \Sigma n = n_{O_2} = \frac{(n_{O_2})^3\times720}{(n_{O_3})^2\times760\times n_{O_2}}$$

$$\therefore \quad (n_{O_3})^2 = \frac{(n_{O_2})^2\times720}{760\times K_P} = \frac{(7.74\times10^7)^2\times720}{760\times1.3\times10^{57}}$$

$$\therefore \quad n_{O_3} = 2.09\times10^{-21}$$

$$\therefore \text{ molecules of } O_3 = 2.09\times10^{-21}\times6.023\times10^{23}$$

$$= \mathbf{12.58\times10^2}$$

64.

	$I_2(g)$	$\rightleftharpoons 2I(g)$
Initial pressure	0.074	0
Final pressure	$(0.074-P)$	$2P$

where I_2 equivalent to pressure P dissociates

$\therefore$ $0.074 - P + 2P = 0.112$ or $P = 0.112 - 0.074 = 0.038$

Now, $K_P = \frac{(P_I')^2}{P_{I_2}'} = \frac{(2\times0.038)^2}{(0.074-0.038)} = \mathbf{0.160\ atm}$

65.

	$S_8(g)$	$\rightleftharpoons 4S_2(g)$
Initial pressure	1	0
Pressure of equilibrium	$(1-0.29)$	(4×0.29)
	0.71	4×0.29

$\because$ Pressure of S_8 reduces by 0.29 atm

Now, $K_P = \frac{[P_{S_2}']^4}{[P_{S_8}']} = \frac{[4\times0.29]^4}{0.71} = \mathbf{2.55\ (atm)^3}$

NOTE : It would have been better, if the physical state of S_2 have also been reported as gaseous state.

66.

	$CO(g)$	$+ 2H_2(g)$	$\rightleftharpoons CH_3OH(g)$
Initial mole	0.2	a	0
Mole at equilibrium	$(0.2-0.1)$	$(a-0.2)$	0.1

Now total mole at equilibrium are $= 0.1 + a - 0.2 + 0.1 = a$

Also, mole $(n) = \frac{PV}{RT} = \frac{4.92\times5}{0.0821\times600} = 0.499$

$$\therefore \quad a = 0.499$$

$$\therefore \quad [CH_3OH] = \frac{0.1}{5};\ [CO] = \frac{0.2-0.1}{5} = \frac{0.1}{5};$$

$$[H_2] = \frac{0.499-0.20}{5} = \frac{0.299}{5}$$

$$\because \quad K_C = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.1/5}{0.1/5\times(0.299/5)^2}$$

$$= 279.64\ \text{litre}^2\ \text{mol}^{-2}$$

$$K_C = \mathbf{279.64\ litre^2\ mol^{-2}}$$

$$K_P = K_C(RT)^{\Delta n} = 279.64\times(0.0821\times600)^{-2}$$

$$K_P = \mathbf{0.115\ atm^{-2}}$$

67. (i) Given,

	$CO(g)$	$+ 2H_2(g)$	$\rightleftharpoons CH_3OH(g)$
Mole before reaction	0.15	a	0
Mole after reaction	$(0.15-x)$	$(a-2x)$	x
and			$x = 0.08$

Total mole at equilibrium $= 0.15 - x + a - 2x + x$

$$= 0.15 + a - 2x$$

$$= 0.15 + a - 0.16 = a - 0.01$$

Also total mole at equilibrium are obtained by $n = \frac{PV}{RT}$

$$n = \frac{8.5\times2.5}{0.0821\times750} \quad \left.\begin{array}{l} \because \ P = 8.5\text{atm} \\ V = 2.5\text{lit.} \\ T = 750\text{K} \end{array}\right\} \text{at equilibrium}$$

$$\therefore \quad n = 0.345$$

$$\therefore \quad a - 0.01 = 0.345$$

$$\therefore \quad a = 0.355$$

At equilibrium : Mole of $CO = 0.15 - 0.08 = 0.07$

Mole of $H_2 = 0.355 - 0.16 = 0.195$

Mole of $CH_3OH = 0.08$

$$\therefore \quad K_C = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.08/2.5}{\left(\frac{0.07}{2.5}\right)\left(\frac{0.195}{2.5}\right)^2}$$

$$= \mathbf{187.85\ mol^{-2}\ litre^2}$$

Also $K_P = K_C (RT)^{\Delta n}$

$= 187.85 \times (0.0821 \times 750)^{-2} = \mathbf{0.05\ atm^{-2}}$

(ii) If reaction does not take place, then

Mole of CO = 0.15

Mole of H_2 = 0.355

$\therefore$ Total mole = 0.505 $\therefore$ $P \times 2.5 = 0.505 \times 0.0821 \times 750$

$\therefore$ $P = \mathbf{12.438\ atm}$

68. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

Pressure at $t = 0$	0.02		
Pressure at eq.	$\frac{0.02 \times 99}{100}$	P	$\frac{0.02 \times 1}{100}$

$\because$ $K_P = \dfrac{[P_{NOCl}]^2}{[P_{NO}]^2 [P_{Cl_2}]} = \dfrac{(0.02 \times 0.01)^2}{(0.99 \times 0.02)^2 \times P} = 1 \times 10^{-3}$

$\therefore$ $P = 0.102$ atm

For Cl_2 in vessel, using $PV = nRT$

$0.102 \times V = n \times R \times T$ ...(i)

For a gas in vessel, $1 \times V = 9.2 \times R \times T$ ...(ii)

By Eqs. (i) and (ii),

$\therefore$ mole of Cl_2 (n) at equilibrium = 0.0204

2 atm of NO reacts with 1 atm of Cl_2 (If V, T are constant)

$\frac{0.02 \times 1\text{atm}}{100}$ NO react with $\frac{0.02 \times 1}{2 \times 100} = 0.0001\text{atm}\ Cl_2$

Thus, $0.0001 \times V = n_{Cl_2\ used} \times RT$ ...(iii)

By Eqs. (ii) and (iii),

$\therefore$ n_{Cl_2} which have reacted = 2×10^{-5} mol

$\therefore$ Total Cl_2 added = $0.0204 + 2 \times 10^{-5} = \mathbf{0.02042\ mol}$

69. van't Hoff isochore is :

$$\log_{10} K = \log_{10} A - \frac{\Delta H}{2.303RT}$$

(i) Thus, intercept = $\log_{10} A = 10$ $\therefore$ $A = \mathbf{10^{10}}$

(ii) Also, slope = $\tan\theta = 0.5 = -\dfrac{\Delta H}{2.303R}$

$\therefore$ $\Delta H = \mathbf{-2.303\ cal\ mol^{-1}}$

(iii) Also, $\log_{10} K = 10 + \dfrac{2.303}{2.303 \times 2 \times 298}$

$\therefore$ $K = \mathbf{1.004 \times 10^{10}}$

(iv) Also, $\log_{10} K = 10 + \dfrac{2.303}{2.303 \times 2 \times 800}$

$\therefore$ $K = \mathbf{1.001 \times 10^{10}}$

70. van't Hoff equation for variation of K_P with temperature can be written as,

$$2.303 \log_{10} \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H[T_2 - T_1]}{R T_1 T_2}$$

$K_{P_1} = 1.6 \times 10^{-4}$; $T_1 = 673$ K, $K_{P_2} = ?$;

$T_2 = 773$ K, $\Delta H = -25.14 \times 10^3$ cal

$\therefore$ $2.303 \log_{10} \dfrac{K_{P_2}}{1.6 \times 10^{-4}} = \dfrac{-25.14 \times 10^3}{2} \left[\dfrac{773 - 673}{773 \times 673}\right]$

$\therefore$ $K_{P_2} = \mathbf{1.462 \times 10^{-5}\ atm^{-2}}$

71. $2.303 \log_{10} \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$2.303 \log_{10} \dfrac{0.0129}{0.0266} = \dfrac{\Delta H}{2}\left[\dfrac{673 - 623}{673 - 623}\right]$

$\therefore$ $\Delta H = -12140$ cal $= \mathbf{-12.140\ kcal}$

72. $2.303 \log_{10} \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$\therefore$ $2.303 \log_{10} \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{42.4 \times 10^3}{2}\left[\dfrac{1405 - 1338}{1405 \times 1338}\right]$

$\therefore$ $\dfrac{K_{P_2}}{K_{P_1}} = 2.129$

$\therefore$ $K_{P_2} = 2.129 \times 0.0118 = \mathbf{0.025\ atm}$

73. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\Delta n = \Sigma n$ products $- \Sigma n$ reactants $= 2 - 4 = -2$

$\because$ $K_P = K_C (RT)^{\Delta n}$

$1.64 \times 10^{-4} = K_C (0.0821 \times 673)^{-2}$

$\therefore$ $K_C = \mathbf{0.5006\ mol^2\ litre^{-2}}$

Now since $\Delta G^\circ = -2.303 RT \log_{10} K$

If $K = K_P$

Then $\Delta G^\circ = -2.303 \times 2 \times 673 \log_{10} (1.64 \times 10^{-4})$

$= \mathbf{+11.733\ kcal}$

If $K = K_C$

Then $\Delta G^\circ = -2.303 \times 2 \times 673 \log_{10} (0.5006) = \mathbf{+931\ cal}$

where ΔG° is the Gibb's energy change when all the reactants and products are in the standard state. For $\Delta G^\circ = -2.303RT \log_{10} K_P$, standard state means the partial pressure of each as 1 atm. When $\Delta G^\circ = -2.303RT \log_{10} K_C$, standard state means that concentration of each is 1 mol litre^{-1}. So the values are different.

74. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium

$-\Delta G^\circ = 2.303 RT \log_{10} K_P$ ...(1)

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Given ΔH° for $NH_3 = -46$ kJ)

and $\Delta S^\circ_{Reaction} = 2 \times S^\circ_{NH_3} - S^\circ_{N_2} - 3 \times S^\circ_{H_2}$

$= 2 \times 192 - 191 - 3 \times 130 = -197$ J

Also, $T = 273 + 25 = 298$ K

Thus, $\Delta G^\circ = -92 \times 10^3 - 298 \times (-197) = -92000 + 58706$

(ΔH° for reaction $= -46 \times 2$ kJ)

$\Delta G^\circ = -33294$ J

Thus, from Eq. (1)

$+33294 = 2.303 \times 298 \times 8.3 \log_{10} K_P$ $\therefore$ $\log_{10} K_P = \mathbf{5.845}$

75. $-\Delta G^\circ = 2.303 RT \log_{10} K_P$

$-(-16.5 \times 10^3) = 2.303 \times 8.314 \times 298 \log_{10} K_P$

$\log_{10} K_P = \dfrac{16500}{2.303 \times 8.314 \times 298}$

$\therefore$ $K_P = \mathbf{779.41\ atm^{-1}}$

Also, K_{P_1} for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$K_{P_1} = (K_P)^2 = (779.41)^2$

$K_{P_1} = 6.07\times10^5$ **atm**$^{-2}$

Also, $-\Delta G_1^\circ = 2.303\times8.314\times298\log_{10}(6.07\times10^5)$ J

$= 32.998$ kJ

$\therefore \quad \Delta G_1^\circ = \mathbf{-32.998\ kJ}$

76. $d\ln K_P = \dfrac{\Delta H^\circ}{RT^2}$

On integration $\ln K_P = -\dfrac{\Delta H}{RT} + C$

or $\log_{10} K_P = -\dfrac{\Delta H^\circ}{2.303RT} + C$

Thus, $\text{slope} = -\dfrac{\Delta H^\circ}{2.303R} = 4.95\times10^3$

$\therefore \quad \Delta H^\circ = -2.303\times8.314\times4.95\times10^3 = \mathbf{-9.48\times10^4}$ **J**

Also, $\Delta S^\circ = S^\circ_{SO_3} - S^\circ_{SO_2} - \dfrac{1}{2}\times S^\circ_{O_2}$

$= 256.8 - 248.2 - \dfrac{1}{2}\times205.1 = -93.95\,\text{JK}^{-1}\text{mol}^{-1}$

$\therefore \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -9.48\times10^4 - 298\times(-93.95) = -6.68\times10^4$

Now, $\Delta G^\circ = -2.303RT\log K_P$

$-6.68\times10^4 = -2.303\times8.314\times298\log K_p$

$K_P = \mathbf{5.1\times10^{11}}$

77. $-\Delta G^\circ = 2.303RT\log_{10}K$, also $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Thus, $-(\Delta H^\circ - T\Delta S^\circ) = 2.303RT\log_{10}K$

or $2.303\log_{10}K = -\dfrac{\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$

78. $\Delta G^\circ = -2.303RT\log K$

$\therefore \quad 33 = -2.303\times8.314\times10^{-3}\times920\log K$

$\therefore \quad K$ at 920 K $= 1.34\times10^{-2}$

Now using, $2.303\log\dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\dfrac{[T_2 - T_1]}{T_1T_2}$

if $K_1 = 1.34\times10^{-2}$ and $K_2 = 1$; $T_1 = 920$ K, then,

$$2.303\log\frac{1}{1.34\times10^{-2}} = \frac{\Delta H}{R}\left[\frac{T_2 - 920}{T_2\times920}\right]$$

$T_2 = \mathbf{1078.5\ K}$

Thus, at any temperature above this temperature K will be greater than 1.

79. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $G^\circ = H^\circ - TS$

$\Delta G^\circ = \Delta G^\circ_B - \Delta G^\circ_A$

$= [25.44\times10^3 - (300\times253.3)] - [24.27\times10^3 - (300\times246.4)]$

$= -50550 + 49650 = -900$ J

$\Delta G^\circ = -2.303RT\log K_P$

$-900 = -2.303\times300\times8.314\log K_P$

$K_P = 1.434$

Also, $K_P = \dfrac{[B]}{[A]} = 1.434$

$\therefore \quad [B] = 1.434$ and total of $[A]$ and $[B] = 1 + 1.434 = 2.434$

$\therefore \quad$ mole % of $[B]$ in mixture $= \dfrac{1.434}{2.434}\times100 = \mathbf{58.92}$

mole % of A in mixture = **41.08**

80.

	Pentyne-1 $\overset{\text{KOH alc.}}{\rightleftharpoons}$	Pentyne-2 +	Pentadiene-1-2
	(*A*)	(*B*)	(*C*)
At eq.	1.3	95.2	3.5

$$K_{eq.} = \frac{[B][C]}{[A]} = \frac{95.2\times3.5}{1.3} = 256.31 \qquad ...(i)$$

Now, for $B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]} \qquad ...(ii)$$

Then from Eqs. (i) and (ii), $K_1 = \dfrac{[C]}{K_{eq.}} = \dfrac{3.5}{256.31} = 0.013$

$\therefore \quad \Delta G^\circ = -2.303RT\log_{10}K$

$= -2.303\times8.314\times448\ \log\ 0.013 = 16178$ J

$= \mathbf{16.178\ kJ}$

Stability order for A and B is $B > A$.

Similarly for $B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_{eq.}[A]}{[B]^2} = \frac{256.31\times1.3}{95.2\times95.2} = 0.037$$

$\therefore \quad \Delta G^\circ = -2.303RT\log_{10}K$

$= 2.303\times8.314\times448\log0.037 = 12282$ J $= \mathbf{12.282\ kJ}$

Thus, stability order for B and C is $B > C$.

The total stability order is $B > C > A$.

$CH_3\cdot CH_2\cdot CH_2\cdot C\equiv CH \xrightarrow{\text{KOH alc.}} [CH_3CH_2CH=C=CH_2] \longrightarrow [CH_3CH_2C\equiv C-CH_3]$

81. (i) $N_2O_4 \rightleftharpoons 2NO_2$; $\quad G^\circ_{N_2O_4} = 100\,\text{kJ mol}^{-1}$

conc. at $t = 0$	5	5	$G^\circ_{NO_2} = 50\,\text{kJ mol}^{-1}$

ΔG° for reaction $= 2\times G^\circ_{NO_2} - G^\circ_{N_2O_4} = 2\times50 - 100 = 0$

Now $\quad \Delta G = \Delta G^\circ + 2.303\ RT\log Q$

$\Delta G = 0 + 2.303\times8.314\times10^{-3}\times298\log\dfrac{5^2}{5} = \mathbf{+3.99\ kJ}$

(ii) Since ΔG is +ve and thus reaction will not proceed in forward direction.

Also for reverse reaction :

$2NO_2 \rightleftharpoons N_2O_4$

Mole at $t = 0$	5	5
Mole at eq.	$(5-2x)$	$(5+x)$

$\therefore \quad \Delta G^\circ = -2.303RT\log K_C$

$\therefore \quad \Delta G^\circ = 0 \quad \therefore \ K_C = 1$ or $1 = \dfrac{5+x}{(5-2x)^2} \quad \therefore \ x = 1.25$

Thus, $[NO_2]_{\text{at eq.}} = 5 - 2.5 = 2.5$ M

$[N_2O_4]_{\text{at eq.}} = 5 + 1.25 = \mathbf{6.25\ M}$

82. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ...(1)

ΔH° for reaction $= \Delta H^\circ_B - \Delta H^\circ_A = 25.44 - (-24.27)$

$= -1.17$ kJ

ΔS° for reaction $= S^\circ_B - S^\circ_A = 252.3 - 246.4$

$= 5.9$ J $= 5.9\times10^{-3}$ kJ

$\therefore \quad \Delta G^\circ_{reaction} = -1.17 - (298 \times 5.9 \times 10^{-3})$

$= -1.17 - 1.76 = -2.93\,kJ$

Now at equilibrium : $\Delta G^\circ = -2.303\,RT \log K_C$

$\therefore \quad -2.93 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_C$

$\therefore \quad K_C = 3.26$

Thus, $\dfrac{[B]}{[A]} = K_C = 3.26$

or the mixture contains $[B]$ and $[A]$ in the ratio **3.26 : 1**

83. **Case I :** $N_2O_4 \rightleftharpoons 2NO_2$

$PV = \dfrac{w}{m}RT$

$\therefore \quad m_{mix} = \dfrac{w}{P \cdot V} \cdot RT = \dfrac{dRT}{P}$

$= 3.62 \times 0.0821 \times 288 = 85.6 \quad \left(\dfrac{w}{V} = \text{g / litre}\right)$

Let a mole of N_2O_4 and $(1-a)$ mole of NO_2 exist at equilibrium

$\therefore \quad a \times 92 + (1-a) \times 46 = 85.6 \qquad \therefore \quad a = 0.86$

$\therefore \quad [n_{N_2O_4}] = 0.86$ mole and $[n_{NO_2}] = 0.14$ mole

$\therefore \quad K_P = \dfrac{0.14 \times 0.14}{0.86} \times \left[\dfrac{1}{1}\right]^1 = 0.028$ atm at 288 K

Case II: $m_{mix} = 1.8 \times 0.0821 \times 348 = 52.57$

Let a' mole of N_2O_4 and $(1-a')$ mole of NO_2 exist at equilibrium.

$\therefore \quad a' \times 92 + (1-a') \times 46 = 52.57 \qquad \therefore \quad a' = 0.14$

$\therefore \quad [n_{N_2O_4}] = 0.14 \quad [n_{NO_2}] = 0.86$

$\therefore \quad K_P = \dfrac{0.86 \times 0.86}{0.14} \times \left[\dfrac{1}{1}\right]^1 = 5.283$ atm at 348 K

Now, $2.303 \log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$\therefore \quad 2.303 \log \dfrac{5.283}{0.0228} = \dfrac{\Delta H}{2}\left[\dfrac{348-288}{348 \times 288}\right]$

$\therefore \quad \Delta H = 18196\,cal = \mathbf{18.196\ kcal}$

Also, $-\Delta G = 2.303\,RT \log K_P$

$\therefore \quad \Delta G = -2.303 \times 2 \times 348 \times \log 5.283 = -1158.7$ cal

$\therefore \quad \Delta S = \dfrac{\Delta H - \Delta G}{T} = \dfrac{18196 + 1158.7}{348} = \mathbf{55.62\ cal}$

84.

	A	+	B	$\rightleftharpoons$	C	+	D
At $t=0$	2		2		0		0
At eq.	$(2-x)$		$(2-x)$		x		x

$K_C = \dfrac{[C][D]}{[A][B]} = \dfrac{[C]^2}{[A]^2} \quad [\because [C] = [D] \text{ and } [A] = [B]]$

Also, $\Delta G^\circ = -2.303\,RT \log K_C$

or $460 = -2.303 \times 2 \times 300 \log \dfrac{[C]^2}{[A]^2}$

or $\log \dfrac{[C]^2}{[A]^2} = -0.3329$ or $\dfrac{[C]^2}{[A]^2} = 0.464$

or $\dfrac{[C]}{[A]} = \mathbf{0.68}$

85. $\Delta G^\circ = -2.303\,RT \log_{10} K_C$

$\therefore \quad 77.77 \times 10^3 = -2.303 \times 8.314 \times 1000 \log_{10} K_C$

$\therefore \quad K_C = 8.67 \times 10^{-5}$

$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$

Initial pressure	0.8	0.2	0
Final pressure	$\left(0.8 - \frac{x}{2}\right)$	$\left(0.2 - \frac{x}{2}\right)$	x

$\therefore \quad 8.67 \times 10^{-5} = \dfrac{x}{\left(0.8 - \frac{x}{2}\right)^{1/2}\left(0.2 - \frac{x}{2}\right)^{1/2}}$

$x = \mathbf{3.47 \times 10^{-5}\ atm}$

86. **At 1000 K :**

	$CO_2(g)$	+	$C(s)$	$\rightleftharpoons$	$2CO(g)$
Mole at $t=0$	$\frac{88}{44} = 2$		$\frac{30}{12} = 2.5$		0
Mole at equilibrium	$(2-a)$		$(2.5-a)$		$2a$

mass of gaseous mixture $= [(2-a) \times 44] + (2a \times 28)$

$= 88 - 44a + 56a = (88 + 12a)$ g

$\therefore \quad$ density of mixture $= \dfrac{88 + 12a}{5} = 18.3$ g / litre

$\therefore \quad 88 + 12a = 5 \times 18.3 \qquad \therefore \quad a = 0.29$

$\therefore$

	$CO_2(g)$	+	$C(s)$	$\rightleftharpoons$	$2CO$
Mole at eq.	$(2 - 0.29) = 1.71$		$(2.5 - 0.29) = 1.71$		$2 \times 0.29 = 0.58$

$K_c = \dfrac{[CO]^2}{[CO_2]} = \dfrac{0.58 \times 0.58}{5 \times 1.71} = 3.93 \times 10^{-2}$

$\therefore \quad K_P = K_c (RT)^{\Delta n} = 3.93 \times 10^{-2} \times (0.0821 \times 1000) \quad (\because \Delta n = 2 - 1 = 1)$

$= \mathbf{3.23\ atm}$

At 1100 K : $\dfrac{88 + 12a'}{5} = 18.9 \quad \therefore \quad a' = 0.54$

$\therefore$

	$CO_2(g)$	+	$C(s)$	$\rightleftharpoons$	$2CO$
Mole at eq.	$(2 - 0.54) = 1.46$		$(2.5 - 0.54) = 1.08$		1.08

$K_c = \dfrac{1.08 \times 1.08}{5 \times 1.46} = 0.16$

$\therefore \quad K_P = 0.16 \times 0.0821 \times 1100 = 14.43$ atm

Also, $2.303 \log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{R}\dfrac{T_2 - T_1}{T_1 T_2}$

$2.303 \log \dfrac{14.43}{3.23} = \dfrac{\Delta H}{2}\left[\dfrac{1100 - 1000}{1100 \times 1000}\right]$

$\therefore \quad \Delta H = 32936\,cal = \mathbf{32.936\ kcal}$

87. $2.303 \log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H^\circ}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

or $2.303[\log K_{P_2} - \log K_{P_1}] = \dfrac{\Delta H^\circ}{2}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$2.303[1.305 - 2.025] = \dfrac{\Delta H^\circ}{2}\left[\dfrac{1218 - 1023}{1218 \times 1023}\right]$

$\therefore \quad \Delta H^\circ = 21190.67\,cal = 21.19$ kcal

$\Delta G^\circ = -2.303\,RT \log_{10} K_P$

$= -2.303 \times 2 \times 1023 \times 2.025$

$= -9541.6$ cal $= -9.5416$ kcal

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-9541.6 = -21190.67 - 1023 \times \Delta S^\circ$

$\Delta S^\circ = \frac{11649}{1023}$

$\Delta S^\circ = \mathbf{+11.38\ cal}$

88.

$$A(g) \rightleftharpoons 2B(g) + 3C(g)$$

Initial pressure	10	0	0
Final pressure	$(10-P)$	$2P$	$3P$

$\because\ 10 - P + 2P + 3P = 15.76\ \therefore\ P = 1.44$

$\therefore\ P'_A = 10 - 1.44 = 8.56$ atm

$P'_B = 2 \times 1.44 = 2.88$ atm

$P'_C = 3 \times 1.44 = 4.32$ atm

$$\therefore\ K_P = \frac{(4.32)^3 \times (2.88)^2}{8.56} = 78.12$$

Also, $\Delta G^\circ = -2.303 RT \log K_P$

$= -2.303 \times 8.314 \times 298 \times \log 78.12 = -10799.8$ J

$= \mathbf{-1.08 \times 10^4\ kJ}$

89.

$$2.303 \log_{10} K_P = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\text{or } 2.303 \log_{10} K_P = \frac{98320}{8.314 \times 300} - \frac{95}{8.314}$$

(Put ΔH° and R in J)

$$\therefore\ K_P = \mathbf{1.44 \times 10^{12}\ atm^{-1/2}}$$

90.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Pressure at equilibrium	P	P

$\therefore$ Total pressure at equilibrium $= 2P = 1.12$ atm

$\therefore\ P = 1.12/2$ atm

$\because\ K_P = P'_{NH_3} \times P'_{H_2S}$

$$\therefore\ K_P = \frac{1.12}{2} \times \frac{1.12}{2} = \mathbf{0.3136\ atm^2}$$

91. For the dissociation equilibrium,

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Pressure before dissociation	0.5	0
Pressure after dissociation	$(0.5+P)$	P

Let pressure equivalent to P atm is developed by NH_3 and H_2S on dissociation of NH_4HS, when 0.5 atm of NH_3 is already present.

$\therefore\ K_P = P'_{NH_3} \times P'_{H_2S} = (0.5+P)P$ or $0.11 = (0.5+P)P$

$\therefore\ P = 0.1653$

$\therefore\ P'_{NH_3} = 0.5 + 0.1653 = \mathbf{0.6653\ atm}$

$P'_{H_2S} = \mathbf{0.1653\ atm}$

92.

$$NH_4CN(s) \rightleftharpoons NH_3(g) + HCN(g)$$

Partial pressure at equilibrium	P	P

$\because$ Total pressure at equilibrium $= 2P = 0.298$ atm

$\therefore\ P = 0.149$ atm

Also, $K_P = P'_{NH_3} \times P'_{HCN} = 0.149 \times 0.149 = \mathbf{0.0222\ atm^2}$

Now dissociation is made when, $P_{NH_3} = 0.25$ atm

$$NH_4CN(s) \rightleftharpoons NH_3(g) + HCN(g)$$

Initial pressure	0.25	0
Pressure at equilibrium	$0.25 + P'$	P'

$\therefore\ K_P = P'(P' + 0.25)$

$\therefore\ 0.0222 = (P')^2 + 0.25P'$

$\therefore\ P' = \mathbf{0.0694\ atm}$

93.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Initial mole	$\frac{3.06}{51}$	0	0
Mole at eq.	$\frac{3.06}{51} \times \frac{70}{100}$	$\frac{3.06}{51} \times \frac{30}{100}$	$\frac{3.06 \times 30}{51 \times 100}$

Given, $V = 2$ litre; $T = 27^\circ$C; $\Delta n = 2 - 0 = 2$

$$K_C = [NH_3][H_2S] = \frac{3.06 \times 30}{51 \times 100 \times 3} \times \frac{3.06 \times 30}{51 \times 100 \times 2}$$

$$= \mathbf{8.1 \times 10^{-5}\ mol^2\ litre^{-2}}$$

Also, $K_P = K_C (RT)^{\Delta n} = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$

$$= \mathbf{4.90 \times 10^{-2}\ atm^2}$$

Addition of more NH_4HS on this equilibrium will cause no effect because concentration of NH_4HS is not involved in formulae of K_P or K_C.

94.

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

Let pressure at equilibrium of CO_2 be P, then

$P_{NH_3} = 2P$ and total pressure at equilibrium $= 3P$

$$\therefore\ K_P = (2P)^2 \times P = 4P^3 \qquad \ldots(1)$$

If NH_3 is added and the pressure of NH_3 after addition at equilibrium is $3P$, *i.e.*, equal to initial pressure.

$$K_P = 4P^3 = (P'_{NH_3})^2 \times P'_{CO_2} = (3P)^2 \times P'_{CO_2}$$

$$\therefore\ P'_{CO_2} = \frac{4}{9}P$$

Thus, Total pressure in II equilibrium is $= 3P + \frac{4}{9}P = \frac{31}{9}P$

$$\frac{\text{Total pressure in II equilibrium}}{\text{Total pressure in I equilibrium}} = \frac{31P/9}{3P} = \mathbf{\frac{31}{27}}$$

95.

$$K_C = \frac{[CO_2]}{[CO]}$$

$$\therefore\ 5 = \frac{[CO_2]}{2.5 \times 10^{-2}}$$

$\therefore\ [CO_2]$ at equilibrium $= 2.5 \times 10^{-2} \times 5$

$$= \mathbf{12.5 \times 10^{-2}\ mol\ litre^{-1}}$$

96.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Gaseous mole before dissociation	-	1	0
Gaseous mole after dissociation	-	$\left(1 - \frac{50}{100}\right)$	$\frac{2 \times 50}{100}$
	-	0.5	1

$\therefore$ Total mole $= 1.5$ and $\Delta n = 1$

Total pressure given at equilibrium $= 12$ atm

$$K_P = \frac{(n_{CO})^2}{(n_{CO_2})} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n} = \frac{(1)^2}{0.5} \times \left(\frac{12}{1.5}\right)^1$$

$$K_P = \frac{12}{1.5 \times 0.5} = \mathbf{16\ atm}$$

97.

$$CO_2(g) + C(s) \rightleftharpoons 2CO$$

Initial mole	$\frac{1.77}{44}$	$\frac{2}{12}$	0
	$= 0.040$	0.167	0
Final mole	0.017		0.034

$$\left[\because \text{Mole of } CO_2 = \text{mole of } BaCO_3 \quad (CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O)\right.$$
$$\left.\text{left} \quad n_{CO_2} = \frac{3.41}{197} = 0.017\right]$$

$$\therefore \quad K_C = \frac{\left[\frac{0.034}{1}\right]^2}{0.017} = 0.068$$

$$\therefore \quad K_P = 0.068 \times (0.0821 \times 1100)^1 = \mathbf{6.14\ atm}$$

98.
$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial pressure	0.5	0	0
Final pressure	(0.5 – P)	0	2P

$\therefore \quad 0.5 - P + 2P + = 0.8 \quad \therefore \quad P = 0.3$ atm

Therefore, final partial pressure at equilibrium are

$$P'_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$
$$P'_{CO} = 2P = 2(0.3) = 0.6 \text{ atm}$$
$$\therefore \quad K_P = \frac{(P'_{CO})^2}{P'_{CO_2}} = \frac{(0.6)^2}{(0.2)} = \mathbf{1.8\ atm}$$

99. (a) The given equilibrium is,

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial mole	1	0
Final mole	(1 – α)	2α

$$K_P = \frac{(n_{CO})^2}{n_{CO_2}} \times \left[\frac{P}{\Sigma n}\right]^1 = \frac{(2\alpha)^2}{(1-\alpha)} \times \left[\frac{5}{1+\alpha}\right]$$
$$10 = \frac{20\alpha^2}{1-\alpha^2} \quad \text{or} \quad 10 - 10\alpha^2 = 2\alpha^2$$
$$\therefore \quad \alpha^2 = \frac{10}{30}$$
$$\therefore \quad \alpha = \sqrt{\frac{1}{3}} = 0.577$$

Thus, mole of CO_2 at equilibrium $= 1 - \alpha = 1 - 0.577 = 0.423$
and mole of CO at equilibrium $= 2\alpha = 2 \times 0.577 = 1.154$
Total mole present at equilibrium $= 0.423 + 1.154 = 1.577$
At equilibrium, $PV = nRT$
$P = 5$atm; $n = 1.577$, $T = 817 + 273 = 1090$
$5 \times V = 1.577 \times 0.0821 \times 1090 \quad \therefore \quad V = 28.22$ litre

$$\therefore \quad [CO] \text{ at equilibrium} = \frac{1.154}{28.22} = \mathbf{0.041\ mol\ litre^{-1}}$$
$$[CO_2] \text{ at equilibrium} = \frac{0.423}{28.22} = \mathbf{0.015\ mol\ litre^{-1}}$$

(b) For
$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial mole	1	0
Final mole	(1 – α)	2a

Total mole at equilibrium $= 1 - a + 2a = 1 + a$

Given $\frac{1-a}{1+a} = \frac{5}{100} \quad \therefore \quad a = \frac{95}{100}$

$$K_P = \frac{(n_{CO})^2}{(n_{CO_2})} \times \left[\frac{P}{\Sigma n}\right]^1$$
$$10 = \frac{\left(\frac{2 \times 95}{100}\right)^2}{\left(\frac{5}{100}\right)} \times \left[\frac{P}{\frac{105}{100}}\right]^1$$

$$\therefore \quad P = \mathbf{0.145\ atm}$$

100. $K_P = (P_{H_2O}) = \mathbf{23\ mm}$

101.
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Mole before dissociation	$\frac{20}{100}$	0	0
Mole after dissociation	$\left[\frac{20}{100} \times \frac{35}{100}\right]$	$\left[\frac{20}{100} \times \frac{65}{100}\right]$	$\left[\frac{20}{100} \times \frac{65}{100}\right]$

$$\therefore \text{ Mole of } CO_2 \text{ formed} = \frac{20 \times 65}{10^4} = 1.3 \times 10^{-1}$$
$$\because \quad PV = nRT$$
$$P_{CO_2} = \frac{1.3 \times 10^{-1}}{10} \times 0.0821 \times 1073 = 1.145 \text{ atm}$$
Now, $K_P = P'_{CO_2} = \mathbf{1.145\ atm}$

102. Eq. I
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
Given, $K_P = 4 \times 10^{-2} = P'_{CO_2}$
Eq. II Also,
$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$
$$K_P = \frac{(P_{CO})^2}{P'_{CO_2}} = 2.0$$

Now both are at equilibrium and thus $P'_{CO_2} = 4 \times 10^{-2}$ which should remain constant, thus

$$2.0 = \frac{(P'_{CO})^2}{4 \times 10^{-2}} \quad \text{or} \quad P'_{CO} = \sqrt{4 \times 10^{-2} \times 2} = \mathbf{0.28\ atm}$$

103. For, $M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$

$\because$ CO_2 is 1% in air ; $\quad \therefore \quad P'_{CO_2} = \frac{1}{100} \times P_{air}$

$$= \frac{1}{100} \times 1\text{atm} = 0.01\text{atm}$$

Also, for equilibrium $K_P = P'_{CO_2} = 0.0095$atm

$\because$ Given, $P'_{CO_2} = 0.01$ atm

Since, decomposition is carried out in presence of P'_{CO_2} of 0.01 atm and $K_P = 0.0095$ atm, thus, practically **no decomposition of M_2CO_3. Thus, 1% CO_2 is sufficient to prevent any loss in mass.**

If at all reaction is desired the P'_{CO_2} must be lesser than 0.0095 atm as P'_{CO_2} at equilibrium cannot be more than 0.0095 atm.

Alternate solution :

For
$$M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(s)$$
$$\left(\frac{1}{100} + P\right)$$

$\because$ $K_P = P'_{CO_2}$ and the pressure of CO_2 already present in 1/100 atm. Let the decomposition of M_2CO_3 produces the CO_2 of pressure P, then

$$\therefore \quad K_P = \frac{1}{100} + P$$

or $\quad 0.0095 = P + 0.01$ or $P = -0.0005$

The value of pressure comes negative and thus, it may be concluded that M_2CO_3 will not dissociate in pressure of CO_2 of pressure 0.01 atm.

104. $\ln K_P = 7.282 - \frac{8500}{T}$ at $T = 1123\,K$

$\ln K_P = 7.282 - 7.569$

$\ln K_P = -0.287$ $\quad\therefore\ K_P = 0.751$ at $T = 1223\,K$

$\ln K_P = 7.282 - 6.950$

$\ln K_P = 0.332;$ $\quad\therefore\ K_P = 1.394$

$\therefore$ Av. $K_P = \frac{0.751 + 1.394}{2} = \frac{2.145}{2} = 1.0725$

Quiet air means, the state when the decomposition of $CaCO_3$ occurs in a way that the air surrounded to it becomes saturated with a pressure of CO_2 equal to 1 atm (to pushback the air) needed to attain equilibrium.

Thus, when $K_P \geq 1$, then reaction is spontaneous is forward direction or at 950° C, the reaction occurs predominantly in forward direction. Thus, for minimum temperature, putting $K_P = 1$ in given equation.

$\therefore\ \log K_P = 7.282 - \frac{8500}{T}$ or $\log 1 = 7.282 - \frac{8500}{T}$

$\therefore\ T = \mathbf{1167.26\ K}$ or **894.26°C**

105. An efflorescent salt is one that loses H_2O to atmosphere.

For the reaction,

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(v)$$

$$K_P = (P'_{H_2O})^2 = 1.086 \times 10^{-4}$$

$\therefore\ P'_{H_2O} = \mathbf{1.042 \times 10^{-2}\ atm\ =\ 7.92\ mm}$

$\because$ Given P'_{H_2O} at 25°C, (*i.e.*, 23.8) > 7.92 mm and thus, reaction will proceed in backward direction, *i.e.*,

$$CuSO_4 \cdot 3H_2O + 2H_2O(v) \rightleftharpoons CuSO_4 \cdot 5H_2O(s)$$

Thus, $CuSO_4 \cdot 5H_2O$ will not act as efflorescent but on the contrary $CuSO_4 \cdot 3H_2O$ will absorb moisture from the atmosphere under given conditions. The salt $CuSO_4 \cdot 5H_2O$ will effloresce only on a dry day when the aqueous tension or partial pressure of moisture in the air is lesser than 7.92 mm or if relative humidity of air at 25° C $= \frac{7.92}{23.8} = 0.333$ or 33.3%

106. For (i) $K_P = (P_{H_2O})^4$

$\therefore\ P_{H_2O} = \sqrt[4]{K_P} = \sqrt[4]{6.9 \times 10^{-12}} = 1.62 \times 10^{-3}$ atm

For (ii) $K_P = (P_{H_2O})^{10}$

$$P_{H_2O} = \sqrt[10]{K_P} = \sqrt[10]{4.08 \times 10^{-25}} = 3.64 \times 10^{-3}\ \text{atm}$$

For (iii) $K_P = (P_{H_2O})^5$

$\therefore\ P_{H_2O} = \sqrt[5]{K_P} = \sqrt[5]{5.25 \times 10^{-13}} = 3.50 \times 10^{-3}$ atm

All these reactant can be used as drying agent since their P_{H_2O} is lesser than V.P. of H_2O in atmosphere, *i.e.*, 4.58 mm or 6.02×10^{-3} atm. The efficiency order is

$SrCl_2 \cdot 6H_2O > Na_2HPO_4 \cdot 12H_2O > Na_2SO_4 \cdot 10H_2O$

107.

	$SnO_2(s) + 2H_2(g)$	$\rightleftharpoons$	$Sn(l) + 2H_2O(g)$
Case I : 900 K	45		55

$\therefore\ K_{C_1} = \frac{(55)^2}{(45)^2} = \mathbf{1.494}$

	$SnO_2(s) + 2H_2(g)$	$\rightleftharpoons$	$Sn(l) + 2H_2O(g)$
Case II : 1100 K	24		76

$\therefore\ K_{C_2} = \frac{76 \times 76}{24 \times 24} = \mathbf{10.03}$

K_C increases with temperature and thus reaction should be endothermic. Thus, high temperature is preferred for reduction of SnO_2.

108. $\because$ $LiCl \cdot 3NH_3(s) \rightleftharpoons LiCl \cdot NH_3(s) + 2NH_3(g)$ $\quad[K_P = 9\,atm^2]$

$\therefore\ LiCl \cdot NH_3(s) + 2NH_3(g) \rightleftharpoons LiCl \cdot 3NH_3(s)$ $\quad\left[K_P = \frac{1}{9}(atm)^{-2}\right]$

Initial mole	0.1	a	0
Final mole at equilibrium	0	$(a - 0.2)$	0.1

Let initial mole of NH_3 should be a to bring in completion of reaction.

At eq. $\quad K_{P_1} = \frac{1}{(P'_{NH_3})^2}$ or $\frac{1}{9} = \frac{1}{(P'_{NH_3})^2}$

$\therefore\ P'_{NH_3} = 3$ atm

$\because\ PV = nRT$

$3 \times 5 = n \times 0.0821 \times 313$

$\therefore\ n = 0.5837$

i.e., $(a - 0.2) = 0.5837$

$\therefore$ Initial mole of $NH_3 = a = 0.5837 + 0.2 = \mathbf{0.7837\ mol}$

109.

	$2Na(g)$	$\rightleftharpoons$	$Na_2(g)$
mass at eq.	71		29
mole at eq.	$\frac{71}{23}$		$\frac{29}{46}$
	= 3.087		= 0.630

$$K_P = \frac{{}^{n}Na_2}{({}^{n}Na)^2} \times \left[\frac{P}{\Sigma n}\right]^{-1} = \frac{0.630}{(3.087)^2} \times \left[\frac{1.013}{3.717}\right]^{-1}$$

$$= \mathbf{0.242\ M\ Pa^{-1}}$$

110. Volume of room $= 6 \times 5 \times 3 = 90\,m^3 = 90 \times 10^3$ litre

$Hg(l) \rightleftharpoons Hg(v)$ $\quad K_P = P'_{Hg} = \frac{0.002}{760} = 2.63 \times 10^{-6}$ atm

$$n_{Hg(v)} = \frac{PV}{RT} = \frac{2.63 \times 10^{-6} \times 90 \times 10^3}{0.0821 \times 300} = 9.62 \times 10^{-3}\ \text{mol}$$

$\therefore\ w_{Hg}(v) = 9.62 \times 10^{-3} \times 200.5 = 1.928\,g = \frac{1.928}{90 \times 10^3}$

$= 2.14 \times 10^{-5}$ g / litre

$= \frac{2.14 \times 10^{-5} \times 10^3}{10^{-3}}$ mg / m^3 $= 21.4$ mg / m^3

The value is higher than safety limit and thus dangerous to enter in the room.

111.

	$C_2H_5OH + CH_3COOH$	$\rightleftharpoons$	$CH_3COOC_2H_5 + H_2O$
Mole before reaction	1		0 1
Mole at equilibrium	$(1-x)$	$(1-x)$	x $1+x$

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\frac{x}{V} \cdot \frac{(1+x)}{V}}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x(1+x)}{(1-x)^2}$$

Given that, $x = 0.543$ since 54.3% of acid is used up

$\therefore \quad K_C = \mathbf{4.012}$

112. Case I:

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Mole before reaction	1	1	0	0
Mole at equilibrium	$1-x$	$1-x$	x	x

$\therefore \quad x = \frac{2}{3}$

$\therefore$ Mole at equilibrium $\left(1-\frac{2}{3}\right) \quad \left(1-\frac{2}{3}\right) \quad \frac{2}{3} \quad \frac{2}{3}$

$$\therefore \quad K_C = \frac{\frac{2}{3}\times\frac{2}{3}}{\frac{1}{3}\times\frac{1}{3}} = 4$$

NOTE : Volume terms are eliminated as in problem 105.

Case II : $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Mole before reaction	2	2	0	0
Mole at equilibrium	$(2-x)$	$(2-x)$	x	x

$$\therefore \quad K_C = 4 = \frac{x^2}{(2-x)^2} \quad \text{or} \quad \therefore \quad \frac{x}{(2-x)} = 2$$

or $\quad x = \mathbf{1.33}$

113. $\alpha - D$ glucose $\rightleftharpoons \beta - D$ glucose

At equilibrium	36.4	63.6

$$\therefore \quad K_C = \frac{63.6}{36.4} = \mathbf{1.747}$$

114. $KI(aq.) + I_2(aq.) \rightleftharpoons KI_3(aq.)$

Molar mass KI = 166

Mole at $t = 0$	$\frac{1.326}{166}$	0	Molar mass KI_3 = 420
Mole at equilibrium	$\left[\frac{1.326}{166} - \frac{0.105}{420}\right]$	0.0013	$\frac{0.105}{420}$
	$= 7.738\times10^{-3}$	0.0013	2.5×10^{-4}

$$\therefore \quad K_C = \frac{[KI_3]}{[KI][I_2]} = \frac{2.5\times10^{-4}}{7.738\times10^{-3}\times0.0013}$$

($\because$ volume of solution = 1 litre)

$$K_C = \mathbf{24.62}$$

The free iodine should be in solid and solution state.

The I_2 in solution state, *i.e.*, $I_2(aq.) = 0.0013\,M$

Thus, I_2 in solid state = 0.0025 − 0.0013 = 0.0012 mol

115. Given $\quad S(s) + S^{2-} \rightleftharpoons S_2^{2-} \qquad K_{C_1} = 1.7$

$$2S(s) + S^{2-} \rightleftharpoons S_3^{2-} \qquad K_{C_2} = 5.3$$

$$\therefore \quad K_{C_1} = \frac{[S_2^{2-}]}{[S^{2-}]} = 1.7 \qquad \ldots(1)$$

$$K_{C_2} = \frac{[S_3^{2-}]}{[S^{2-}]} = 5.3 \qquad \ldots(2)$$

Now for $\quad S_2^{2-} + S(s) \rightleftharpoons S_3^{2-}$

$$K_C = \frac{[S_3^{2-}]}{[S_2^{2-}]}$$

$\therefore$ By Eqs. (2) and (1), $\quad \frac{K_{C_2}}{K_{C_1}} = \frac{[S_3^{2-}]}{[S_2^{2-}]} = K_C$

$$\therefore \quad K_C = \mathbf{3.11}$$

116. $Ag^+(aq.) + Fe^{2+}(aq.) \rightleftharpoons Fe^{3+}(aq.) + Ag(s)$

Millimole before reaction	500×0.150	500×1.09		
or	$= 75$	$= 545$	0	0
Millimole after reaction	$(75-x)$	$(545-x)$	x	x

$\because$ mM = Meq. (both Ag^+/Ag and Fe^{2+}/Fe^{3+} have valency factor unity)

$$\because \quad K_C = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]}$$

$$\therefore K_C = \frac{\frac{x}{1000}}{\left(\frac{75-x}{1000}\right)\left(\frac{545-x}{1000}\right)} \quad \ldots(1)$$

$\because$ Conc. $= \frac{\text{Millimole}}{\text{Total Volume}}$

$[Ag^+] = \frac{75-x}{1000}$

$[Fe^{2+}] = \frac{545-x}{1000}$

$[Fe^{3+}] = \frac{x}{1000}$

Now 25 mL of mixture requires 30 mL of .0832 *M* or $0.0832\times5\,N$ $KMnO_4$.

$\because$ Fe^{2+} is oxidized by $KMnO_4$.

$\therefore$ Milliequivalent of Fe^{2+} left at equilibrium in 1000 mL = Milliequivalent of $KMnO_4$ for 1000 mL

$$= \frac{30\times0.0832\times5\times1000}{25} = 499.2$$

$\therefore \quad 545 - x = 499.2 \qquad \therefore \quad x = 545 - 499.2 = 45.8$

Thus, by Eq. (1), $\quad K_C = \dfrac{\frac{45.8}{1000}}{\left(\frac{75-45.8}{1000}\right)\times\left(\frac{545-45.8}{1000}\right)}$

$$= \frac{45.8\times1000}{29.2\times499.2}$$

$$K_C = \mathbf{3.1420}$$

117. $2Fe^{3+}(aq.) + (Hg_2)^{2+}(aq.) \rightleftharpoons 2Fe^{2+}(aq.) + 2Hg^{2+}(aq.)$

Conc. before reaction	0.5	0.5	0.03	0.03
Conc. after reaction at eq.	$(0.5-a)$	$(0.5-a/2)$	$(0.03+a)$	$(0.03+a)$

$$K_C = 9.14\times10^{-6} = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[(Hg_2)^{2+}]}$$

$$\therefore \quad 9.14\times10^{-6} = \frac{(0.03+a)^2(0.03+a)^2}{(0.5-a)^2(0.5-a/2)}$$

$$\therefore \quad a = 0.0027$$

$$\therefore \quad [Fe^{3+}] = 0.5 - 0.0027 = \mathbf{0.4973\,M}$$

$$[Hg_2^{2+}] = 0.5 - \frac{0.0027}{2} = \mathbf{0.4987\,M}$$

$$[Fe^{2+}] = 0.03 + 0.0027 = \mathbf{0.0327\,M}$$

$$[Hg^{2+}] = 0.03 + 0.0027 = \mathbf{0.0327\,M}$$

118. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Before reaction	0.1	0.1	0	0
At equilibrium	$(0.1-x)$	$(0.1-x)$	x	x

Meq. of acetic acid left = Meq. of NaOH used
$= 100 \times 0.85 = 85$

$\therefore$ Millimole of acetic acid left = 85 ($\because$ mono basic)

$\therefore$ Mole of acetic acid left = 0.085

or $(0.1-x) = 0.085$ or $x = 0.015$

Now $K_C = \dfrac{x^2}{(0.1-x)^2} = \dfrac{(0.015)^2}{(0.085)^2} = \mathbf{0.031}$

119. For the reaction : $Fe^{2+} + 3dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$

$r_{forward} = K_f \times [Fe^{2+}][3dipy]$
$= 1.45 \times 10^{13} [Fe^{2+}][3dipy]$

$r_{backward} = K_b \times [Fe(dipy)_3]^{2+}$
$= 1.22 \times 10^{-4} [Fe(dipy)_3]^{2+}$

At equilibrium $r_f = r_b$ and $K_C = \dfrac{K_f}{K_b}$

$= [Fe(dipy)_3]^{2+} / [Fe^{2+}][dipy]^3$

Also, stability constant of complex = Equilibrium constt. of reaction $= \dfrac{K_f}{K_b}$

$= \dfrac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = \mathbf{1.188 \times 10^{17}}$

120. $2KCN + AgNO_3 \longrightarrow Ag(CN)_2^- + KNO_3 + K^+$

0.1	0.03	0	0	0
$(0.1-0.06)$	0	0.03	0.03	0.03

$\therefore$ $[Ag(CN)_2^-] = 0.03\,M$

Now use $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$

0.03	0	0.04
$(0.03-a)$	a	$0.04 + 2a = 0.04$

Since, K_C is too small and dissociation of $Ag(CN)_2^-$ is very less and thus,

$\therefore$ $0.04 + 2a \approx 0.04$ and $0.03 - a \approx 0.03$

$\therefore$ $[Ag(CN)_2^-] = 0.03$; $[Ag^+] = a$; $[CN^-] = 0.04$

Now $K_C = \dfrac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = \dfrac{a \times (0.04)^2}{0.03}$

$\therefore$ $a = \mathbf{7.5 \times 10^{-18}}$

121. $H_3BO_3 + \text{glycerine} \rightleftharpoons \text{complex}$; $K = \dfrac{[\text{Complex}]}{[H_3BO_3][\text{glycerine}]} = 0.9$

0.10	a	9
$(0.1-x)$	$(a-x)$	x where $x = 60 \times \frac{0.1}{100} = 0.06$

If 60% of H_3BO_3 gives complex then $[H_3BO_3]$ left = 40%

Given $\dfrac{[\text{Complex}]}{[H_3BO_3]} = \dfrac{60}{40}$

Thus, $0.9 = \dfrac{60}{40[\text{glycerine}]}$

or [glycerine] or $(a-x) = \dfrac{60}{40 \times 0.9} = 1.67\,M$

$\therefore$ $a = 1.67 + x = 1.67 + 0.06 = \mathbf{1.73\,M}$

122. $A + B \rightleftharpoons C$

Conc. at I equilibrium	15	15	a (volume is V litre)
Conc. when V is doubled	$\frac{15}{2}$	$\frac{15}{2}$	$\frac{a}{2}$ (volume is $2V$ litre)

Since, on increasing volume, pressure decreases and the reaction proceeds in the direction where it shows an increase in mole, *i.e.*, backward reaction.

Conc. at II equilibrium $\left(\frac{15}{2}+x\right)$ $\left(\frac{15}{2}+x\right)$ $\left(\frac{a}{2}-x\right)$

$\because$ $\dfrac{15}{2} + x = 10$ $\therefore$ $x = \dfrac{5}{2}$

Now, $K_C = \dfrac{[C]}{[A][B]} = \dfrac{\left[\frac{a}{2} - \frac{5}{2}\right]}{\left[\frac{15}{2} + \frac{5}{2}\right]\left[\frac{15}{2} + \frac{5}{2}\right]}$ ...(1) for II Eq.

$K_C = \dfrac{[C]}{[A][B]} = \dfrac{a}{15 \times 15}$ ...(2) for I Eq.

$\because$ K_C are same

$\therefore$ $\dfrac{(a-5)/2}{10 \times 10} = \dfrac{a}{15 \times 15}$ $\therefore$ $a = \mathbf{45\,M}$

Now, $K_C = \dfrac{45}{15 \times 15} = \mathbf{0.2\ mol^{-1}\ litre^1}$

123. For I equilibrium $2NO_2 \rightleftharpoons N_2O_4$

$K_P = \dfrac{P'_{N_2O_4}}{(P'_{NO_2})^2} = 6.8$ ...(1)

$\because$ $P'_{N_2O_4} = 1.7\text{atm}$ $\therefore$ By Eq. (1); $P'_{NO_2} = 0.5\text{atm}$

The equilibria are maintained using NO and NO_2 in the ratio 1 : 2

For II equilibrium $NO + NO_2 \rightleftharpoons N_2O_3$

Initial pressure	P	$2P$	0
Pressures at equi.	$(P-x)$	$(2P-x-3.4)$	x

$\because$ 3.4 atm of NO_2 are used for I equilibrium to have $P'_{N_2O_4} = 1.7\,\text{atm}$

At equilibrium	$(P-x)$	0.5	x

($\because$ P'_{NO_2} is same for both the equilibria since both reactions are at equilibrium at a time.)

Total pressure at equilibrium (Given 5.05 atm)
$= P'_{NO} + P'_{NO_2} + P'_{N_2O_3} + P'_{N_2O_4}$
$= P - x + 0.5 + x + 1.7$

$\therefore$ $5.05 = P + 2.20$

$\therefore$ $P = 5.05 - 2.20$ $\therefore$ $P = 2.85\,\text{atm}$

$\because$ $2P - x - 3.4 = 0.5$

$2 \times 2.85 - x - 3.4 = 0.5$

$\therefore$ $x = 5.70 - 3.90$ $\therefore$ $x = \mathbf{1.80\ atm}$

$\therefore$ $P'_{NO} = 2.85 - 1.80 = \mathbf{1.05\ atm}$

Now, K_P for $NO + NO_2 \rightleftharpoons N_2O_3$

$K_P = \dfrac{P'_{N_2O_3}}{P'_{NO} \times P'_{NO_2}} = \dfrac{1.80}{1.05 \times 0.5} = \mathbf{3.43\ atm^{-1}}$

124. $3A_2(g) \rightleftharpoons A_6(g)$ $\quad K_P = 1.6\ \text{atm}^{-2}$

$$K_P = 1.6 = \frac{P'_{A_6}}{(P_{A_2})^3}$$

$$P_{A_2} = \sqrt[3]{\frac{0.2}{1.6}} = 0.5\ \text{atm}$$

Also, pressure of A_2 used for the formation of $A_6 = 0.6\text{atm}$

For $\quad A_2(g) + C(g) \rightleftharpoons A_2C(g)$

$t = 0 \quad 2P \quad P \quad 0$

At eq. $\quad 2P - P^1 - 0.6 \quad P - P^1 \quad P^1$

Also, for $\quad 3A_2(g) \rightleftharpoons A_6(g)$

$t = 0 \quad 2P \quad 0$

At eq. $\quad 2P - P^1 - 0.6 \quad 0.2$

$$2P - P^1 - 0.6 = 0.5$$

(since P_{A_2} at eq. is 0.5 for simultaneous equilibria)

Also, pressure of $A_2 + C + A_2C + A_6$

$$= (2P - P^1 - 0.6) + (P - P^1) + P^1 + 0.2 = 1.4$$

$$0.5 + P + 0.2 = 1.4$$

$$P = \mathbf{0.7\ atm}$$

$\therefore \quad 2P - P^1 - 0.6 = 0.5$

$\therefore \quad P^1 = 2\times 0.7 - 0.6 - 0.5$

$$P^1 = 0.3\ \text{atm}$$

$\therefore P_{A_2} = 0.5\ \text{atm}, P_C = 0.7 - 0.3 = 0.4\ \text{atm}, P_{A_2C} = 0.3\ \text{atm}$

Also, K_P for $\quad A_2(g) + C(g) \rightleftharpoons A_2C(g)$

$$K_P = \frac{P_{A_2C}}{P_{A_2} \times P_C} = \frac{0.3}{0.5\times 0.4} = \mathbf{1.5\ atm^{-1}}$$

125. $A(g) \rightleftharpoons B(g) + 2C(g)$ and $C \rightleftharpoons 2D + 3B(g)$

$1 \quad 0 \quad 0$

$1-a \quad (a+3b) \quad 2a-b \quad 2a-b \quad 2b \quad (a+3b)$

$\therefore \quad \Sigma$ mole at eq. $= 1 - a + a + 3b + 2a - b + 2b = 2a + 4b + 1$

Now, $\quad P_{\text{initial}} \propto 1$

$$P_{eq.} \propto 2a + 4b + 1$$

$$\therefore \quad 2a + 4b + 1 = \frac{13}{6}$$

or $\quad 2a + 4b = \frac{7}{6} \quad \ldots(1)$

Also, $\quad [C]_{eq.} = \frac{4}{9}[A]_{eq.}$

$$2a - b = \frac{4}{9} \times (1 - a)$$

$$\therefore \quad 22a - 9b = 4 \quad \ldots(2)$$

By Eqs. (1) and (2), $a = 0.25, b = 0.167$

$$\therefore \quad K_{C_1} = \frac{[B][C]^2}{[A]} = \frac{(a+3b)(2a-b)^2}{(1-a)}$$

$$= \frac{[0.25 + (3\times 0.167)][0.5 - 0.167]^2}{(1 - 0.25)} = 0.11$$

$$K_{C_2} = \frac{[D]^2[B]^3}{[C]} = \frac{(2b)^2(a+3b)^3}{(2a-b)}$$

$$= \frac{[2\times 0.167]^2[0.25 + (3\times 0.167)]^3}{[0.5 - 0.167]} = 0.142$$

126. $NH_4I \rightleftharpoons NH_3 + HI \quad \ldots(1)$

$P \quad P$

For this equilibrium $2P = 275$

$\therefore \quad P = 137.5$

Thus, K_P for Eq. (1) $= P_{NH_3} \times P_{HI} = 137.5 \times 137.5 \ldots(2)$

For $\quad 2HI \rightleftharpoons H_2 + I_2$

$1 \quad 0 \quad 0$

$(1-x) \quad \frac{x}{2} \quad \frac{x}{2}$

$$\therefore \quad K_P = K_C = \frac{x^2}{4(1-x)^2} = (0.015)^2$$

$\therefore \quad x = 0.2$

i.e., degree of dissociation of HI is 0.2. Again since HI decomposes, reaction (1) proceeds in forward direction, *i.e.*,

$$NH_4I \rightleftharpoons NH_3 + HI \quad \ldots(3)$$

$(P+A) \quad (P-a)$

$$2HI \rightleftharpoons H_2 + I_2 \quad \ldots(4)$$

$(P-a) \quad \frac{a}{2} \quad \frac{a}{2} \quad [\because a = 0.2P]$

Also, K_P for final equilibrium Eq. (3) or Eq. (1) is

$$K_P = (P+A)(P-a) = (P+A)(P - 0.2P)$$

$$= 137.5\times 137.5 = (P+A)(0.8P)$$

$\therefore \quad P + A = 171.875$

$\therefore \quad A = 34.375$

$$a = 0.2P \times 0.2 = 27.5$$

Total pressure at equilibrium $= \frac{NH_3}{P+A} + \frac{HI}{P-a} + \frac{H_2}{a/2} + \frac{I_2}{a/2}$

$$= 2P + A = 2\times 137.5 + 34.375$$

$$= \mathbf{309.75\ atm}$$

127. $N_2 + O_2 \rightleftharpoons 2NO$

Initial Vol. % $\quad a \quad b \quad 0$

Final Vol. % $\quad\quad\quad x$

Also, $\quad x = \sqrt{K.a.b} - \frac{K(a+b)}{4} \quad \ldots(1)$

The 'x' is maximum only when condition of maximum are fulfilled, *i.e.*,

$$\frac{\delta x}{\delta a} \quad \text{and} \quad \frac{\delta x}{\delta b} = 0$$

By partial differentiation of 'x' w.r.t. 'b' keeping 'a' constant.

From Eq. (1), $\quad \frac{\delta x}{\delta a} = \frac{K.b}{2\sqrt{K.a.b}} - \frac{K}{4} = \frac{\sqrt{K.b}}{2\sqrt{a}} - \frac{K}{4} = 0 \ldots(2)$

By partial differentiation of 'x' w.r.t. 'b' keeping 'a' constant.

From Eq. (1), $\quad \frac{\delta x}{\delta b} = \frac{K.a}{2\sqrt{K.a.b}} - \frac{K}{4} = \frac{\sqrt{K.a}}{2\sqrt{b}} - \frac{K}{4} = 0 \ldots(3)$

By Eq. (2), $\quad K \cdot a \cdot b = 4b^2$

By Eq. (3), $\quad K \cdot a \cdot b = 4a^2$

$\therefore \quad a = b$

NOTE : Also, this is valid only when $K < 4$, because if $a = b$, Eq. (1) yields $x = \sqrt{Ka^2} - \frac{Ka}{2} = a\left(\sqrt{K} - \frac{K}{2}\right)$

If x is +ve $\quad \sqrt{K} > K/2 \quad$ or $\quad 4K > K^2$

or $\quad K(4-K) > 0 \quad$ or $\quad 0 < K < 4$

128. $\Delta G^\circ = -2.303RT\log_{10} K_P$ (at 1 atm)

$11.8\times10^3 = -2.303\times8.314\times230\log_{10} K_P$

$\therefore \quad K_P = 2.09\times10^{-3}$

Also, for $2AB \rightleftharpoons A_2 + B_2$

	1	0	0
	$(1-\alpha)$	$\frac{\alpha}{2}$	$\frac{\alpha}{2}$

$\therefore \quad K_P = \dfrac{\alpha^2}{4(1-\alpha)^2}$ or $\dfrac{\alpha}{2(1-\alpha)} = \sqrt{2.09\times10^{-3}}$

$\therefore \quad \alpha = \mathbf{0.0837}$ or $\mathbf{8.37\%}$

129. $XA \rightleftharpoons D + C$

	$a(1-\alpha)$	$\frac{a\alpha}{x}$	$\frac{a\alpha}{x}$

$\therefore \quad K_C = \dfrac{a^2\alpha^2}{V^2\cdot x^2\left[\frac{a(1-\alpha)}{V}\right]^x} = \dfrac{\alpha^2\cdot a^{2-x}}{x^2(1-\alpha)^x\cdot V^{2-x}}$

Since, α is independent of a $\therefore \quad 2-x=0 \ \therefore \quad x=\mathbf{2}$

130. Given that $\Delta E - \Delta H = 1200$ cal

where ΔE is heat of reaction at constant volume and ΔH is heat of reaction at constant pressure.

Also, we have $\Delta H = \Delta E + \Delta nRT$

$\therefore \quad \Delta nRT = -1200$ or $\Delta n = \dfrac{-1200}{2\times300} = -2 \quad (R = 2\text{ cal})$

Now, $K_P = K_C(RT)^{\Delta n}$

$\therefore \quad \dfrac{K_P}{K_C} = (0.0821\times300)^{-2} = \mathbf{1.648\times10^{-3}}$

131. Meq. of H_2S = Meq. of PbS $= \dfrac{1.029\times1000}{238/2} = 8.6$

$\therefore \quad$ Mole of H_2S formed $= \dfrac{8.6}{1000\times2} = 0.0043$

Also, $Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$

Initial mole	0.01	0.01	0	0
Final mole	$(0.01-x)$	$(0.01-3x)$	$2x$	$3x$

$\because \quad 3x = 0.0043; \ \therefore \ [H_2S] = \left[\dfrac{0.0043}{2.5}\right]M$

and $[H_2] = \left[\dfrac{0.01-0.0043}{2.5}\right]M$

Thus, $K_C = \dfrac{[H_2S]^3}{[H_2]^3}$

Thus, $K_C = \dfrac{\left[\frac{0.0043}{2.5}\right]^3}{\left[\frac{0.01-0.0043}{2.5}\right]^3} = \mathbf{0.43 = 4.3\times10^{-1}}$

132. Let mole of A and B diffused out are n_A and n_B respectively. Initially they were present in the ratio $\dfrac{P_A'}{P_B'} = 1$

$\therefore \quad \dfrac{n_A}{n_B} = \sqrt{\dfrac{m_B}{m_A}} = \sqrt{\dfrac{4}{16}} = \dfrac{1}{2}$

Thus, mole ratio of n_A and n_B goes out in the ratio 1 : 2. Thus, mole of A and B are left after diffusion in the ratio 2 : 1. Total pressure after diffusion is 2 atm thus,

P_A' left $= \dfrac{4}{3}$ at 27°C

P_B' left $= \dfrac{2}{3}$ at 27°C

Now, vessel is heated to 127°C, thus new pressures becomes

$P_A' = \dfrac{4}{3}\times\dfrac{4}{3} = \dfrac{16}{9} \qquad \left(\dfrac{P_1}{P_2} = \dfrac{T_1}{T_2}\right)$

$P_B' = \dfrac{2}{3}\times\dfrac{4}{3} = \dfrac{8}{9}$

Now, $A + B \rightleftharpoons C$

Initial P	$\frac{16}{9}$	$\frac{8}{9}$	0
P at eq.	$\left[\frac{16}{9}-P\right]$	$\left[\frac{8}{9}-P\right]$	P

$\therefore \quad K_P = 0.1 = \dfrac{P}{\left[\frac{16}{9}-P\right]\left[\frac{8}{9}-P\right]} = \dfrac{81P}{(16-9P)(8-9P)}$

or $81P = 12.8 - 21.6P + 8.1P^2$

or $P^2 - 12.67P + 1.58 = 0 \quad \therefore \quad P = \mathbf{0.126\text{ atm}}$

133. $V = 0.224\,dm^3$, $P = 1$ atm, $T = 273$ K

$\therefore$ Mole input per minute at eq.

$= \dfrac{PV}{RT} = \dfrac{1\times0.224}{0.0821\times273} = 99.941\times10^{-4}$

$ZnO(s) + CO(g) \rightleftharpoons Zn(g) + CO_2(g) + N_2(g)$

Initial Mole	$99.941\times0.45\times10^{-4}$ $=44.97\times10^{-4}$	$99.941\times10^{-4}\times0.50$ $=49.97\times10^{-4}$	$99.941\times10^{-4}\times0.05$ $=4.997\times10^{-4}$

$ZnO(s) + CO(g) \rightleftharpoons Zn(g) + CO_2(g) + N_2(g)$

Mole at eq.	$[44.97-5]\times10^{-4}$ $=39.97\times10^{-4}$	5×10^{-4}	$[49.97+5]\times10^{-4}$ $=54.97\times10^{-4}$	4.997×10^{-4}

$\therefore$ Total mole in gaseous phase at equilibrium

$= [39.97 + 5 + 54.97 + 4.997]\times10^{-4} = 104.937\times10^{-4}$

Now, $K_P = \dfrac{n_{Zn}\times n_{CO_2}}{n_{CO}}\times\left[\dfrac{P}{\Sigma n}\right]^1$

$= \dfrac{54.97\times10^{-4}\times5\times10^{-4}}{39.97\times10^{-4}}\times\left[\dfrac{770}{104.937\times10^{-4}}\right]^1$

$= 50.45\text{ mm} = \dfrac{50.45}{760} = \mathbf{0.0664\text{ atm.}}$

134. For the equilibrium :

$nA \rightleftharpoons [A_n]$

Initially	1	0
At eq.	$1-\alpha$	$\frac{\alpha}{n}$

$\therefore$ Total mole at equilibrium $= 1-\alpha+\dfrac{\alpha}{n}$

$\because \quad PV = nRT$

Thus at equilibrium

$\therefore \quad PV = \left[1-\alpha+\dfrac{\alpha}{n}\right]RT$ or $\dfrac{P}{RT} = \dfrac{1-\alpha+\frac{\alpha}{n}}{V}$ ...(i)

Given, $\frac{PV}{RT}=1-\frac{(n-1)K_C}{V^{n-1}}$

or $\frac{P}{RT}=\frac{1}{V}-\frac{(n-1)K_C}{V^n}=\frac{1}{V}-\frac{(n-1)\times\frac{\alpha}{nV}}{V^n\times\frac{(1-\alpha)^n}{V^n}}$

$$\left[\because K_C=\frac{\frac{\alpha}{nV}}{\left[\frac{1-\alpha}{V}\right]^n}\right]$$

$$=\frac{1}{V}\left[1-\frac{(n-1)\alpha}{n(1-\alpha)^n}\right]$$

[since α is small, $\therefore (1-\alpha)^n=1$]

$$=\frac{1}{V}\left[1-\frac{(n-1)\alpha}{n}\right]$$

$$=\frac{1}{V}\left[1-\alpha+\frac{\alpha}{n}\right] \quad ...(ii)$$

Eqs. (i) and (ii) are identical.

135. Equilibrium constant K is given dimension less which means that

$$K=\frac{(a_{H_2})\times(a_{CO})}{(a_{H_2O})\times(a_C)}=\frac{\left(\frac{P_{H_2}}{P^\circ}\right)\left(\frac{P_{CO}}{P^\circ}\right)}{\frac{P_{H_2O}}{P^\circ}\times 1} \quad (\text{for solid } a=1)$$

The term a represents relative activity, *i.e.*, $a=\frac{P}{P^\circ}$ where P° standard state pressure = 100 kPa for gases and P is partial pressure of that gaseous component.

Thus for the equilibrium :

$$\underset{1}{C(s)}+\underset{1}{H_2O(g)}\rightleftharpoons\underset{0}{CO(g)}+\underset{0}{H_2(g)}$$

$$\underset{(1-x)}{\quad}\quad\underset{(1-x)}{\quad}\quad\underset{x}{\quad}\quad\underset{x}{\quad}$$

$\therefore$ $K=\frac{x\cdot x}{(1-x)}\times\left[\frac{P_T}{P^\circ\times(1+x)}\right]^1$

$1.34=\frac{x^2}{1-x^2}\times\frac{200}{100}$ $\quad\therefore x=0.633$

$\therefore$ Mole fraction of CO = mole fraction of

$H_2=\frac{x}{1+x}=\frac{0.633}{1.633}=\mathbf{0.388}$

Mole fraction of $H_2O=\frac{1-0.633}{1.633}=\mathbf{0.224}$

136. $K_c^\circ=\frac{P_{H_2}\times[OH^-]^2}{[I^-]^2}$

$\therefore$ $[OH^-]^2=\frac{K_c\times[I^-]^2}{P_{H_2}}$

$=\frac{1.2\times10^{-23}\times(0.1)^2}{\frac{60}{100}}\left(P_{H_2}^\circ=\frac{\text{Pressure of } H_2}{100\text{ kPa}}\right)$

$[OH^-]=\sqrt{2\times10^{-25}}=4.472\times10^{-13}$

$\therefore$ pOH = 12.35

$\therefore$ pH = **1.65**

137. $AB_2(g)+A(s)\rightleftharpoons 2AB(g)$

Initial pressure	P	0	0
Pressure at eq.	$P-P_1$		$2P'$

Given, $P=0.7$ and $P+P'=0.95$ bar $\therefore$ $P'=0.25$ bar

$$K_{P_1}=\frac{(P_{AB})^2}{P_{AB_2}}=\frac{(2\times0.25)^2}{(0.7-0.25)}=0.55$$

Let after reversible and isothermal expansion pressure of AB_2 and AB be a and b bar respectively at equilibrium

$$K_{P_1}=0.55=\frac{b^2}{a}z$$

Also $a+b=0.4$

$\therefore$ $b=0.27$ bar

$a=0.13$ bar

Thus, mole % of $AB_2=\frac{0.13}{0.4}\times100=\mathbf{32.5}$

mole % of $AB=\frac{0.27}{0.4}\times100=\mathbf{67.5}$

138. $CH_3COCH_3(g)\rightleftharpoons CO(g)+C_2H_6(g)$

Initial mole	a	0	0
at eq.	$(a-x)$	x	x

$\because$ $P\propto a$

$\therefore$ $100\propto a$ (Initial prressue is 100 mm)

Also given mole fraction of CO $=\frac{x}{a+x}=\frac{1}{3}$

$\therefore$ $3x=a+x$

or $x=\frac{a}{2}$

Let pressure at equilibrium be P', $P'\propto a+x$

$\therefore$ $P'\propto a+\frac{a}{2}=\frac{3a}{2}$

Then $P'=\frac{3\times100}{2}=150$ mm

and pressure of $x=50$ mm

$\therefore$ $K_p=\frac{P_{CO}\times P_{C_2H_6}}{P_{CH_3COCH_3}}=\frac{50\times50}{50}=\mathbf{50\text{ mm}}$

SINGLE INTEGER ANSWER PROBLEMS

1. Maximum number of phases in which sulphur exists are.....
2. For $2A+2B \rightleftharpoons 2C+2D$ $K_c = 1/16$ then K_c for $C+D \rightleftharpoons A+B$ is .....
3. For the reaction $2P \underset{K_2}{\overset{K_1}{\rightleftharpoons}} Q \underset{K_4}{\overset{K_3}{\rightleftharpoons}} R+S; K_1, K_2, K_3$ and K_4 are $4\times10^3, 2\times10^4, 16\times10^2$ and 40 respectively. The overall equilibrium constant is .....
4. In the reaction : $C(s)+CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 6 atm. If 50% of CO_2 reacts then K_P of the reaction is .....
5. The mole at equilibrium obtained during experiment for the given reaction in 1 litre vessel are shown below the reactants and products.

$$2A(g)+B(g) \rightleftharpoons 3C(g)+3D$$

Mole at equilibrium 8 16 4 4

If reaction in forward direction is to be made, the initial conc. of reactants and products should be such that reaction Quotient should be less than.....

6. The rate of disappearance of A in the reaction at equilibrium $A \rightleftharpoons B$ is given by

$$-\frac{d[A]}{dt} = 2\times10^{-2}[A]-4\times10^{-3}[B] \text{ at } 300 \text{ K}.$$

The equilibrium constant K_c is .....

7. If $K_p = K_c \times [RT]^{\Delta n}$, for the reaction

$$2CO_2(g)+2CaCO_3(s) \rightleftharpoons 2CaC_2(s)+5O_2(g);\ \Delta n$$

is equal to .....

8. Negative slope of the line drawn as In K_c *vs.* $\frac{1}{T}$ for a given reaction is -1. The heat of reaction is ..... cal.
9. If $\Delta G°$ for a reaction is -8290.8 cal. The K_c for the reaction 300 K is 10^n. The value of n is :
10. The plot of ln K *vs.* $\frac{1}{T}$ shows an intercept of ln $a = 4$. The change in standard entropy for the reaction at equilibrium is ..... cal.
11. What is the % dissociation of H_2S, if one mole of H_2S is introduced in 1 litre vessel at 1000 K, if K_c for the reaction :

$$2H_2S(g) \rightleftharpoons 2H_2(g)+S_2(g) \text{ is } 4\times10^{-6}$$

12. In a reaction at equilibrium, 'x' mole of the reactant, A decompose to give 1 mole each of B and C. The experimental studies suggest that the decomposition of A at equilibrium is independent of initial concentration of A. Calculate 'x'.
13. Given below are two reversible reactions:

$$A+B \rightleftharpoons Z;\ K_{c_1} = 24$$

$$2B+C \rightleftharpoons 2Y;\ K_{c_2} = 16$$

The equilibrium constant K_c for the reaction

$$A+Y \rightleftharpoons Z+\frac{C}{2} \text{ is .....}$$

14. For a reversible reaction $A \rightleftharpoons B$, $\log_{10} K = 1.737 - \frac{2500}{T}$ (in litre atm unit). The standard entropy, change to the closest value in cal K^{-1} is.....
15. For a reversible reaction $\frac{K_p}{K_c} = (RT)^{\Delta n}$ at 300 K. If $K_p / K_c = 14941.5$ (in litre atm unit) for a given reaction then Δn for the reaction is..... (given $\log K_p / K_c = 4.17$ and $\log 24.93 = 1.39$).
16. If pK_a of HCN is 10 and of HCO_3^- is 9, the $pK_{eq.}$ for the given reaction is.....

$$CO_3^{2-}+HCN \longrightarrow CN^- + HCO_3^-$$

17. Δn for the reaction :

$$NH_4Cl(s) \rightleftharpoons NH_3(v)+HCl(g) \text{ is.....}$$

18. The variation of ln K_C *vs.* $\frac{1}{T}$ gives a straight line having an angle of 45°. The value of heat of reaction in cal is.....
19. Vapour density of N_2O_4 at temperature T K is 43.80. The % dissociation of N_2O_4 to NO_2 is.....
20. For the reaction : $AB(g) \rightleftharpoons A(g)+B(g)$, the total pressure P at which AB is 50% dissociated is given by $P = a \times K_p$. The value of a is.....
21. Total number of present of equilibrium in the given reaction are.....

$$CuSO_4(s)3NH_3(l) \rightleftharpoons CuSO_4 \cdot 3NH_3(l)$$

22. 5 mole of PCl_5 are heated to attain the equilibrium at constant volume V and temperature T as :

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$; the degree of dissociation of PCl_5 is 0.2 at these conditions. Now 2 mole of N_2 are added to maintain V and T. The total mole of gases present at new equilibrium are.....

23. A one litre container was used to study the following equilibria occuring simultaneously

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If 10 mole of each CH_4 and H_2O, were used and if 2 mole of H_2O reacts with CH_4 and CO separately, to attain equilibria, then mole of H_2 formed are.....

24. For the reaction : $2CO(g)+O_2(g) \rightleftharpoons 2CO_2(g)$ $K_c = 0.75$

Conc at eq. 4 3 a

What is the value of a?

25. The variation of ln K_c *vs.* $\frac{1}{T}$ gives a straight line having an angle of 45°. The value of heat of reaction in cal is.....
26. For the equilibrium at temperature T :

$Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2 \cdot HPO_4 \cdot XH_2O(s) + YH_2O(g)$;

$K_p = 25\times10^{-3Y}$. If vapour pressure of H_2O at T K is 5×10^{-3} atm, how many molecule of H_2O are lost by $Na_2HPO_4\cdot12H_2O$ at equilibrium ?

27. For an equilibrium reaction : $A+2B \rightleftharpoons 2C+D$; A and B are mixed in a reaction vessel at 300 K. The initial concentration of B was 1.5 times the initial concentration of A. After the equilibrium, the equilibrium concentrations of A and D are same. What is K_c ?
28. Vapour density of N_2O_4 at temperature T K is 43.80. What is % dissociation of N_2O_4 to NO_2 ?
29. Hot copper turnings are used to absorb O_2 in order to produce inert gas atmosphere. At 500 K,

$$2Cu(s)+\frac{1}{2}O_2(g) \rightleftharpoons Cu_2O(s),$$

the value of $(K_p)^2$ is $2.5\times10^{+21}$ atm^{-1}. If $R=0.08$ and Av.no. is 6×10^{23}, how many molecules of O_2 are left at equilibrium in 1 litre container ?

30. For the reaction $AB(g) \rightleftharpoons A(g)+B(g)$, the total pressure P at which AB is 50% dissociated is given by $P=a\times K_p$. The value of a is.....
31. A certain gas A polymerises as $nA \rightleftharpoons (A)_n$. If $n=2$ and degree of polymerisation is 20% then if reaction is carried out by taking 10 mole of A, then total mole at equilibrium are.....
32. Total number of phases present at equilibrium in the reaction

$$CuSO_4(s)+3\,NH_3(l) \rightleftharpoons CuSO_4\cdot3NH_3(l)$$

33. For the reaction at 300 K, $A(g) \rightleftharpoons B(g)+C(g)$, $\Delta_rH^\circ=-30$ kJ mol^{-1} and $\Delta_rS^\circ=-100$ JK^{-1} mol^{-1}, then equilibrium constant K for the reaction is ..... .
34. The value of ΔG°, when $K_C=1$ for a reaction in equilibrium is ..... .
35. A vessel of 250 litre containing 0.01 mole of Sb_2S_3 was filled with 0.01 mole of H_2 and reaction at 440°C,

$$Sb_2S_3(s)+3H_2(g) \longrightarrow 2Sb(s)+3H_2S(g)$$

was allowed to attain equilibrium. The H_2S formed was just sufficient to react with $Pb(NO_3)_2$ to give 1.19 g of PbS. The value of K_C at 440°C is ..... .

36. The value of $\frac{K_p \text{ (in atm)}}{K_C \text{ (in M)}}$ for the reaction, $SO_2Cl_2(g) \rightleftharpoons SO_2(g)+Cl_2(g)$ at temperature 365.4 K is 3×10^a. The value of a is ..... .
37. The values of K_{p_1} and K_{p_2} for the reaction given below are in the ratio 2 : 1. If degree of dissociation of X and A are equal, then total pressure at eq. (1) and eq. (2) are in the ratio.

$$X \rightleftharpoons Y+Z; \quad K_{p_1}$$
$$A \rightleftharpoons 2B; \quad K_{p_2}$$

38. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$; $G^\circ_{N_2O_4}$ and $G^\circ_{NO_2}$ are 100 kJ mol^{-1} and 50 kJ mol^{-1} at 298 K when 5 mole of each are taken initially than the approximate value of Gibbs energy change for the above reaction in kJ is ..... .
39. The degree of dissociation of PCl_5 at 1 atm and 400 K is 60%. Assuming ideal behaviour the density of equilibrium mixture is approximately in g/litre is ..... .
40. K_p for $NH_4HS(s) \rightleftharpoons NH_3(g)+H_2S(g)$ is 9 (atm)^2 at T K. The total pressure at equilibrium at T K is ..... .
41. For the decomposition of $NH_4HS \rightleftharpoons NH_3+H_2S$, if $K_p=n_{NH_3}\times n_{H_2S}\times\left(\frac{P}{\Sigma n}\right)^a$, then a is equal to ..... .
42. If K_p for $LiCl\cdot3NH_3(s) \rightleftharpoons LiCl\cdot NH_3(s)+2NH_3(g)$, is 9 atm^2. If 0.1 mole of $LiCl\cdot NH_3$ at equilibrium, the pressure of NH_3 at equilibrium is ..... .
43. 2 mol SO_2 and 1 mol O_2 are heated in closed vessel to attain equilibrium : $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ The equilibrium mixture shows a pressure of 5 atm and requires $\frac{1}{3}$ mol of $K_2Cr_2O_7$ in acidic medium for oxidation. What is K_p in atm^{-1}.
44. Consider a reaction : $AB_2(g) \rightleftharpoons AB(g)+B(g)$ in equilibrium. The initial pressure and equilibrium pressure are 100 and 120 torr respectively. The equilibrium constant in torr is ... .

ANSWERS

1. Four	2. Four	3. Eight	4. Eight	5. Four	6. Five	7. Three	8. Two	9. Six	10. Eight	11. Two	12. Two	
13. Six	14. Eight	15. Three	16. One	17. Two	18. Two	19. Five	20. Three	21. Two	22. Eight	23. Eight	24. Six	
25. Two	26. Two	27. Four	28. Five	29. Six	30. Three	31. Nine	32. Two	33. One	34. Zero	35. One	36. One	
37. Eight	38. Four	39. Four	40. Six	41. Two	42. Three	43. One	44. Five					

OBJECTIVE PROBLEMS (One Answer Correct)

1. The rate for the $A_2 + C \longrightarrow$ Product for which mechanism is given below is 5.0 mol litre^{-1} s^{-1} when the concentration of reactant A_2 and C are 10 mol/litre and 4 mol/litre respectively :

Step I. $A_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2A$ $K_1 = 10^{10}$ s^{-1}

and $K_2 = 10^9$ litre mol^{-1} sec^{-1}

Step II. $A + C \longrightarrow AC$

The rate constant for the change $A + C \longrightarrow AC$ is :

(a) 1.25×10^{-1} (b) 1.25×10^{-3}

(c) 1.25×10^{-2} (d) 1.25

2. The equilibrium constant K_c for $A_{(g)} \longrightarrow B_{(g)}$ is 1 : 1. The gas having its concentration at equilibrium greater than 1 is :

(a) only A

(b) only B

(c) both A and B

(d) both $[A]$ and $[B]$ if $[A] \geq 1$ and only $[B]$ if $0.91 < A \leq 1$

3. For the reaction in equilibrium : $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ if $P_{Cl_2} = \frac{P}{4}$, when P is initial pressure of NOCl, then total pressure at equilibrium is :

(a) $\frac{5P}{4}$ (b) $2P$

(c) $\frac{P}{4}$ (d) $\frac{3P}{4}$

4. The standard internal energy change during the course of reaction at equilibrium at 300 K : $2A_g + B_g \rightleftharpoons A_2B_g$ is : (Given, $K_p = 10^{-10}$ atm^{-2} and $\Delta S° = 5$ JK^{-1})

(a) –63.93 kJ (b) +63.93 kJ

(c) +58.94 kJ (d) –58.94 kJ

5. An aquatic species needs atleast 4 mg/litre O_2 for their survival. The solubility of O_2 in water at 273 K and 1 atm pressure is 2.21×10^{-3} mol litre^{-1}. The partial pressure of O_2 above water (in atmosphere at 273 K) needed for survival of species is :

(a) 0.56 atm (b) 5.525×10^{-3} atm

(c) 5.525 atm (d) 0.056 atm

6. The equilibrium constants for the reactions are :

$NO_{2(g)} \rightleftharpoons NO_{(g)} + O_{(g)}$ $K_{P_1} = 6.0 \times 10^{-50}$

$O_3 + NO_{(g)} \rightleftharpoons NO_{2(g)} + O_{2(g)}$ $K_{P_2} = 5.0 \times 10^{-35}$

The equilibrium constant for $O_{2(g)} + O_{(g)} \rightleftharpoons O_{3(g)}$ is :

(a) 8.3×10^{14} (b) 1.2×10^{-15}

(c) 3.0×10^{-84} (d) 3.3×10^{83}

7. If K_{a_2} for $H_2S = 1.0 \times 10^{-15}$ and K_{sp} of $Ba_3(AsO_4)_2$, Ag_2S and Ag_3AsO_4 are 7.70×10^{-51}, 2.0×10^{-49} and 1.0×10^{-22} respectively. The equilibrium constant for the reaction :

$3Ag_2S_{(s)} + Ba_3(AsO_4)_{2(s)} + 3H^+ \rightleftharpoons 2Ag_3AsO_{4(s)} + 3HS^- + 3Ba^{2+}$ is :

(a) 5.6×10^{-124} (b) 3.0×10^{-109}

(c) 5.6×10^{-108} (d) 4.63×10^{-108}

8. Vapour density of N_2O_4 at 60°C is found to be 30.6. The degree of dissociation of N_2O_4 is :

(a) 10 % (b) 20 %

(c) 40 % (d) 50 %

9. The dissociation equilibrium pressure of $NH_4HS_{(s)}$ is 60 cm at 27°C. The total pressure at equilibrium when the NH_4HS is dissociated in presence of 45 cm of NH_3 is :

(a) 85 cm (b) 100 cm

(c) 105 cm (d) 75 cm

10. The rate of disappearance of A at two temperatures is given by : $A \rightleftharpoons B$

I. $-\frac{d[A]}{dt} = 2 \times 10^{-2}[A] - 4 \times 10^{-3}[B]$ at 300 K

II. $-\frac{d[A]}{dt} = 4 \times 10^{-2}[A] - 16 \times 10^{-4}[B]$ at 400 K

The heat of reaction for the change is :

(a) 3.863 kcal (b) 6.93 kcal

(c) 1.68 kcal (d) 1.68×10^2 kcal

11. The decomposition of HNO_3 represented below attains equilibrium at a given $P_{eq.}$ and T. If we start $4HNO_{3(g)} \rightleftharpoons 4NO_{2(g)} + 2H_2O_{(g)} + O_{2(g)}$ with pure HNO_3 having initial pressure P_i, then at equilibrium which one is not correct ?

(a) $K_p = \frac{1024(P_{O_2})^7}{(P_{eq.} - 7P_{O_2})^4}$ (b) $K_P = \frac{1024(P_{O_2})^7}{(P_i - 4P_{O_2})^4}$

(c) $K_p^\circ = \frac{1024(P_{O_2})^7}{(P_{eq.} - 7P_{O_2})^4} \times \left(\frac{1}{P^\circ}\right)^3$

(d) All of these

12. Hot copper turnings can be used as oxygen getter for inert gas supplies by slowly passing the gas over the turnings at 600 K.

$2Cu_{(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons Cu_2O_{(s)}$; $K_p = 7.5 \times 10^{10}$ atm$^{-1/2}$

The number of molecules per litre left after equilibrium has reached are :

(a) 2.17 (b) 2.17×10^{23}
(c) 3.61×10^{24} (d) 1.78×10^{22}

13. 0.2 mole of NH_4Cl are introduced into an empty container of 10 litre and heated to 327 to attain equilibrium as : $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$; $K_p = 0.36\ atm^2$. The quantity of solid NH_4Cl left is :
(a) 0.02 mol (b) 0.078 mol
(c) 0.095 mol (d) 0.035 mol

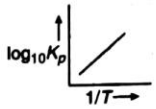
14. For the reaction :
$2CaSO_{4(s)} \rightleftharpoons 2CaO_{(s)} + 2SO_{2(g)} + O_{2(g)}$;
$K_p^\circ = 0.143$ dimension less. If mole fraction of SO_2 is 0.4 at equilibrium, the dissociation pressure at equilibrium (in mm) is :
(a) 868 mm (b) 40.3 mm
(c) 76 mm (d) 86.8 mm

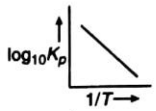
15. The dissociation of N_2O_4 is carried out at constant volume and temperature T. The degree of dissociation α of N_2O_4 is : ($P_{eq.}$ and P_{ini} are pressure at equilibrium and initial pressure at equilibrium and initial pressure before dissociation and assume ideal gas nature)
(a) $\dfrac{P_{eq.} - P_{ini}}{P_{ini}}$
(b) $\left[\dfrac{K_P}{4P + K_p}\right]^{1/2}$
(c) dependent of initial mass of N_2O_4
(d) all of the above

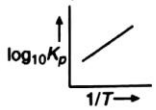
16. NO and NO_2 are mixed in a container at constant volume to attain for the equilibrium :
$2NO_2 \rightleftharpoons N_2O_4 \quad NO + NO_2 \rightleftharpoons N_2O_3$
If partial pressures of P'_{NO_2} and $P'_{N_2O_4}$ are 0.5 and 1.7 atm respectively and equilibrium pressure is 5.05 atm, the initial pressure (atm) of NO would be :
(a) 2.20 (b) 2.85
(c) 3.20 (d) 3.85

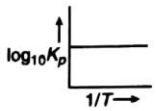
17. The equilibrium constant K_p for the reaction has the following characteristics :
(a) $K_p = K_p^\circ$ if pressure are expressed in bar or in standard state
(b) K_p° values rises exponentially with the constant, if reaction is multiplied by the constant
(c) on increasing the temperature equilibrium is shifted towards high enthalpy side whereas on decreasing temperature, it is shifted towards low enthalpy side :
(d) all of the above

18. Which graph correctly represents for $\log_{10} K_p$ *vs.* $\dfrac{1}{T}$ plots ?

(a) Exothermic reaction : 

(b) Exothermic reaction : 

(c) Endothermic reaction : 

(d) Endothermic reaction : 

19. The intercepts and plots of graph of $\log_{10} K_p^\circ$ *vs.* $\dfrac{1}{T}$ are :
(a) $\Delta G^\circ, \Delta H^\circ$ (b) $\dfrac{\Delta G^\circ}{2.303R}, \dfrac{\Delta H^\circ}{2.303R}$
(c) $\dfrac{\Delta S^\circ}{2.303\,R}, -\dfrac{\Delta H^\circ}{2.303\,R}$ (d) $\dfrac{\Delta H^\circ}{2.303R}, \Delta S^\circ$

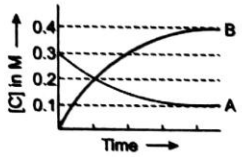
20. If S° for N_2, O_2, N_2O, NO, NO_2 and N_2O_4 are 45.7, 49.0, 48.2, 50.24, 57.24 and 72.77 cal respectively and
$N_2 + \frac{1}{2}O_2 \rightleftharpoons N_2O$; $\Delta H^\circ = 19.49$ kcal at 300 K
$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$; $\Delta H^\circ = 21.60$ kcal at 300 K
$\frac{1}{2}N_2 + O_2 \rightleftharpoons NO_2$; $\Delta H^\circ = 8.09$ kcal at 300 K
$N_2 + 2O_2 \rightleftharpoons N_2O_4$; $\Delta H^\circ = 2.19$ kcal at 300 K
For which ΔG° is more +ve :
(a) N_2O (b) NO
(c) NO_2 (d) N_2O_4

21. For the reaction : $AB_{2(g)} \rightleftharpoons AB_{(g)} + B_{(g)}$, the degree of dissociation of AB_2 is negligible compared to unity, then which one is not correct ?
(a) $K_{eq.} = \dfrac{C\alpha^2}{4}$ (b) $\alpha = \sqrt{\dfrac{K_{eq.}}{C}}$
(c) $\alpha = \sqrt{\dfrac{K_p}{P}}$ (d) $K_{eq.} = \dfrac{\alpha^2 \times P}{(1+\alpha)}$

22. In a reaction at equilibrium 'x' mole of the reactant A decompose to give 1 mole of C and D. It has been found that the fraction of A decomposed at equilibrium is independent of initial concentration of A. The value of 'x' is :
(a) 1 (b) 2
(c) 3 (d) 4

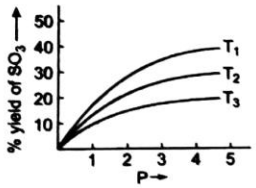
23. A certain reaction has equilibrium constant 10 and 100 at 300 K and 400 K respectively. The ratio of ΔG° at 300 K and 400 K respectively is :
(a) $\frac{1}{10}$ (b) $\frac{3}{8}$
(c) $\frac{1}{2}$ (d) $\frac{3}{4}$

24. The equilibrium constant K_c for the reaction,
$$A(g) \rightleftharpoons 2B(g),$$
obeying the graph is :



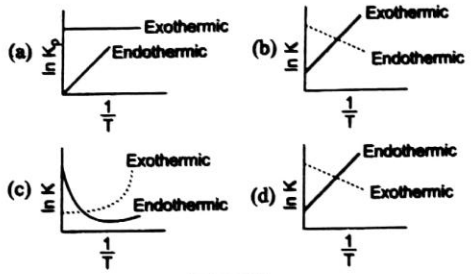
(a) 1.6 (b) 1.0
(c) 1.3 (d) 4

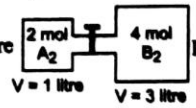
25. The preparation of $SO_3(g)$ by the reaction,
$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$



shows the following figure in % yield against pressure at different temperature then :
(a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$
(c) $T_1 = T_2 = T_3$ (d) $T_2 > T_1 > T_3$

26. Which of the following is correct for the equilibrium constant involving exothermic and endothermic change :



27. Gases are 

present in two containers at 300 K separated by a narrow tube of negligible volume having valve in between. On opening the valve the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ attains equilibrium at 300 K. If $K_c = 4$ at 300 K, the concentration of AB at equilibrium is :
(a) 1.33 M (b) 2.66 M
(c) 1.66 M (d) 0.66 M

28. Two solid compounds A_1 and A_2 in a container dissociates at temperature T to show the equilibrium :
$$A_1(s) \rightleftharpoons A(g) + 2B(g); \quad K_{p_1} = 9 \times 10^{-3}$$
$$A_2(s) \rightleftharpoons C(g) + 2B(g); \quad K_{p_2} = 4.5 \times 10^{-3}$$
The total pressure of gases at equilibria will be :
(a) 1.5 atm (b) 0.45 atm
(c) 0.6 atm (d) 2 atm

29. 10% of a mixture of 0.2 mole of N_2 and 0.6 mole of H_2 react to give NH_3 according to the equation to give NH_3 following the reaction equilibrium :
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
at constant temperature. The ratio between the initial moles and final mole is:
(a) 1.05 (b) 2.20
(c) 0.8 (d) 0.6

30. At a definite temperature, the equilibrium constant for a reaction, $A + B \rightleftharpoons 2C$, was found to be 81. Starting with 1 mole A and 1 mole of B, the mole fraction of C at equilibrium is :
(a) $\frac{9}{11}$ (b) $\frac{1}{11}$
(c) $\frac{2}{11}$ (d) $\frac{7}{11}$

31. Addition of 1 mole of N_2 is made to an equilibrium mixture of PCl_5 in a piston fitted cylinder. Which of the following is correct :
(a) No effect on equilibrium constant K_c or K_p
(b) The degree of dissociation of PCl_5 decreases
(c) The volume of container does not change
(d) No effect on equilibrium concentration

32. Which of the following represent chemical equilibria on mixing?
(a) 20 mL of 0.1 M HCl + 20 mL of 0.1 M NaOH
(b) 20 mL of 0.1 M NH_4OH + 20 mL of 0.1 M HCl
(c) 20 mL of 0.1 M $AgNO_3$ + 20 mL of 0.1 M KCl
(d) 20 mL of 0.1 M K_2CrO_4 + 20 mL of 0.1 M $Pb(NO_3)_2$

33. Which of the following relation correctly represents the equilibrium constant in terms of standard state for the dissociation of :
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
Partial pressure at eq. P_1 P_2 P_3
(in kPa)
(a) $K_{P_{SS}} = \frac{(P_3)^2}{(P_1)^2 \times (P_2)}$
(b) $K_{P_{SS}} = \frac{(P_3)^2}{(P_1)^2 \times (P_2)} \times 100$

(c) $K_{p_{ss}} = \frac{(P_3)^2}{(P_1)^2 \times (P_2)} \times 1000$

(d) $K_{p_{ss}} = \frac{(P_3)^2}{(P_1)^2 \times (P_2)} \times 10$

34. Select the incorrect statement :
(a) Solubility of hydrated salts usually increases with temperature
(b) $P_W \longrightarrow P_R$; $\Delta H = +ve$
(c) Dissolution of water soluble gas is always exothermic
(d) Le chatelier principle is not valid for solid-solid systems

35. Select the incorrect statement :
(a) m.pt. of ice is lowered at higher altitute
(b) m.pt. of solid is raised at higher altitude
(c) Ice melts slowly at higher altitude
(d) Melting of ice takes place slowly on spraying NaCl at same pressure

36. Select the incorrect statement :
(a) On dissolution 0.1 mole of CH_3COONa in 10 mL water in a beaker shows equilibrium
(b) Chemical equilibrium is attained only at constant P or at constant V
(c) On dissolving $CuSO_4$ in water a turbid solution is formed which forms a transparent solution on addition of little CH_3COOH
(d) $SbCl_3$ in aqueous solution gives a transparent solution

37. For the reaction,
$$X + Y \rightleftharpoons 3Z,$$
if α mole of each X and Y per litre are taken initially in the container, which are correct at equilibrium :
(a) $[X]+[Y]=0$ (b) $3[X]+[Z]=3\alpha$
(c) $[X]-\frac{1}{3}[Y]=\alpha$ (d) $[X]+[Z]=3\alpha$

38. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if :
(a) temperature is increased and pressure is kept constant
(b) temperature is reduced and pressure is increased
(c) both temperature and pressure are increased
(d) both temperature and pressure are reduced

39. For the reaction,
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g),$$
the equilibrium constant K_p changes with :
(a) total pressure
(b) catalyst
(c) the amounts of H_2 and I_2 present
(d) temperature

40. Pure ammonia is placed in a vessel at a temperature where its dissociation constant a is appreciable. At equilibrium :
(a) K_p does not change significantly with pressure
(b) a does not change with pressure
(c) concentration of NH_3 does not change with pressure
(d) concentration of hydrogen is less than that of nitrogen

41. An example of a reversible reaction is :
(a) $Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$
(b) $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
(c) $2Na(s) + H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
(d) $KNO_3(aq) + NaCl(aq) \rightarrow KCl(aq) + NaNO_3(aq)$

42. The reaction which proceeds in the forward direction is :
(a) $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$
(b) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$
(c) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2HgCl_2$
(d) $2CuI + I_2 + 4K^+ = 2Cu^{2+} + 4KI$

43. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under 1 atm. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is :
(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) 1.0 atm

44. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by :
(a) temperature and pressure
(b) temperature only
(c) pressure only
(d) temperature, pressure and catalyst

45. Consider a hypothetical equilibrium :
$$A(aq.) \rightleftharpoons 2B(aq.) + C(aq.)$$
Before the reaction, A and B were present such that mole fraction of B is 1/3 as well as molar concentration of B is M. At equilibrium the reaction mixture has mole fraction of A equal to 1/2. The equilibrium constant of the reaction can be given by :
(a) $\frac{27M^3}{28}$ (b) $\frac{28M^3}{27}$
(c) $\frac{M^2}{7}$ (d) $\frac{9M^2}{28}$

46. One mole of A at pressure P in a closed container of 1 litre shows the following equilibria :
$$A(g) \rightleftharpoons B(g) + C(g) \quad ; \quad K_1$$
$$C(g) \rightleftharpoons D(g) + B(g) \quad ; \quad K_2$$
The pressure at equilibrium is $2P$ and $\frac{[C]_{eq.}}{[A]_{eq.}} = 2.1$. The ratio of $\frac{K_1}{K_2}$ can be given by :
(a) 3 : 1 (b) 4 : 1
(c) 2 : 1 (d) 1 : 2

47. Consider a hypothetical reaction : $A + B \rightleftharpoons C$; $K_C = 0.9$. The mole of A added to 1 litre of 0.1 M B so that 60% of B is converted to C are :

(a) 1.83 (b) 1.93
(c) 1.73 (d) 1.63

48. For the given endothermic equilibrium, the heat of reaction at constant volume is 1200 cal more than that of heat of reaction at constant pressure at 300 K. The ratio of equilibrium constants K_p and K_C for the above equilibrium is :
(a) 3.6×10^{5} (b) 6.2×10^{6}
(c) 3.6×10^{-5} (d) 1.64×10^{-3}

49. The concentrations of A and B are $3M$ and $4M$ respectively in the state of equilibrium of $A(g)+2B(g)\rightleftharpoons C(g)$. After the equilibrium is attained, the volume of container is doubled so that equilibrium is restablished and at this state $[B]_{eq.}$ is $3M$. The equilibrium constant K_C for the reaction is :
(a) 0.083 (b) 12
(c) 4 (d) 0.25

50. Equal volumes of 0.06 M $AgNO_3$ and 0.2 M KCN solutions are mixed. K_C for the reaction $Ag(CN)_2^-(aq.)\rightleftharpoons Ag^+(aq.)+2CN^-(aq.)$ is 1.6×10^{-19} at 25°C. The concentration of $Ag^+(aq.)$ in solution is :
(a) $3\times10^{-18}\,M$ (b) $1.5\times10^{-19}\,M$
(c) $1.5\times10^{-18}\,M$ (d) $3\times10^{-20}\,M$

51. Two solids A and C shows the following dissociation equilibria :
$A(s)\rightleftharpoons B(g)+D(g)$
$C(s)\rightleftharpoons E(g)+D(g)$
The pressure over excess solid A is 40 atm and over excess C is 80 atm. The total pressure of the gaseous mixture over the solid mixture is :
(a) 67.0 atm (b) 89.4 atm
(c) 134 atm (d) 178.8 atm

52. For the equilibrium : $A(s)\rightleftharpoons 2B(g)+3C(g)$, the concentration of B and C are x and y mole litre^{-1} respectively at equilibrium. If concentration of C is two times of y at equilibrium then what would be the value of $[B]$ at equilibrium?
(a) $2x$ (b) $3x$
(c) $8x$ (d) $\frac{x}{2\sqrt{2}}$

53. The colour of given reaction mixture is blue at room temperature. On
$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}}(aq.)+4Cl^-\rightleftharpoons\underset{\text{Blue}}{[CoCl_4^{2-}]}(aq.)+6H_2O$$
cooling it becames pink, this indicates that :
(a) reaction is exothermic
(b) reaction is endothermic
(c) reaction shifts in forward direction on cooling
(d) none of the above

54. The activation energy for the forward and backward reactions are 10.303 and 8.0 k cal respectively at 500 K. Assuming pre exponential factor same for both forward and reverse reaction are same and R = 2cal, the equilibrium constant for the reaction $A\rightleftharpoons B$ is :
(a) 10 (b) 100
(c) 1000 (d) 0.1

55. N_2O_4 is dissociated to 33% and 40% at total pressure P_1 and P_2 respectively at equilibrium. The ratio of $\frac{P_1}{P_2}$ is :
(a) 2.0 (b) 1.55
(c) 2.5 (d) 3.0

56. For the reaction at equilibrium :
$$2NOBr(g)\rightleftharpoons 2NO(g)+Br_2(g)$$
if $P_{Br_2}=\frac{P}{9}$ at equilibrium and total pressure is P, then ratio of $\frac{K_p}{P}$ is equal to :
(a) $\frac{1}{9}$ (b) $\frac{1}{81}$
(c) $\frac{1}{27}$ (d) $\frac{1}{3}$

57. 500 mL vessel contains 1.5 M each of A, B, C and D at equilibrium. If 0.5 M each of C and D are taken out, the value of K_C for $A+B\rightleftharpoons C+D$ is :
(a) 1.0 (b) $\frac{1}{9}$
(c) $\frac{4}{9}$ (d) $\frac{8}{9}$

58. For the reaction at 500 K, $2A+B\rightleftharpoons 2C$; $\Delta G^\circ=2$ kJ mol^{-1}. What is the value of K for the reaction $A+\frac{1}{2}B\longrightarrow C$ at 500 K.
(a) 0.786 (b) 0.527
(c) 0.22 (d) 0.46

59. N_2O_4 dissociates to NO_2 for which equilibrium constant (K_p) is 0.2 at 300 K. Find out the fraction of N_2O_4 dissociated at total pressure of 4 atm pressure having 1 mole of Argon at equilibrium. Assume α being small for solving the problem.
(a) 0.158 (b) 0.058
(c) 0.250 (d) 0.015

60. 4 mole of SO_3 shows dissociation equilibrium in 2 litre flask as :
$$2SO_3\rightleftharpoons 2SO_2+O_2$$
The equilibrium mixture requires 6.4 mL of 0.1 M acidified $KMnO_4$ for the redox change. K_c for the reaction equilibrium is mol litre^{-1} is :
(a) 0.178 (b) 0.356
(c) 0.702 (d) 0.0178

61. The ΔU° and ΔS° for the change :
$$2A(g)\rightleftharpoons 2B(g)+C(g)$$

are 30 kcal and 100 cal/° at 300 K. The equilibrium constant for the reaction is :

(a) e^{-2} (b) e^{-1}

(c) e (d) e^{-3}

62. The equilibrium pressure of the reaction mixture :

$$NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$$

is P atm at temperature T K. The standard Gibbs energy change for the reaction is :

(a) $-2RT[\ln P - \ln 2]$ (b) $-RT[\ln P - \ln 2]$

(c) $-RT[\ln 2 - \ln P]$ (d) $-2RT \ln P$

63. Variation of equilibrium constant 'K' with temperature is given by :

$$\ln K = 4 - \frac{100}{T}$$

The value of ΔS_r (in cal) for the reaction : $A \rightleftharpoons B$ at 300 K is :

(a) 2 (b) 4

(c) 6 (d) 8

64. A 20 litre container at 400 K contains $CO_2(g)$ at pressure 0.4 atm and an excess of SrO neglect the volume of solid (SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be :

(Given that : $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$ $K_p = 1.6$ atm)

(a) 5 litre (b) 10 litre

(c) 4 litre (d) 2 litre

65. The equilibrium constants of the following are :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ K_1

$N_2 + O_2 \rightleftharpoons 2NO$ K_2

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ K_3

The equilibrium constant (K) of the reaction :

$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$; will be :

(a) $\frac{K_1K_3^3}{K_2}$ (b) $\frac{K_2K_3^3}{K_1}$

(c) $\frac{K_2K_3}{K_1}$ (d) $\frac{K_2^3K_3}{K_1}$

SOLUTIONS (One Answer Correct)

1. (a) The step II is slow since I K_1 and K_2 are very high

$$\therefore \quad K_C = \frac{[A]^2}{[A_2]} = \frac{K_1}{K_2} = \frac{10^{10}}{10^9} = 10^1$$

$$\therefore \quad [A] = \sqrt{[A_2]\times 10}$$

$$r = K[A][C]$$
$$= K\times\sqrt{[A_2]\times 10}\times[C]$$

or $\quad 5 = K\sqrt{10\times 10}\times 4$

$$\therefore \quad K = \frac{5}{4\times 10} = 0.125$$

2. (d) Mathematical observation.

3. (a) $\underset{P-\frac{P}{2}}{2NOCl} \rightleftharpoons \underset{P/2}{2NO} + \underset{P/4}{Cl_2}$

$$\therefore \quad P_r = \frac{P}{2}+\frac{P}{2}+\frac{P}{4} = \frac{5P}{4}$$

4. (b) $\quad \Delta G^\circ = -2.303\,RT\log K_p$

$$\therefore \quad = -2.303\times 8.314\times 10^{-3}\times 300\log 10^{-10}$$
$$= +57.44\text{ kJ}$$

Now, $\quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$+57.44 = \Delta H^\circ - 300\times 5\times 10^{-3}$$
$$\Delta H^\circ = +58.94\text{ kJ}$$

Also, $\quad \Delta H^\circ = \Delta U^\circ + \Delta nRT$ kJ

$$58.94 = \Delta U^\circ + (-2)\times 8.314\times 10^{-3}\times 300,\ \Delta U^\circ = 63.93\text{kJ}$$

5. (d) Acc. to Henry's law $K_p = \frac{a}{p} = \frac{2.21\times 10^{-3}}{1}$

$$= 2.21\times 10^{-3}\text{ mol atm}^{-1}$$

Now, O_2 required for survival $= 4\times 10^{-3}$ g/litre

$$= \frac{4\times 10^{-3}}{32}\text{ mol litre}^{-1}$$

Now, $\quad 2.21\times 10^{-3} = \frac{4\times 10^{-3}}{P\times 32}$

$$\therefore \quad P = 0.056\text{ atm}$$

6. (d) $\quad K_{P_1} = \frac{[NO][O]}{[NO_2]}$ and $K_{P_2} = \frac{[NO_2][O_2]}{[O_3][NO]}$

$$\therefore \quad \frac{1}{K_{P_1}}\times\frac{1}{K_{P_2}} = \frac{[NO_2]}{[NO][O]}\times\frac{[O_3][NO]}{[NO_2][O_2]}$$
$$= \frac{[O_3]}{[O][O_2]} = K$$

$$\therefore \quad K = \frac{1}{6\times 10^{-50}\times 5\times 10^{-35}} = 3.3\times 10^{83}$$

7. (d) $\quad K_{2_{H_2S}} = \frac{[H^+][S^{2-}]}{[HS]}$ ...(i)

$$K_{sp_{Ag_2S}} = [Ag^+]^2[S^{2-}]$$ ...(ii)

$$K_{sp_{Ba_3(AsO_4)_2}} = [Ba^{2+}]^3[AsO_4^{3-}]^2$$ ...(iii)

$$K_{sp_{Ag_3AsO_4}} = [Ag^+]^3[AsO_4^-]$$ ...(iv)

$$K_{eq.} = \frac{[HS^-]^3[Ba^{2+}]^3}{[H^+]^3}$$ ...(v)

By Eqs. (i), (ii), (iii) and (iv)

$$K = K_{sp_{Ba_3AsO_4}}\times\left(\frac{1}{K_{2_{H_2S}}}\right)^3\times(K_{sp_{Ag_2S}})^3\times\left(\frac{1}{K_{sp_{Ag_3AsO_4}}}\right)^2$$

$$= \frac{7.70\times 10^{-51}\times(2.0\times 10^{-49})^3}{(1.10\times 10^{-15})^3\times(1.0\times 10^{-22})^2} = 4.63\times 10^{-108}$$

8. (d) $\quad \underset{1-\alpha}{N_2O_4} \rightleftharpoons \underset{2\alpha}{2NO_2}$

$$2\times 30.6 = \frac{(1-\alpha)\times 92+2\alpha\times 46}{(1+\alpha)} \quad \therefore\ \alpha = 0.5$$

9. (d) $\quad NH_4HS_{(s)} \rightleftharpoons NH_3 + H_2S$

K_p for NH_4HS $\quad = P\times P = P^2$ $\quad$ Also given $2P = 60$ cm

$\therefore\ P = 30$ cm

$$K_p = 30\times 30 = 900\text{cm}^2$$

$$\underset{P'+45}{NH_4HS_{(s)}} \rightleftharpoons \underset{P'}{NH_3} + H_2S$$

$$(P'+45)\times P' = 900$$

$$\therefore \quad P' = 15\text{ cm}$$

$$\therefore \quad P_r = 15+45+15 = 75\text{cm}$$

10. (a) $\quad K_1 = \frac{K_f}{K_b} = \frac{2\times 10^{-2}}{4\times 10^{-3}} = 5$ at 300 K

$$K_2 = \frac{K_f}{K_b} = \frac{4\times 10^{-2}}{16\times 10^{-4}} = 25\text{ at }400\text{ K}$$

$$\therefore \quad 2.303\log\frac{25}{5} = \frac{\Delta H}{2}\times\left[\frac{400-300}{400\times 300}\right]$$

or $\quad \Delta H = 3863.3\text{ cal} = 3.86\text{ kcal}$

11. (d) $\quad 4HNO_{3(g)} \rightleftharpoons 4NO_{2(g)} + 2H_2O_{(g)} + O_2$;

Pressure at equilibrium is $P_{eq.}$

$$\underset{P_i-4P}{\overset{P_i}{}} \quad \underset{4P}{0} \quad \underset{2P}{0} \quad \underset{P}{0}$$

$$P_{eq.} = P_i - 4P + 4P + 2P + P$$

$$\therefore \quad P_i - 4P = P_{eq.} - 7P = P_{eq.} - 7P_{O_2};\quad P = P_{O_2}$$

$$K_P = \frac{(P_{NO_2})^4(P_{H_2O})^2 P_{O_2}}{(P_{HNO_3})^4}$$

$$= \frac{1024(P_{O_2})^7}{(P_{eq.}-7P_{O_2})^4} = \frac{1024(P_{O_2})^7}{(P_i-4P_{O_2})^4}$$

and $\quad K_P^\circ = \frac{(P_{NO_2})^4\times(P_{H_2O})^2 P_{O_2}}{(P_{HNO_3})^4}\times\frac{1}{(P^0)^3}$

$$= \frac{(4P)^{21}\times(2P)^2\times P}{(P_{eq.}-7P_{O_2})^4}\times\frac{1}{(P^0)^3}$$

$$= \frac{1024(P_{O_2})^7}{(P_{eq.}-7P_{O_2})^4}\times\frac{1}{(P^\circ)^3}$$

12. (a) $K_P = (P_{O_2})^{-1/2}$

$\therefore \quad 7.5\times10^{10} = (P_{O_2})^{-1/2}$

$\therefore \quad P_{O_2} = 1.78\times10^{-22}$

Now, $PV = nRT$

$\therefore \quad n = \dfrac{1.78\times10^{-22}\times1}{600\times0.0821} = 3.61\times10^{-24}$

$\therefore$ Number of molecules of O_2 left

$= 3.61\times10^{-24}\times6.023\times10^{23} = 2.17$

13. (b) $NH_4Cl \rightleftharpoons NH_3 + HCl$

mole at t = 0	0.20	0	0
mole at eq.	(0.20–a)	a	a

Also, $K_p = P_{NH_3}\times P_{HCl} = P^2$

$P = \sqrt{K_P} = \sqrt{0.36} = 0.6$ atm

Now, NH_3 formed $n = \dfrac{PV}{RT} = \dfrac{0.6\times10}{0.0821\times600}$

$= 0.122$ mol

= mole of NH_4Cl decomposed

$\therefore$ NH_4Cl left = 0.2 – 0.122 = 0.078 mol

14. (a) $2CaSO_{4(s)} \rightleftharpoons 2CaO_{(s)} + 2SO_{2(g)} + O_{2(g)}$

$K_P = (P_{SO_2})^2\cdot P_{O_2}$ and $K_P^\circ = \dfrac{(P'_{SO_2})^2\cdot P'_{O_2}}{(P^\circ)^3}$

$(P^\circ = 1$ atm$)$

$\therefore \quad (P_{SO_2})^2\cdot P_{O_2} = K_P^\circ\times(P^\circ)^3 = 0.143 = 0.143$ atm

Let dissociation pressure be P atm, then $P'_{SO_2} = P\times0.4$ and $P'_{O_2} = P\times0.6$

$\therefore \quad 0.143 = (P\times0.4)^2\times P\times0.6$

$\therefore \quad P = 1.14$ atm $= 1.14\times760$ mm $= 867.96$ mm

15. (d) $N_2O_4 \rightleftharpoons 2NO_2$

mole at t = 0	a	0
mole at eq.	$(a-a\alpha)$	$2a\alpha$

where, α is degree of dissociation.

$\therefore \quad P_{ini} = \dfrac{aRT}{V}, \quad P_{eq.} = \dfrac{(a+a\alpha)\cdot RT}{V}$

$\therefore \quad \dfrac{P_{ini}}{P_{eq.}} = \dfrac{1}{(1+\alpha)}$ or $\alpha = \dfrac{P_{eq.}-P_{ini}}{P_{ini}}$

Also, $K_p = \dfrac{(2a\alpha)^2}{(a-a\alpha)}\times\left[\dfrac{P}{a+a\alpha}\right]^1 = \dfrac{4\alpha^2P}{1-\alpha^2}$

$\therefore \quad \alpha = \sqrt{\dfrac{K_p}{4P+K_p}}$

16. (b) $2NO_2 \rightleftharpoons N_2O_4$

At eq.	0.5	1.7

$NO + NO_2 \rightleftharpoons N_2O_3$

At eq.	$P-x$	0.5	x

(where, P is initial pressure)

$\therefore$ Eq. pressure $= P - x + 0.5 + x + 1.7$

or $\quad 5.05 = P + 2.20$

$\therefore \quad P = 2.85$ atm

17. (d) $A + B \rightleftharpoons C + D$: $\quad K_{P_1} = \dfrac{P'_C\times P'_D}{P'_A\times P'_B}$

$nA + nB \rightleftharpoons nC + nD$; $\quad K_{P_2} = \dfrac{(P'_C)^n\times(P'_D)^n}{(P'_A)^n\times(P'_B)^n}$

$\therefore \quad K_{P_2} = (K_{P_1})^n$

18. (a) $-\dfrac{\Delta H}{2.303R} = +ve$

$\therefore \quad \Delta H = -ve$

19. (c) $-\Delta G^\circ = 2.303RT\log K_p$

$-(\Delta H^\circ - T\Delta S) = 2.303RT\log K_P$

$\therefore \quad \log K_p = -\dfrac{\Delta H^\circ}{2.303RT} + \dfrac{\Delta S^\circ}{2.303R}$

20. (a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ_{f_{N_2O}} = 19.49 - \left[48.2 - 45.7 - \dfrac{49.0}{2}\right]\times300\times10^{-3}$

$= 26.09$ kcal

$\Delta G^\circ_{f_{NO}} = 21.60 - \left[50.24 - \dfrac{45.7}{2} - \dfrac{49.0}{2}\right]\times300\times10^{-3}$

$= 20.73$ kcal

$\Delta G^\circ_{f_{NO_2}} = 8.09 - \left[57.24 - \dfrac{45.7}{2} - 49.0\right]\times300\times10^{-3}$

$= 12.47$ kcal

$\Delta G^\circ_{f_{N_2O_4}} = 2.19 - [72.77 - 45.7 - 98.0]\times300\times10^{-3}$

$= 23.47$ kcal

21. (a) $AB_2 \rightleftharpoons A + B$

	1	0	0
	$1-\alpha$	α	α

$\therefore \quad K_{eq.} = \dfrac{C\alpha^2}{1-\alpha}$ and $K_p = \alpha^2\left[\dfrac{P}{1+\alpha}\right]^1$

22. (b) $XA \rightleftharpoons D + C$

$a(1-\alpha) \quad \dfrac{a\alpha}{x}\cdot\dfrac{a\alpha}{x}$

$\therefore \quad K_c = \dfrac{a^2\alpha^2}{V^2\cdot X^2\left[\dfrac{a(1-\alpha)}{v}\right]^x} = \dfrac{\alpha^2a^{2-x}}{X^2(1-\alpha)^x\cdot V^{2-x}}$

Since, α is independent of a

$\therefore \quad 2 - x = 0$

$x = 2$

23. (b) $\Delta G^\circ = -RT\ln K$

$\dfrac{\Delta G^0_1}{\Delta G^0_2} = \dfrac{300\ln10}{400\ln100} = \dfrac{300}{400}\times\dfrac{1}{2} = \dfrac{3}{8}$

24. (a) At. eq. $[B] = 0.4\ M$; $[A] = 0.1\ M$

$\therefore \quad K_c = \dfrac{0.4\times0.4}{0.1} = 1.6$

25. (a) The formation of SO_3 is exothermic and thus at high temperature backward reaction will proceed to give lower percentage yield.

26. (b) $\ln K = \dfrac{-\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$

For endothermic change $\Delta H^\circ = +$ ve

$\therefore$ slope of $\ln K$ vs $\dfrac{1}{T}$ is negative.

For exothermic change $\Delta H^\circ = -$ ve

$\therefore$ slope of $\ln K$ vs $\dfrac{1}{T}$ is positive.

27. (d)

$$\underset{\text{at eq.}}{\underset{\text{mole at } t=0}{}} \quad \underset{2}{A_2} + \underset{4}{B_2} \rightleftharpoons \underset{0}{2AB}$$
$$\qquad\qquad (2-x) \quad (4-x) \qquad 2x$$

Total volume at equilibrium is $1+3=4$ litre

$$\therefore \quad K_c = 4 = \frac{\left[\frac{2x}{4}\right]^2}{\left[\frac{2-x}{4}\right]\left[\frac{4-x}{4}\right]} = \frac{4x^2}{8-6x+x^2} = 4$$

$$\therefore \quad 4x^2 = 32-24x+4x^2$$

$$\therefore \quad x = \frac{32}{24} = \frac{4}{3} = 1.33$$

$$\therefore \quad [AB] = \frac{2\times 1.33}{4} = 0.66$$

28. (b) $A_{1(s)} \rightleftharpoons A_{(g)} + 2B_{(g)}$

$\qquad\qquad {}^{*}P_1 \quad 2P_1 + 2P_2$

$A_2 \rightleftharpoons C + 2B_{(g)}$

$\qquad\qquad {}^{*}P_2 \quad 2P_1 + 2P_2$

$$\therefore \quad \frac{K_{P_1}}{K_{P_2}} = \frac{(2P_1+2P_2)^2 \times P_1}{(2P_1+2P_2)^2 \times P_2}$$

$$\frac{P_1}{P_2} = 2$$

$$P_1 = 2P_2$$

Also, from $K_{P_1} = P_1(2P_1+2P_2)^2$;

$P_1 = 0.1$ atm and $P_2 = 0.05$ atm

Total pressure $= P_1 + P_2 + 2P_1 + 2P_2$

$$= 3(P_1+P_2) = 3(0.1+0.05)$$

$$= 0.45 \text{ atm}$$

29. (a)

$$\underset{\text{Initial mole}}{\underset{\text{Mole at eq.}}{}} \quad \underset{(0.2-0.02)}{\underset{0.18}{N_2(g)}} + \underset{(0.6-0.06)}{\underset{0.54}{3H_2}} \rightleftharpoons \underset{\text{Total mole present} = 0.8}{\underset{0.04}{2NH_3}}$$

10% of the react *i.e.*, 0.08 mole react. Let x mole of N_2 and $3x$ mole of H_2 react, then

$$\therefore \quad 4x = 0.08$$

$$x = 0.02$$

Total mole at eq. $= 0.18+0.54+0.04 = 0.76$

$$\therefore \quad \frac{\text{Mole at } t=0}{\text{Mole at } eq.} = \frac{0.80}{0.76} = 1.05$$

under similar conditions of P & T, this is also volume ratio.

30. (b)

$$\underset{1-x}{\underset{1}{A}} + \underset{1-x}{\underset{1}{B}} \rightleftharpoons \underset{2x}{\underset{0}{2C}}$$

$$\therefore \quad 81 = \frac{4x^2}{(1-x)^2}$$

$$\text{or} \quad \frac{2x}{(1-x)} = 9$$

$$\therefore \quad x = \frac{1}{11}$$

Thus,

$$\underset{\frac{10}{11}}{\underset{\frac{10}{11}}{A}} + \underset{\frac{10}{11}}{\underset{\frac{10}{11}}{B}} \rightleftharpoons \underset{\frac{2}{11}}{2C}$$

$$\left(\text{Total mole} = \frac{10}{11}+\frac{10}{11}+\frac{2}{11} = \frac{22}{11}\right)$$

$$\therefore \text{ Mole fraction of } C = \frac{\frac{2}{11}}{\frac{22}{11}} = \frac{1}{11}$$

31. (a) Addition of inert gas either at constt. P or V does not bring any effect on K_c or K_p values. Volume increases and thus degree of dissociation of PCl_5 increases.

32. (b) $PbCrO_4$ and AgCl are precipitated out. Salt of strong acid + weak base shows hydrolysis equilibrium.

33. (b) In standard state,

$$K_{p_{st}} = \frac{\left(\frac{P_{SO_3}}{P^\circ}\right)^2}{\left(\frac{P_{SO_2}}{P^\circ}\right)\times\left(\frac{P_{O_2}}{P^\circ}\right)} = K_p \times P^\circ$$

Also $P^\circ = 100$ kPa or 1 bar in standard state.

34. (b) White phosphorus is more reactive than red P and possess more enthalpy.

35. (d) Melting of ice takes place fastly on spraying salt at same pressure.

36. (d) $SbCl_3 + H_2O \rightleftharpoons \underset{\text{turbid}}{SbOCl} + 2HCl$

37. (b)

$$\underset{(\alpha-a)}{\underset{\alpha}{X}} + \underset{(\alpha-a)}{\underset{\alpha}{Y}} \rightleftharpoons \underset{3a}{\underset{0}{3Z}}$$

$$\therefore \quad (\alpha-a)-(\alpha-a) = 0 = [X]-[Y]$$

Also, $\quad 3[X]+[Z] = 3\alpha$

$$3(\alpha-a)+3a = 3\alpha$$

38. (b) $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$; $\Delta H = -ve$;

Follow Le Chatelier principle.

39. (d) K_p depends only on temperature.

40. (a) Follow solution 39.

41. (d) An irreversible reaction is one in which either of the product is precipitated or separated out as solid or escaped out as gas.

42. (a) Acid-base reactions occur spontaneously.

43. (b)

$$\underset{1-0.20}{\underset{1}{N_2O_4}} \rightleftharpoons \underset{2\times 0.20}{\underset{0}{2NO_2}}$$

Mole of $N_2O_4 = 1$ mol

Dissociated $N_2O_4 = \frac{1\times 20}{100} = 0.2$ mol

$P_{N_2O_4}$ at 300 K = 1 atm. $\therefore$ $P_{N_2O_4}$ at 600 K = 2 atm

$\therefore$ Total mole present at eq. $= 1-0.20+0.40 = 1.20$

$$\because \quad \frac{P_1}{P_2} = \frac{n_1}{n_2} \qquad \text{(at constant } T, V\text{)}$$

$$\therefore \quad \frac{2}{P_2} = \frac{1}{1.2} \qquad \therefore \quad P_1 = 2.4 \text{ atm}$$

44. (a) The formation of product is favoured by increase in P for this reaction and change in temperature.

45. (d)

$$A(aq.) \rightleftharpoons 2B(aq.) + C(aq.)$$

mole fraction at $t=0$	$\frac{2}{3}$	$\frac{1}{3}$	0
molarity $t=0$	$2M$	$1M$	0
At eq.	$(2M-x)$	$(M+2x)$	x

(Since mole fraction are in the ratio 2 : 1 for A and B thus their molarity will also show same ratio)

Thus total mole at equilibrium

$$= 2M - x + M + 2x + x = 3M + 2x$$

Given mole fraction of A at eq. $= \frac{1}{2} = \frac{2M-x}{3M+2x}$

$\therefore \quad x = \frac{M}{4}$;

Thus $[B] = M + \frac{2M}{4} = \frac{3M}{2}$

and $[A] = 2M - \frac{M}{4} = \frac{7M}{4}$

Now, $K_C = \frac{[B]^2[C]}{[A]} = \frac{\left[\frac{3M}{2}\right]^2\left[\frac{M}{4}\right]}{\frac{7M}{4}} = \frac{9M^2}{28}$

46. (b)

$$A(g) \rightleftharpoons B(g) + C(g)$$

Initial mole	1	0	0
final mole at eq.	$1-x$	$x+y$	$x-y$

$$C(g) \rightleftharpoons D(g) + B(g)$$

x	0	0
$(x-y)$	y	$x+y$

Given $\frac{[C]}{[A]} = \frac{x-y}{1-x} = 2$

$\therefore \quad 3x - y - 2 = 0 \quad \ldots$ (i)

Also pressure $\propto$ mole (V and T are constant)

Thus, $P \propto 1$

$$2P \propto 1 - x + (x+y) + (x-y) + y = 1 + x + y$$

$\therefore \quad 1 + x + y = 2 \quad \ldots$ (ii)

From (i) and (ii)

$\therefore \quad x = \frac{3}{4}$ and $y = \frac{1}{4}$

Therefore $K_1 = \frac{(x+y)(x-y)}{(1-x)}$

$$K_2 = \frac{(x+y)y}{(x-y)}$$

$\therefore \quad \frac{K_1}{K_2} = \frac{(x-y)^2}{(1-x)y} = \frac{\left(\frac{3}{4} - \frac{1}{4}\right)^2}{\frac{1}{4}\left(1 - \frac{3}{4}\right)} = 4$

47. (c)

$$A + B \rightleftharpoons C \qquad K_C = 0.9$$

at $t=0$	a	0.1	0	x = 60% of 0.1 or 0.06
at equilibrium	$(a-0.06)$	$(0.1-0.06)$	0.06	
	$(a-0.06)$	0.04	0.06	

$\therefore \quad K_C = \frac{[C]}{[A][B]}$

$$0.9 = \frac{0.06}{(a-0.06)\times 0.04}$$

$$0.9 = \frac{3}{2a - 0.12}$$

or $1.8a - 0.108 = 3$

$\therefore \quad a = \frac{3.108}{1.8} = 1.73$

48. (d)

$$\Delta H = \Delta U + \Delta nRT$$

$\therefore \quad \Delta n = \frac{\Delta H - \Delta U}{RT} = -\frac{1200}{2\times 300} = -2$

Now $\frac{K_p}{K_C} = (RT)^{\Delta n} = (0.0821\times 300)^{-2}$

$$= 1.64 \times 10^{-3}$$

49. (a)

$$A(g) + 2B(g) \rightleftharpoons C$$

Concentration at I eq.	3	4	a

$\therefore \quad K_C = \frac{a}{3\times 4^2} = \frac{a}{48}$

Also if volume is doubled *i.e.*, pressure decreases the reaction will proceed in the direction where mole increases, thus

	A	+	$2B$	$\rightleftharpoons$	C
when $V = V$	3		4		a
when $V = 2V$	1.5		2		$\frac{a}{2}$
Re-establishment of eq.	2		3		$\frac{a}{2} - 0.5$

$\therefore \quad K_C = \frac{\left(\frac{a}{2} - 0.5\right)}{2\times 3^2} = \frac{(a-1)}{36}$

or $\frac{a-1}{36} = \frac{a}{48}$

$48a - 48 = 36a$

$\therefore \quad 12a = 48$

$a = 4$ M

or $K_C = \frac{a-1}{36} = \frac{(4-1)}{36} = \frac{1}{12} = 0.083$

50. (a)

$$AgNO_3 + 2KCN \longrightarrow Ag(CN)_2^- + 2K^+ + NO_3^-$$

Initially	$0.06\times V$	$0.2\times V$	0	0	0
After mixing	–	$0.08\times V$	$0.06\,V$	$0.12\,V$	$0.06\,V$

Thus, $[Ag(CN)_2]^- = \frac{0.06V}{2V} = 0.03$ M

$$[CN^-] = \frac{0.08\times V}{2V} = 0.04$$

Now $Ag(CN)_2^-(aq.) \rightleftharpoons Ag^+ + 2CN^-$

0.03	—	0.04
$(0.03-a)$	a	0.04

$$K_C = 1.6\times 10^{-19} = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-}$$

or $1.6\times 10^{-19} = \frac{a\times(0.04)^2}{(0.03-a)}$

a is very small as K_C is very low $0.03 - a \simeq 0.03$

Thus, $a = \frac{1.6\times10^{-19}\times0.03}{(0.04)^2} = 3\times10^{-18}$

51. (b) $A(s) \rightleftharpoons B + D$

$P_B + P_D = 40$

$\therefore \quad 2P = 40$

or $\quad P = 20$ atm

$\therefore \quad K_p = (P)^2 = 20\times20 = 400$

Similarly, $C(s) \rightleftharpoons E(g) + D(g)$

$P_E + P_D = 80$

$\therefore \quad 2P = 80$

or $\quad P = 40$ atm

$\therefore \quad K_p = 40\times40 = 1600$

For simultaneous equilibrium $A(s) \rightleftharpoons \underset{P_1}{B} + \underset{P_1+P_2}{D}$

$C(s) \rightleftharpoons \underset{P_2}{E} + \underset{P_2+P_1}{D}$

$\therefore \quad 400 = P_1\times(P_1+P_2)$

$1600 = P_2(P_1+P_2)$

or $\quad \frac{P_1}{P_2} = \frac{1}{4} \quad$ or $\quad P_2 = 4P_1$

Also, $P_1(P_1+P_2) = 400$

$P_1(P_1+4P_1) = 400$

$5P_1^2 = 400$

$P_1 = 8.94$ atm

Total pressure at eq. $= P_1 + (P_1+P_2) + P_2$

$= 2(P_1+P_2) = 2(P_1+4P_1)$

$= 10P_1 = 10\times8.94 = 89.4$

52. (d) $A(s) \rightleftharpoons 2B(g) + 3C(g)$

$\therefore \quad K_C = [B]^2[C]^3 = x^2(y)^3 = x^2y^3$

If concentration of C is two times to that of y at equilibrium *i.e.*, $2y$ then if concentration of B is B_2

$K_C = [B_2]^2[2y]^3$

or $\quad [x]^2[y]^3 = 8[B_2]^2[y]^3$

$\therefore \quad [B_2] = \frac{x}{\sqrt{8}} = \frac{x}{2\sqrt{2}}$

53. (b) Follow Le-Chatelier principle

54. (d) $K_c = \frac{K_f}{K_b} = \frac{Ae^{-10.303\times10^3/RT}}{Ae^{-8\times10^3/RT}}$

$= e^{-2.303\times10^3/RT} = e^{-2.303\times10^3/2\times500}$

$K_C = e^{-2.303} = 0.1$

55. (b) $N_2O_4 \rightleftharpoons 2NO_2$

$\underset{1-0.33}{1} \qquad \underset{2\times0.33}{0}$

$\therefore \quad K_p = \frac{(2\times0.33)^2}{0.67}\times\frac{P_1}{1.33}$

$\left[\because K_p = \frac{(n_{NO_2})^2}{n_{N_2O_4}}\times\left(\frac{P}{\Sigma n}\right)\right]^1$

Similarly for 40%

$K_p = \frac{(2\times0.4)^2}{0.6}\times\frac{P_2}{1.40}$

$\therefore \quad \frac{P_1}{P_2} = 1.55$

56. (b) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

At eq. $\quad P' \qquad \frac{2P}{9} \qquad \frac{P}{9}$

$\therefore \quad P' + \frac{2P}{9} + \frac{P}{9} = P$

or $\quad P' = \frac{2}{3}P$

$\therefore \quad K_p = \frac{\left(\frac{2P}{9}\right)^2\left(\frac{P}{9}\right)}{\left(\frac{2P}{3}\right)^2} = \frac{P}{81}$

57. (a) K_C does not depend on concentration of reactants or products.

$K_C = \frac{[D][C]}{[A][B]} = \frac{1.5\times1.5}{1.5\times1.5} = 1$

58. (a) $2A + B \rightleftharpoons 2C \quad \Delta G^\circ = 2$ kJ mole^{-1}

$A + \frac{1}{2}B \rightleftharpoons C \quad \Delta G^\circ = 1$ kJ mole^{-1}

Now, $\quad -\Delta G^\circ = 2.303RT\log K$

$-1000 = 2.303\times8.314\times500\log K$

$K = 0.786$

59. (a) $N_2O_4 \rightleftharpoons 2NO_2$

$\underset{1-\alpha}{1} \qquad \underset{2\alpha}{0}$

Σ mole $= 1-\alpha+2\alpha+1 \quad$ (for Ar)

$= 2+\alpha$

$K_p = \frac{(2\alpha)^2}{(1-\alpha)}\left[\frac{P}{2+\alpha}\right]^1 = \frac{4\alpha^2P}{2-\alpha^2-\alpha}$

$\alpha <<< 2$

$\therefore \quad K_p = \frac{4\alpha^2P}{2} = \frac{4\times\alpha^2\times4}{2} = 0.2$

$\therefore \quad \alpha = 0.158$

60. (a) $2SO_3 \rightleftharpoons 2SO_2 + O_2$

Initial mole	4	0	0
At eq.	$4-x$	x	$\frac{x}{2}$

SO_2 will show redox change with $KMnO_4$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}$

$2e + \overset{+6}{S} \longrightarrow S^{4+}$

meq. of SO_2 = meq. of $KMnO_4$

$= 6.4\times0.1\times5 = 3.2$

$\therefore \quad$ mole of SO_2 at eq. $= \frac{3.2}{2} = 1.6$

(n-factor of $SO_2 = 2$)

$\therefore \quad x = 1.6$

$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

$$K_c = \frac{\left(\frac{x}{2}\right)^2\left(\frac{x}{2\times 2}\right)}{\left[\frac{(4-x)}{2}\right]^2} = \frac{\left(\frac{1.6}{2}\right)^2\left(\frac{1.6}{4}\right)}{\left[\frac{4-1.6}{2}\right]^2} \quad (V = 2 \text{ litre})$$

$= 0.178$ mole litre^{-1}

61. (b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Also, $\Delta H^\circ = \Delta U^\circ + \Delta nRT$

$\therefore \quad \Delta H^\circ = 30\times 10^3 + 1\times 2\times 300$

$= 30600$ cal

$\therefore \quad \Delta G^\circ = 30600 - 300\times 100$

$= 600$ cal

$-\Delta G^\circ = RT \ln K_p$

$K_p = e^{-\Delta G^\circ/RT} = e^{-\frac{600}{2\times 300}} = e^{-1}$

62. (a) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$K_p = P'_{NH_3} \times P'_{H_2S} = \frac{P}{2}\times\frac{P}{2} = \frac{P^2}{4}$

$\Delta G^\circ = -RT \ln K_p = -RT \ln \frac{P^2}{4} = -RT \ln \frac{P^2}{2^2}$

$= -2RT[\ln P - \ln 2]$

63. (d) $\Delta G^\circ = -RT \ln K_p$

and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_p$

$\therefore \quad \ln K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

On comparing $\ln K_p = 4 - \frac{100}{T}$

$\therefore \quad \frac{\Delta S^\circ}{R} = 4$

$\Delta S^\circ = 4\times 2 = 8$ cal

64. (a) $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$;

$K_p = P_{CO_2} = 1.6$ atm

The reaction should favour forward direction as $Q < K_p$, but since $SrCO_3$ is not taken initially, reaction cannot take place in forward direction.

$SrO(s) + CO_2(g) \rightleftharpoons SrCO_3$;

$K_p = \frac{1}{1.6} = 0.625$ atm

Thus on increasing pressure, volume of container will decrease till P_{CO_2} becomes 1.6 atm having same mole of CO_2.

The reaction will attain equilibrium till $P = 0.625$

$\therefore$ Initial mole of $CO_2 = \frac{PV}{RT} = \frac{0.4\times 20}{RT} = \frac{8}{RT}$

At eq. $V = \frac{nRT}{P}$

$= \frac{8}{RT}\times\frac{RT}{1.6} = 5$ litre

65. (b) $2NH_3 \rightleftharpoons N_2 + 3H_2$; $\frac{1}{K_1} = \frac{[N_2][H_2]^3}{[NH_3]^2}$ ... (i)

$N_2 + O_2 \rightleftharpoons 2NO$; $K_2 = \frac{[NO]^2}{[N_2][O_2]}$ ... (ii)

$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$; $K_3^3 = \frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}$ ... (iii)

$$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$$

$$K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}}$$

By multiplying (i), (ii) and (iii),

$$\frac{1}{K_1}\times K_2 \times K_3^3 = \frac{[N_2][H_2]^3}{[NH_3]^2}\times\frac{[NO]^2}{[N_2][O_2]}\times\frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}$$

$$= \frac{[NO]^2\times[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = K$$

$\therefore \quad K = \frac{K_2\times K_3^2}{K_1}$

PREVIOUS YEARS PROBLEMS

1. For the reversible reaction :
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 500°C. The value of K_p is 1.44×10^{-5}, when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol L^{-1} is : **(IIT 2000)**
(a) $1.44 \times 10^{-5} / (0.082 \times 500)^2$
(b) $1.44 \times 10^{-5} / (8.314 \times 773)^2$
(c) $1.44 \times 10^{-5} / (0.082 \times 500)^2$
(d) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

2. When two reactants A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction : **(IIT 2000)**
(a) is zero (b) decrease with time
(c) independent of time (d) increase with time

3. At constant temperature, the equilibrium constant (K_P) for the decomposition reaction. $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = 4x^2 p / (1 - x^2)$ where, P is pressure, x is extent of decomposition. Which of the following statement is true ? **(IIT 2001)**
(a) K_p increases with increase of P
(b) K_p increases with increase of x
(c) K_p increases with decrease of x
(d) K_p remains constant with change in P or x

4. Consider the following equilibrium in a closed container : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$. At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α) : **(IIT 2002)**
(a) neither K_p nor α changes
(b) both K_p and α change
(c) K_p changes, but α does not change
(d) K_p does not change, but α changes

5. The following equilibrium are given :
$$N_2 + 3H_2 \rightleftharpoons 2NH_3; \; K_1$$
$$N_2 + O_2 \rightleftharpoons 2NO; \; K_2$$
$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O; \; K_3$$
The equilibrium constant of the reaction :
$$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$$
in terms of K_1, K_2 and K_3 is : **(IIT 2003)**
(a) $\frac{K_1 K_2}{K_3}$ (b) $\frac{K_1 K_2^2}{K_2}$
(c) $\frac{K_2 K_3^3}{K_1}$ (d) $K_1 K_2 K_3$

6. For the reaction : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; ΔH = –ve, the correct statement is : **(IIT 2006)**
(a) Addition of catalyst does not change K_p but changes ΔH.
(b) At equilibrium, $2G_{NH_3} = G_{N_2} + 3G_{H_2}$. ($G$ is Gibbs energy)
(c) At higher temperature, the rate of forward and backward reaction increases by a factor 2.
(d) At 400 K, addition of catalyst increase rate of forward reaction by 2 times and backward by 1.7 times

7. If $Ag^+ + NH_3 \; [Ag(NH_3)]^+$; $K_1 = 3.5 \times 10^{-3}$ and $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 = 1.74 \times 10^{-3}$ the formation constant of $[Ag(NH_3)_2]^+$ is : **(IIT 2006)**
(a) 6.08×10^{-6} (b) 6.08×10^{6}
(c) 6.08×10^{-9} (d) none of these

8. The value of $\log_{10} K$ for the reaction : $A \rightleftharpoons B$, if $\Delta H° = -54.07$ kJ mol^{-1} at 298 K, $\Delta S° = 10 JK^{-1}$ mol^{-1} at 298 K, R = 8.314 JK^{-1} mol^{-1} and 2.303×8.314×298 = 5705, is : **(IIT 2007)**
(a) 5 (b) 10
(c) 95 (d) 100

9. For the reaction $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$ if $K_P = K_C (RT)^x$ where the symbols have usual meaning then the value of x is : (assuming ideality) **[JEE (Main) 2014]**
(a) –1 (b) $-\frac{1}{2}$
(c) $\frac{1}{2}$ (d) 1

10. The following reaction is performed at 298 K.
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K ? ($K_p = 1.6 \times 10^{12}$) **[JEE (Main) 2015]**
(a) $R(298) \ln (1.6 \times 10^{12}) - 86600$
(b) $86600 + R(298) \ln (1.6 \times 10^{12})$
(c) $86600 - \frac{\ln (1.6 \times 10^{12})}{R (298)}$
(d) $0.5 [2 \times 86600 - R(298) \ln (1.6 \times 10^{12})]$

11. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$

and $[C]=\frac{1}{2}$. The reaction proceeds in the :

[R = 8.314 J/K/mol, e = 2.718] **[JEE (Main) 2015]**

(a) forward direction because $Q > K_c$

(b) reverse direction because $Q > K_c$

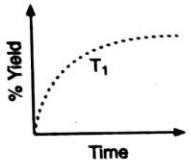
(c) forward direction because $Q < K_c$

(d) reverse direction because $Q < K_c$

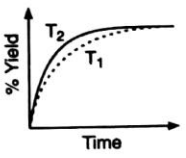
12. The % yield of ammonia as a function of time in the reaction **[JEE (Advanced I) 2015]**

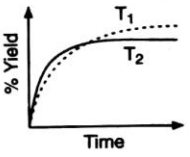
$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H<0$$

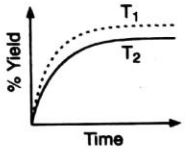
at (P, T_1) is given below :

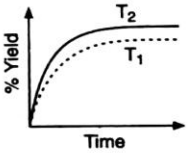


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by :

(a) 

(b) 

(c) 

(d) 

13. The equilibrium constant at 298 K for a reaction $A+B \rightleftharpoons C+D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be : **[JEE (Main) 2016]**

(a) 0.818 (b) 1.818

(c) 1.182 (d) 0.182

SOLUTIONS (Previous Year Problems)

1. (d) $K_p = K_c \times (RT)^{\Delta n}$;

Δn for the change $= 2-(1+3) = -2$

Thus, $K_p = K_c \times (RT)^{-2}$

or $K_c = \dfrac{K_p}{(RT)^{-2}} = \dfrac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

2. (d) At the initial state if only reactants are used $Q = 0$, but from initial stage to attain equilibrium is continuously increase with time till it because equal to K_c.

3. (d) K_P is a characteristic constant for a given reaction and changes only with temperature.

4. (d) For the reaction ; $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$$K_c = \frac{4\alpha^2 a^2}{(a-a\alpha)V} \quad ...(1)$$

where, a is initial mole on N_2O_4 in V litre vessel and α is degree of dissociation of N_2O_4.

If volume is reduced to $V/2$, the initial concentration of N_2O_4 becomes $\dfrac{\frac{a}{V}}{2} = \dfrac{2a}{V}$.

An increase in concentration of reactants leads to forward reaction, *i.e.*, the decomposition of N_2O_4 to have constant value of K_p.

5. (c) $K_1 = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ ...(i)

$K_2 = \dfrac{[NO]^2}{[N_2][O_2]}$ ...(ii)

$K_3 = \dfrac{[H_2O]}{[H_2]^2[O_2]^{1/2}}$ ...(iii)

$K = \dfrac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}}$

By inspection of (i), (ii) and (iii)

$$\frac{K_2 \times K_3^3}{K_1} = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[N_2][H_2]^3}{[NH_3]^2} \times \frac{[H_2O]^3}{[H_2]^3[O_2]^{3/2}}$$

$$= \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = K$$

6. (b) $\Delta G = 2G_{NH_3} - G_{N_2} - 3\times G_{H_2}$

and $\Delta G = 0$ at equilibrium.

7. (a) $K_1 = 3.5\times10^{-3} = \dfrac{[Ag(NH_3)]^+}{[Ag^+][NH_3]}$

$K_2 = 1.74\times10^{-3} = \dfrac{[Ag(NH_3)_2]^+}{[Ag(NH_3)^+[NH_3]}$

$K_3 = K_1 \times K_2 = \dfrac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$

$\therefore$ Formation constant K_3 for

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$

$K_3 = 3.5\times10^{-3} \times 1.74\times10^{-3}$

$= 6.08\times10^{-6}$

8. (b) $\Delta G^\circ = -2.303\,RT \log K$

$\Delta H^\circ - T\Delta S^\circ = -2.303\,RT \log K$

$[-54.07\times10^3 - 298\times10] = -2.303\times8.314\times298 \log K$

$\therefore \quad \log K = \dfrac{57050}{5705} = 10$

9. (b) $\Delta n_{(g)}$= (Number of product molecules − Number of reactant molecules) in gaseous state $= 1-\left(1+\frac{1}{2}\right) = -\frac{1}{2}$

10. (d) $\Delta G_f^\circ = 2\times G^\circ NO_2 - [2\times G_{NO}^\circ + G_{O_2}^\circ]$

$= 2G_{NO_2}^\circ - 2G_{NO}^\circ \qquad [G_{O_2}^\circ = 0]$

$\therefore \quad G_{NO_2}^\circ = \frac{1}{2}\Delta G_f^\circ + G_{NO}^\circ$

$= \frac{1}{2}[-RT \ln K_p] + G_{NO}^\circ$

$= \frac{1}{2}[-R\times298 \ln (1.6\times10^{12})] + 86600$

$= 0.5[-R\times298 \ln 1.6\times10^{12} + 2\times86600]$

11. (b) $Q = \dfrac{[B][C]}{[A]^2} = \dfrac{2\times\frac{1}{2}}{\left(\frac{1}{2}\right)^2} = 4$

$\Delta G^\circ = -2.303\,RT \log K_C$

$2494.2 = -2.303\times8.314\times300 \log K_C$

$\therefore \quad K_C = 0.36$

$\because \; Q > K_C$ thus backward reaction.

12. (c) The combination of N_2 and H_2 to give NH_3 takes place at slower rate if temperature is reduced to 473 K (200°C) because fewer energetic collisions occurs between molecules, however yield of NH_3 is 88%. On the other hand the combination occurs at faster rate at 723 K (450°C) but the yield of NH_3 is 15%. Actually it is the number of energetic collisions which really matters to lead a chemical reaction and the rate of reaction is reduced at low temperature (473 K). The 15% yield of NH_3 is better at 723 K because equilibrium is achieved earlier. The NH_3 formed is dissolved in water and is drained off as $NH_3(aq)$ from the system so that unreacted N_2 and H_2 recombines again to produce NH_3 in order to maintain constant value of K_c. Thus, all the N_2 and H_2 are converted to NH_3 with a faster rate.

13. (b)

	A +	B ⇌	C +	D
Concentration at $t=0$	1	1	1	1
Concentration at eq.	$1-x$	$1-x$	$1+x$	$1+x$

$\because \quad K_c = \dfrac{[C][D]}{[A][B]} = \dfrac{(1+x)^2}{(1-x)^2} = 100$

or $\dfrac{1+x}{1-x} = 10$

or $1+x = 10-10x$

$\therefore \quad x = \dfrac{9}{11}$

Now $[D] = 1+x = 1+\dfrac{9}{11} = 1.818$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statements :
   (a) An increase in pressure increases the boiling point of liquid.
   (b) An increase in pressure increases the melting point of water.
   (c) On spraying NaCl on ice, the melting point of ice is lowered and it does not melt.
   (d) The three phases of a substance exists at triple point only.
2. Which are heterogeneous systems ?
   (a) Ice $\rightleftharpoons$ Water (b) Water $\rightleftharpoons$ Liquid
   (c) $S_{Rhombic} \rightleftharpoons S_{Monoclinic}$ (d) $C_{Daimond} \rightleftharpoons C_{Amorphous}$
3. Select the incorrect statements :
   (a) K_P or K_c are dimensionless if pressure or concentrations are expressed in standard state.
   (b) The numerical value of K_P changes with experimental conditions, *i.e.* P, T and C at which equilibrium is attained.
   (c) Active mass of a reactant = concentration of reactant.
   (d) Dissolution of NH_3 in water obeys Henry's law.
4. Select the correct statements :
   (a) Volume of gas dissolved per unit volume of solvent $\propto (P)^{\circ}$ at constant T.
   (b) Amount of gas dissolved per unit volume of solvent $\propto P$ at constant T.
   (c) Mole fraction of gas dissolved per unit of solvent $\propto P$ at constant T.
   (d) Henry law is a special case of Nernst distribution law
5. A reaction $S_{8(g)} \rightleftharpoons 4S_{2(g)}$ is carried out by taking 2 mole of $S_{8(g)}$ and 0.2 mole of $S_{2(g)}$ in a reaction vessel of 1 litre. Which are correct if $K_c = 6.30 \times 10^{-6}$:
   (a) reaction quotient is 8×10^{-4}
   (b) reaction proceeds in backward direction
   (c) $K_p = 2.55$ atm^3
   (d) reaction proceeds in forward direction
6. The equilibrium is attained in a reaction as :

$$N_2 + 3H_2 \overset{\underset{Fe}{500\,K}}{\rightleftharpoons} 2NH_3;\ \Delta H = -ve.$$

   The yield of NH_3 can be predicted as :
   (a) the yield of NH_3 is lesser (15%) at 500 K than at 200 K (88%)
   (b) the reaction equilibrium at 500 K attains equilibrium earlier at 500 K than at 200 K
   (c) the yield of NH_3 can be increased by forcing a jet of water in vessel
   (d) the rate of forward reaction is faster at 500 K
7. Which are true for the reaction : $A_2 \rightleftharpoons 2C + D$?
   (a) If $\Delta H = 0$; K_p and dissociation of A_2 are independent of temperature
   (b) If $\Delta H = +ve$; K_p increases with temperature and dissociation of A_2 increases
   (c) If $\Delta H = -ve$; K_p decreases with temperature and dissociation of A_2 decreases
   (d) $K_p = 4\alpha^3\left[\frac{P}{1+2\alpha}\right]^2$
8. For given two equilibria attained in a container which are correct if degree of dissociation of A and A' are α and α'.
   $A_{(s)} \rightleftharpoons 2B_{(g)} + C_{(g)}$; $K_{p_1} = 8 \times 10^{-2}$
   $A'_{(s)} \rightleftharpoons 2B_{(g)} + D_{(g)}$; $K_{p_2} = 2 \times 10^{-2}$
   (a) $\frac{K_{p_1}}{K_{p_2}} = \left[\frac{(3\alpha'+2\alpha)}{(3\alpha+2\alpha')}\right]^3 \times \frac{\alpha}{\alpha'}$
   (b) $P'_C / P'_D = 4$
   (c) $P'_B = 2P'_C + 2P'_D$
   (d) $\alpha > \alpha'$
9. For the equilibrium at 298 K : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$; $G^{\circ}_{N_2O_4} = 100$ kJ mol^{-1} and $G^{\circ}_{NO_2} = 50$ kJ mol^{-1}. If 5 mole of N_2O_4 and 2 moles of NO_2 are taken initially in one litre container then which statements are correct :
   (a) Reaction proceeds in forward direction
   (b) $K_C = 1$
   (c) $\Delta G = -0.55$ kJ, $\Delta G^{\circ} = 0$
   (d) At equilibrium $[N_2O_4] = 4.894\,M$ and $[NO_2] = 0.212\,M$
10. Plots of log K *vs.* $\frac{1}{T}$ plots shows an intercept of 2 on Y-axis with a slope of 45° for the studied reaction. Which of the following are correct assuming ΔH° and ΔS° as temperature independent :
    (a) $\Delta S^{\circ} = 4.606$ cal (b) $\Delta H^{\circ} = -4.606$ cal
    (c) $\Delta G^{\circ} = -2.75$ kcal (d) $K = 100.8$
11. The rate of effusion of an equilibrium mixture in one litre vessel of at 300 K $A_2 \rightleftharpoons 2A$ through a pin hole is 0.707 times of rate of diffusion of O_2 under identical conditions of P and T. Which of the following are correct if at. wt. of A is 46 :
    (a) mole ratio of A / A_2 = 0.643
    (b) $K_c = 25.16$ mol / litre
    (c) $\Delta G^{\circ} = -8.01 \times 10^3$ J
    (d) molar mass of mixture = 64
12. For the gas phase reaction :
    $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal) carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) Increasing the temperature
(b) Decreasing the pressure
(c) Removing some H_2
(d) Adding some C_2H_6

13. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium :
(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

14. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$, is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?
(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 do not change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed

15. For the reaction, $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$. The forward reaction at constant temperature is favoured by :
(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

16. For the reaction,
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$$
at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by :
(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of $CO(g)$

17. Which of the following are correct :
(a) A plot of $\log K_p$ *vs* $\frac{1}{T}$ is linear
(b) A plot of $\log [x]$ *vs* time is linear for a I order reaction
(c) A plot of $\log P$ *vs* $\frac{1}{T}$ is linear at constant volume
(d) A plot of P *vs* $\frac{1}{V}$ is linear at constant temperature

18. In a flask, colourless N_2O_4 is in equilibrium with NO_2. At equilibrium when the flask is heated at 100°C, the brown colour deepens and on cooling it fades. Which statements are correct :
(a) $\Delta H = +$ ve (b) $\Delta H = -$ ve
(c) $\Delta S = +$ ve (d) $\Delta S = -$ ve

19. For the reaction : $X(g) \rightleftharpoons nY(g)$,
the degree of dissociation is α, then which one is not correct.
(a) $K_c = \frac{n^n \alpha^n}{(1-\alpha)} \text{mol}^{n-1}\text{litre}^{1-n}$
(b) $K_p = \left[\frac{n\alpha}{1-\alpha}\right]\left[\frac{P}{1-\alpha+n\alpha}\right]^{n-1} \text{atm}^{n-1}$
(c) $K_c = \frac{n\alpha^n}{(1-\alpha)n} \text{mol}^{n-1}\text{litre}^{1-n}$
(d) $K_p = \frac{(n\alpha)^n}{(1-\alpha)}\left[\frac{P}{1-\alpha+n\alpha}\right]^{n-1} \text{atm}^{n-1}$

20. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions.
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
For this equilibrium, the correct statement(s) is (are) :
[JEE (Advanced) II 2013]
(a) ΔH is dependent on T
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of the catalyst, if any

SOLUTIONS (More Than One Answer Correct)

1. (a,b,d,) On spraying NaCl on ice, m.pt. of ice is lowered and at melts earlier.
2. (a,b,c,d) Heterogeneous have $P > 1$; two solids have two phases.
3. (b,c,d) NH_3 show H-bonding with H_2O.
4. (a,b,c,d) Distribution of gas occurs between gaseous and solution phase.

$$\underset{\text{Phase I}}{\text{Gas}} + H_2O \rightleftharpoons \underset{\text{Phase II}}{\text{Solution}}$$

5. (a,c,d) $Q = \dfrac{[S_2]^4}{[S_8]} = \dfrac{(0.2)^4}{[2]} = 8\times10^{-4}$, $K_c = 6.3\times10^{-6}$

$$K_p = K_c \times (RT)^{\Delta n}$$

$$= 6.3\times10^{-6} \times (0.0821\times900)^3 = 2.55$$

Thus, reaction proceeds in backward direction since $Q > K_c$.

6. (a,b,c,d) All are facts about Haber's process. For concept of this reaction follow concepts of physical chemistry by P.Bahadur, Prakash publications, Muzaffarnagar.
7. (a,b,c,d)

$$\underset{1-\alpha}{A_2} \rightleftharpoons \underset{2\alpha}{2C} + \underset{\alpha}{D}$$

$$\therefore \quad K_p = (2\alpha)^2 \cdot \alpha \times \left[\frac{P}{\Delta n}\right]^2 = \frac{4\alpha^3 \cdot P^2}{(1+2\alpha)^2}$$

Use $2.303 \log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$ for effect of temperature on K.

8. (a,b,c,d)

$$\underset{2\alpha + 2\alpha'}{A_{(s)}} \rightleftharpoons \underset{\alpha}{2B_{(g)}} + C_{(g)}$$

$$\underset{2\alpha'+2\alpha}{A_s'} \rightleftharpoons \underset{\alpha'}{2B} + D$$

$$\therefore \quad K_{p_1} = (2\alpha + 2\alpha')^2 \alpha' \times \alpha \times \left[\frac{P}{(3\alpha + 2\alpha')}\right]^3$$

$$K_{p_2} = (2\alpha + 2\alpha')^2 \alpha' \times \left[\frac{P}{(3\alpha' + 2\alpha)}\right]^3$$

$$\therefore \quad \frac{K_{p_1}}{K_{p_2}} = \frac{[3\alpha'+2\alpha]^3}{[3\alpha + 2\alpha']^3} \times \frac{\alpha}{\alpha'}$$

Also, $K_{p_1} = (P_B')^2 \times P_C'$

$$K_{p_2} = (P_B')^2 \times P_D' \; ; \frac{P_C'}{P_D'} = \frac{K_{p_1}}{K_{p_2}} = \frac{8\times10^{-2}}{2\times10^{-2}} = 4$$

Also, $P_B' = 2\times(P_C' + P_D')$

$K_{p_1} > K_{p_2} \quad \therefore \; \alpha > \alpha_1$

9. (a,b,c,d) $\Delta G = \Delta G^\circ + 2.303 RT \log Q$

$$\Delta G^\circ = 2\times G^\circ_{NO_2} - G^\circ_{N_2O_4} = 2\times50 - 100 = 0$$

$$\therefore \; \Delta G = 0 + 2.303\times8.314\times10^{-3}\times298 \log\frac{2^2}{5} = 0 - 0.55\,\text{kJ}$$

$\therefore \; \Delta G = -0.55$ kJ *i.e.*, reaction proceeds in forward direction.

Also, $\Delta G^\circ = 0 = 2.303 RT \log K \quad \therefore \; K = 1$

Now,

$$\underset{5}{N_2O_4} \rightleftharpoons \underset{2}{2NO_2}$$

$$\underset{(5-x)}{} \qquad \underset{(2+2x)}{}$$

$$\therefore \quad 1 = \frac{(2+2x)^2}{(5-x)} \text{ or } x = 0.106$$

10. (b,c,d) $\Delta G^\circ = -2.303 RT \log K$,

$\Delta H^\circ - T\Delta S^\circ = -2.303 RT \log K$

$$2.303 \log K = -\frac{\Delta H^\circ}{R} + \frac{\Delta S^\circ}{R}, \text{Slope} = -\frac{\Delta H^\circ}{2.303R} = \tan 45^\circ$$

$$\therefore \quad \Delta H^\circ = -2.303\times2\times1\,\text{cal}$$

$$= -4.606\,\text{cal}, \text{Intercept} = \frac{\Delta S^\circ}{2.303R} = 2$$

$\therefore \; \Delta S^\circ = 2.303\times2\times2 = 9.212$ cal

$\therefore \; \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -4.606 - 298\times9.212$

$= -2.75$ kcal

11. (a,b,c,d) $\dfrac{r_m}{r_{O_2}} = \sqrt{\dfrac{M_{O_2}}{M_{mix}}} = \sqrt{\dfrac{32}{M}} = 0.707$ or $M = 64$

Let a mole of A_2 be present in mixture, then

$$\therefore \quad 64 = \frac{a\times92 + (100-a)\times46}{100}$$

$A = a = 39.13$ mole and $A_2 = 60.87$ mole

$$\therefore \quad K_C = \frac{[A]^2}{[A_2]} = \frac{(39.13)^2}{60.87} = 25.16;$$

$\Delta G^\circ = -2.303 RT \log K$

$\therefore \; \Delta G^\circ = -2.303\times300\times8.314\log25.16 = -8.01\times10^3$ J

12. (a,b,c,d) Increase in C_2H_4 means backward reaction predominates. This can be done by increasing T, decreasing P, lowering $[H_2]$, increasing $[C_2H_6]$ according to Le-Chatelier principle.
13. (c, d) $NaNO_3\,(s) \rightleftharpoons NaNO_2\,(s) + \frac{1}{2}O_2$;

ΔH = +ve for dissociation.

14. (a) No effect of addition of inert gas at constant volume. However, if addition is made at constant pressure answer will be (b). Both types are possible in closed container.
15. (c,d,e) Follow effect of addition of inert gas at constant P and Le-Chateliers principle.
16. (c) Forward reaction predominates if [reactants] is increased.
17. (a,c,d) Plots of $\log(a-x)$ *vs* time is linear for I order reaction.

18. (a,c) $N_2O_4 \rightleftharpoons 2NO_2$; $\Delta H = +ve$

The reaction absorbs heat and N_2O_4 shows decomposition. Also entropy increases due to the formation of 2 mole of NO_2 by 1 mole of N_2O_4.

19. (a,b)

$$\underset{1}{X(g)} \rightleftharpoons \underset{0}{nY(g)}$$
$$\underset{1-\alpha}{} \quad \underset{n\alpha}{}$$

$$\therefore \quad K_C = \frac{(n\alpha)^n}{(1-\alpha)} \text{mol}^{n-1} \text{ litre}^{1-n}$$

and $K_p = \frac{n\alpha}{(1-\alpha)} \times \left[\frac{P}{1-\alpha+n\alpha}\right]^{n-1} \text{atm}^{n-1}$

20. (a,b,d)

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$\Delta H_{T_2} - \Delta H_{T_1} = \Delta(nC_P)dT$

$\Delta(nC_P) \neq 1$

$\therefore$ ΔH is temperature dependent.

Equilibrium constant is not dependent on amount of $CaCO_3$ K remains constant with temperature since $K_p = P^1_{CO_2}$. Catalyst does not alter the heat of reaction.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : For the equilibrium : $NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2(g)$, one mole of NO_2 is placed in a vessel and allowed to attain the equilibrium at pressure 1 atm. Given that P_{NO} / P_{NO_2} at 700 K and 800 K are 0.872 and 2.5 respectively.

[1] K_p at 700 K and 800 K in $atm^{1/2}$ for the given reaction are respectively
(a) 13.632 (b) 0.585, 0.385 g
(c) 0.385, 1.30 (d) 1.30, 0.385

[2] Heat of reaction for the change is :
(a) 1.3632×10^3 J (b) 13.632 cal
(c) 13.632×10^3 cal (d) 13.632 J

[3] K_c for the given reaction at 700 K is :
(a) 0.02 (b) 0.01
(c) 0.03 (d) 0.04

Comprehension 2: Two solid compounds A and B dissociate into gaseous products at 20° C as
(i) $A(s) \rightleftharpoons A'(g) + H_2S(g)$
(ii) $B(s) \rightleftharpoons B'(g) + H_2S(g)$

At 20°C pressure over excess solid A is 50 mm and that over excess solid B is 68 mm.

[1] The dissociation constants of A and B in mm^2 are :
(a) 1156, 625 (b) 625, 1156
(c) 578, 312 (d) 312, 578

[2] Relative numbers of mole of A' and B' in the vapour phase over a mixture of the solids A and B are :
(a) 0.54 (b) 0.64
(c) 0.44 (d) 0.74

[3] The total pressure of gas over the solid mixture in mm is :
(a) 86.21 (b) 84.38
(c) 73.69 (d) 74.38

Comprehension 3 : 10 mole of NH_3 is heated at 15 atm from 27°C to 347°C assuming volume constant. The pressure at equilibrium is found to be 50 atm. The equilibrium constant for dissociation of NH_3 :

$$2NH_3 \rightleftharpoons N_2 + 3H_2; \ \Delta H = 91.94 \text{ kJ}$$

can be written as $K_p = \dfrac{P_{N_2} \times (P_{H_2})^3}{(P_{NH_3})^2} (\text{atm})^2$

[1] The degree of dissociation of NH_3 is :
(a) 61.3% (b) 20%
(c) 48% (d) none of these

[2] The equilibrium constant K_p for the reaction is :
(a) 7.08×10^2 (b) 3.06×10^2
(c) 7.6×10^2 (d) 1.53×10^3

[3] The volume of container in which gas is heated is :
(a) 16.42 litre (b) 8.21 litre
(c) 20 litre (d) 15 litre

[4] The increase in pressure and temperature on the reaction in equilibrium favours :
(a) forward reaction in both cases
(b) less dissociation of NH_3
(c) backward reaction and forward reaction respectively
(d) more formation of N_2 but less formation of H_2

[5] The vapour density of mixture at equilibrium is :
(a) 6.97 (b) 28.42
(c) 14.14 (d) 5.27

[6] The change in internal energy (in kJ) during the reaction is :
(a) 91.94 kJ (b) 81.63 kJ
(c) 102.25 kJ (d) 86.20 kJ

[7] The equilibrium constant for NH_3 at 247°C would be :
(a) 49.58 atm^2 (b) 45.28 atm^2
(c) 54.98 atm^2 (d) 40.18 atm^2

Comprehension 4 : For a reversible reaction at a certain temperature when it is at equilibrium or equilibrium has been attained whether physical or chemical, a change in certain variables might change the state of equilibrium. These variables include pressure, volume, concentration and temperature. Due to these changes, a system under equilibrium changes its state in such manner, *i.e.*, the equilibrium moves in forward direction or backward direction, so that the effect of change is annuled. For a gaseous phase endothermic decomposition of phosphorus pentachloride, can be made spontaneous by increasing concentration of PCl_5, lowering the pressure and increasing temperature of the system.

[1] Which of the following reactions proceeds in forward direction with increase in temperature are :
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 3000$ cal
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43200$ cal
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22400$ cal
(d) $C(s) + O_2(g) \longrightarrow CO_2(g) + 94300$ cal

[2] The equilibrium, solid $\rightleftharpoons$ liquid $\rightleftharpoons$ gas, will shift in forward direction when :
(a) temperature is raised (b) no effect of temperature
(c) temperature is lowered (d) pressure is increased

[3] The change in free energy for a reaction at equilibrium, *e.g.*, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, on addition of an inert gas at constant pressure and then at constant volume respectively are :
(a) decreases, no change (b) increases, no change
(c) no change, no change (d) no change, decreases

Comprehension 5 : Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G°$, of this reaction is positive. At the start of the reaction, there is one

mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : $R = 0.083$ L bar K^{-1} mol^{-1})

[1] The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is : **[JEE (Advanced) II 2016]**

(a) $\frac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (b) $\frac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

(c) $\frac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (d) $\frac{4\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

[2] The **INCORRECT** statement among the following, for this reaction, is : **[JEE (Advanced) II 2016]**

(a) Decrease in the total pressure will result in formation of more moles of gaseous X

(b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(c) $\beta_{equilibrium} = 0.7$

(d) $K_C < 1$

SOLUTIONS

Comprehension 1

$$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2$$

P	0	0
$P-P'$	P'	$\frac{P'}{2}$

[1] (c) **At 700 K**

Given, $\frac{P'}{P-P'} = 0.872$ at 700 K

$$P' = \frac{0.872P}{1.872} = 0.47P$$

Also, $P - P' + P' + \frac{P'}{2} = 1$

$$P + \frac{0.47P}{2} = 1$$

$\therefore$ $P = 0.81$ atm

$\therefore$ $P' = 0.47 \times 0.81 = 0.38$ atm

$\therefore$ $K_p = \frac{(P_{O_2})^{1/2} \times (P_{NO})}{(P_{NO_2})}$

$$= \frac{\left[\frac{0.38}{2}\right]^{1/2} \times 0.38}{(0.81-0.38)} = \mathbf{0.385\ atm^{1/2}}$$

Similarly, at 800 K $\frac{P'}{P-P'} = 2.5$ $\therefore$ $P' = 0.71P$

Also, $P + \frac{0.71P}{2} = 1$

$P = 0.74$ atm $\therefore$ $P' = 0.74 \times 0.71 = 0.53$ atm

$\therefore$ $K_P = \frac{\left[\frac{0.53}{2}\right]^{1/2} \times 0.53}{[0.74-0.53]} = \mathbf{1.30\ atm^{1/2}}$

[2] (c) Now, $2.303 \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$$2.303 \log \frac{1.30}{0.385} = \frac{\Delta H}{2}\left[\frac{100}{800 \times 700}\right]$$

$\therefore$ $\Delta H = \mathbf{13.632 \times 10^3\ cal}$

[3] (b) $K_p = K_c(RT)^{\Delta n}$

$0.385 = K_c \times (2 \times 700)^{1/2}$

$\therefore$ $K_c = 0.0102\ mol^{1/2}\ litre^{-1/2}$

Comprehension 2

[1] (b) For dissociation of $A(s) \rightleftharpoons A'(g) + H_2S(g)$

$\because$ $P'_{A'} + P'_{H_2S} = 50$

$\therefore$ $P'_{A'} = 25$ mm and $P'_{H_2S} = 25$ mm ($\because$ 1:1 ratio)

$K_{P_1} = P'_{A'} \times P'_{H_2S} = 25 \times 25 = \mathbf{625\ (mm)^2}$

Similarly, for $B(s) \rightleftharpoons B'(g) + H_2S(g)$

$K_{p_2} = P'_{B'} \times P'_{H_2S} = 34 \times 34 = \mathbf{1156\ (mm)^2}$

[2] (a) For mixture showing an equilibrium simultaneously,

$A(s) \rightleftharpoons A'(g) + H_2S$; $B(s) \rightleftharpoons B'(g) + H_2S$

Pressure after dissociation x x y y

$\therefore$ $K_{P_1} = x(x+y)$ and $K_{P_2} = y(x+y)$

$\therefore$ $\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y}$ $\therefore$ $\frac{x}{y} = \frac{625}{1156}$

$\because$ V and T are same and thus, ratio of pressure is ratio of mole, *i.e.*,

$$\frac{n_{A'}}{n_{B'}} = \frac{625}{1156} = \mathbf{0.5407}$$

[3] (b) $\because$ $\frac{x}{y} = \frac{625}{1156}$ and $x(x+y) = 625$

$\therefore$ $x = 14.81$ mm and $y = 27.38$ mm

$\therefore$ $P_T = P'_{A'} + P'_{B'} + P'_{H_2S} = x + y + (x+y)$

$= 2(x+y) = 2(14.81 + 27.38)$

$= \mathbf{84.38\ mm}$

Comprehension 3

[1] (a) $2NH_3 \rightleftharpoons N_2 + 3H_2$

10	0	0	at 300 K
(10–2x)	x	$3x$	at 620 K

Pressure increase due to increases in temperature as well as due to increase in mole.

Initially $P \propto T$

$\therefore$ $15 \propto 300$

$P \propto 620$

$\therefore$ $P = \frac{620}{300} \times 15 = 31$ atm of 10 mole of NH_3 at 620 K

Now, NH_3 is dissociated to attain 50 atm at 620 K.

Thus, $P \propto n$ or $10 \propto 31$

$10 + 2x \propto 50$

$\therefore$ $2x = 6.13$

$\therefore$ $\alpha = \frac{2x}{10} \times 100 = \frac{6.13 \times 100}{10} = \mathbf{61.3\%}$

[2] (d) $K_p = \frac{n_{N_2} \times (n_{H_2})^3}{(n_{NH_3})^2} \times \left[\frac{P}{\Sigma n}\right]^2$

$$= \frac{\frac{6.13}{2} \times \left[\frac{6.13 \times 3}{2}\right]^3}{[10-6.13]^2} \times \left[\frac{50}{10+6.13}\right]^2$$

$= \mathbf{1.528 \times 10^3\ atm^2}$

[3] (a) $PV = nRT$

$15 \times V = 10 \times 0.0821 \times 300$

$\therefore V = \mathbf{16.42\ litre}$

[4] (c) Increase in pressure favours the reaction showing decrease in volume, *i.e.*, backward reaction and increase in temperature favours endothermic reaction, *i.e.*, forward one.

[5] (d) V.D. $= \frac{\text{Molar mass}}{2}$

$$= \frac{3.87\times 17+\frac{6.13}{2}\times 28+\frac{6.13}{2}\times 3\times 2}{2\times\left[3.87+\frac{6.13}{2}+\frac{6.13}{2}\times 3\right]} = \mathbf{5.27}$$

[6] (b) $\Delta H = \Delta U + \Delta nRT$

$\therefore \Delta U = 91940 - 2\times 8.314\times 620 = \mathbf{81630.6\ J}$

[7] (a) $2.303\log\frac{K_{P_2}}{1.53\times 10^3} = \frac{91940}{8.314}\left[\frac{-100}{620\times 520}\right]$

$\therefore K_{P_2} = \mathbf{49.58\ atm^2}$

Comprehension 4

[1] (b) Endothermic reactions are favoured with increase in temperature.

$N_2 + O_2 \longrightarrow 2NO;\ \Delta H = +ve$ (Endothermic)

[2] (a) Increase in temperature will favour the change showing absorption of heat.

[3] (a) At equilibrium, addition of inert gas at constant V does not change pressure, the condition. However addition at constant pressure, the equilibrium get shifted to right. No doubt ΔG° remains constant but ΔG decrease as the reaction goes spontaneously in forward direction to attain new equilibrium conditions.

Comprehension 5

[1] (b) Given,

$$X_2(g) \rightleftharpoons 2X(g)$$

Initial mole	1	0
At. eq.	$(1-a)$	$2a$

Where a mole of X_2 are decomposed at equilibrium

Given $2a = \beta_{\text{equilibrium}}$

So $a = \frac{\beta_{\text{equilibrium}}}{2}$

Total mole at equilibrium $= (1+a) = \left[1+\left(\frac{\beta_{eq}}{2}\right)\right]$

Let P_T be total pressure at equilibrium

$$K_P = \frac{(n_X)^2}{n_{X_2}}\times\left[\frac{P}{\Sigma n}\right]^1$$

So $$K_P = \frac{\left[\frac{2\beta_{eq}}{2}\right]^2}{\left[1-\frac{\beta_{eq}}{2}\right]}\times\left[\frac{P}{1+\frac{\beta_{eq}}{2}}\right]^1$$

$$K_P = \frac{4\beta_{eq}^2}{4-\beta_{eq}^2}\times P_T = \left(\frac{8\beta_{eq}^2}{4-\beta_{eq}^2}\right) \qquad (\because P_T = 2\ \text{bar})$$

[2] (c)

(a) is correct as on decreasing pressure reaction proceeds in the direction where no. of gaseous molecules increase *i.e.*, forward reaction.

(b) is correct. No doubt ΔG is positive but since given dissociation takes place at 298 K and equilibrium is attained. At the start of reaction $Q_P < K_P$ so dissociation of X_2 take place spontaneously.

$$Q_P = \left[\frac{(P_X)^2}{P_{X_2}}\right] = 0$$

(c) is incorrect, $K_P = \frac{8\beta_{eq}^2}{4-\beta_{eq}^2} = \frac{8\times(0.7)^2}{4-(0.7)^2} > 1$

(d) is correct.

As ΔG° positive and $\Delta G^\circ = -RT\ln K_P$

So K_P should be less than 1.

So $K_P < 1$

$K_P = K_C(RT)^{\Delta n_{(g)}}$ $\quad [\Delta n_{(g)} = 1]$

$K_C = \frac{K_P}{RT}$

$K_C < K_P$ So $K_C < 1$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E). Choose the correct answers from the codes (a), (b), (c) and (d) given for each question :

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. S : Recent convention to represent K_p is dimensionless.
   E : The standard state of pure gas is 1 bar and the partial pressure of reactants and products measured with respect to this standard are used to determine K_p for the equilibrium.
   $$A(g) + 2B(g) \longrightarrow C(g)$$
2. S : A reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$; has K_p at 298 K and 500 K as 4.0×10^{24} and 8.5×10^{10} respectively.
   E : The E_a for the forward reaction is lesser than E_b for the backward reaction.
3. S : K_c, K_p and K_x are the equilibrium constant of a reaction in terms of concentration, pressure and mole fraction respectively.
   E : The values of K_c or K_p or K_x change with temperature.
4. S : Vapour pressure of H_2O is constant at given temperature.
   E : The equilibrium $H_2O(l) \rightleftharpoons H_2O(v)$ at a temperature has $K_p = P_{H_2O}$ and K_p is constant at the given temperature.
5. S : A dynamic equilibrium means a balance between the tendency towards minimum and maximum enthalpies.
   E : The reaction having ΔH = – ve; occurs from high enthalpy side to low enthalpy side and the reaction ΔH = + ve; occurs from low enthalpy side to high enthalpy side.
6. S : Melting of ice at 10°C is a reversible process.
   E : Evaporation of water at 100°C and 1 atm pressure is a reversible process.
7. S : The equilibrium in physical system is also dynamic in nature.
   E : The equilibrium ice $\rightleftharpoons$ water is static in nature.
8. S : An increase in temperature disturbs,
   Gas + Solvent $\rightleftharpoons$ Solution, in backward direction.
   E : Gaseous molecules escape out of solution due to increase in kinetic energy.
9. S : The m.pt. of ice is lowered on increasing the pressure, whereas m.pt. of solids other than ice is raised upon increasing pressure.
   E : Ice show H-bonding and leads to the three dimensional solid of more volume.
10. S : The red colour shown by $[Fe(SCN)]^{2+}$ (aq) in a reversible reaction between Fe^{3+} and SCN^-
    $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$ deepens if few more drops KCNS are added in equilibrium mixture.
    E : Addition of KCNS favours backward reaction.
11. S : Water boils at higher temperature in pressure cooker.
    E : Increase in pressure leads an increase in boiling temperature.
12. S : Snow does not melt easily at mountains.
    E : A decrease in pressure leads to an increase in freezing point.
13. S : The solubility of gases always increases with increase in pressure.
    E : High pressure favours the change where volume decreases.
14. S : The melting point of solid (except ice) increases with increase in pressure
    E : An increase in pressure favours the change where volume decreases.
15. S : Addition of an inert gas at constant pressure to dissociation equilibrium of $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ favours forward reaction.
    E : $K_c = \dfrac{\alpha^2}{V(1-\alpha)}$ for the dissociation equilibrium of PCl_5 where α is degree of dissociation of PCl_5.
16. S : $\Delta G = \Delta G° + 2.303RT \log Q$, where Q is reaction quotient.
    E : Q may be greater or lesser than K_c but equal to K_c, if $\Delta G = 0$.
17. S : The equilibrium constant K_c or K_p has the unit (mol litre^{-1})$^{\Delta n}$ or (atm)$^{\Delta n}$ respectively.
    E : The numerical value of $K_c = K_p$ at $\Delta n = 0$.
18. S : A catalyst does not influence equilibrium constant of reaction but it simply helps in attaining the equilibrium earlier.
    E : A catalyst increases both the rate of forward reaction and backward reaction.
19. S : The synthesis of NH_3 in Haber's process needs 500°C and 200 atm pressure inspite of the fact that reaction is favoured at high P and low T according to Le Chatelier's principle.
    E : The high temperature is required to attain higher energy of activation for the reaction because bond energy of N_2 and H_2 are high.

20. **S :** The equilibrium constant may show higher or lower values with increase in temperature.
E : The change depends on the heat of reaction at equilibrium.

21. **S :** The dissociation of PCl_5 decreases on increasing pressure.
E : An increase in pressure favours the forward reaction.

22. **S :** When a soda water bottle is opened, the gas fizzes out.
E : Sealed soda water bottle contains CO_2 gas dissolved at high pressure. On releasing seal, the pressure decreases and CO_2 comes out.

23. **S :** The solubility of a gas in water decreases with rise in temperature.
E : Rise in temperature increases the kinetic energy of gaseous molecules dissolved in water.

24. **S :** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
E : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **[IIT 2008]**

25. **S :** The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at high temperature.
E : When a system in equilibrium is disturbed by changing the temperature. It will tend to adjust itself so as to overcome of the effect of change. **[IIT 2008]**

ANSWERS (Statement Explanation Problems)

1. (c) Let partial of reactants and products are a, b, c bar respectively with respect to standard state, then
For $A(g)+2B(g)\longrightarrow C(g)$
$P'_A=\frac{a\text{ bar}}{1\text{ bar}}=a$; Similarly, $P'_B=b$ and $P'_C=c$.
Thus, $K_c=\frac{a\times b^2}{c}$ is dimensionless.

2. (c) K_p decreases with temperature and thus, $\Delta H=-$ve. Also, $\Delta H=E_a(f)-E_a(b)$. The negative value of ΔH is possible only when $E_a(b)>E_a(f)$.

3. (d) Consider a reaction : $aA\rightleftharpoons bB$

$$K_c=\frac{[B]^b}{[A]^a};\quad K_p=\frac{(P'_B)^b}{(P'_A)^a}$$

$$\because\quad K_p=\frac{(P'_B)^b}{(P'_A)^a}=\frac{(P_T\cdot X_B)^b}{(P_T\cdot X_A)^a}=\frac{(X_B)^b}{(X_A)^a}\times(P_T)^{b-a}$$

$$K_p=K_x\times(P_T)^{b-a}$$

or $$K_x=K_p\times(P_T)^{a-b}=K_P(P_T)^{-\Delta n}$$

Thus, eq. constant K_c,K_p or K_x varies with temperature.

4. (c) Explanation is correct reason for statement.

5. (c) $A+B\rightleftharpoons C+D$; $\Delta H=+$ ve, then
$C+D\rightleftharpoons A+B$; $\Delta H=-$ ve, *i.e.*, a balance in enthalpies is noticed at equilibrium.

6. (b) Water $\rightleftharpoons$ Vapour at b.pt. V.P. = 760 mm.

7. (a) Ice $\rightleftharpoons$ Water shows dynamic equilibrium.

8. (c) Explanation is correct reason for statement.

9. (c) Ice $\rightleftharpoons$ Water
$V_S>V_W$
Thus, forward reaction occurs on increasing pressure, *i.e.*, more ice will melt or m.pt. is lowered.
Solid $\rightleftharpoons$ Liquid
$V_S<V_L$
Thus, more solid will be formed on increasing pressure.

10. (a) Addition of KCNS favours forward reaction.

11. (c) Boiling of a liquid occurs when its vapour pressure becomes equal to atmospheric pressure.

12. (c) Ice $\rightleftharpoons$ water, increase in pressure leads to melting of ice as it favours the change showing decrease in volume.

13. (c) Gas + solvent $\rightleftharpoons$ solution; Increase in pressure leads to the change showing decrease in volume.

14. (c) Solid $\rightleftharpoons$ Liquid $V_L>V_S$; follow answer 12.

15. (c) Inert gas addition at constant pressure leads to an increase in volume. To have K_c constant 'α' must increase.

16. (d) $Q<K_c$ forward reaction
$Q>K_c$ backward reaction
$Q=K_c$ if $\Delta G=0$

17. (d) $\Delta n=0$
$\therefore\quad K_p=K_c$

18. (c) Explanation is correct reason for statement.

19. (c) Explanation is correct reason for statement.

20. (c) $2.303\log\frac{K_{c_2}}{K_{c_1}}=\frac{\Delta H}{R}\frac{[T_2-T_1]}{T_1T_2}$; if $\Delta H=-$ ve, $K_{c_2}<K_{c_1}$
if $\Delta H=+$ve, $K_{c_2}>K_{c_1}$

21. (a) $PCl_5\rightleftharpoons PCl_3+Cl_2$
$\underset{1-\alpha}{1}\qquad\underset{\alpha}{0}\qquad\underset{\alpha}{0}$

$$K_p=\left[\frac{\alpha^2}{1-\alpha}\right]\left[\frac{P}{1+\alpha}\right]^1$$

An increase in pressure will decrease α, to have K_p constant and thus backward reaction occurs.

22. (c) Explanation is correct reason for statement.

23. (c) Explanation is correct reason for statement.

24. (b) $\Delta G^\circ\neq 0$ at equilibrium
$\Delta G=0$ at equilibrium

25. (b) Follow Le Chatelier's principle.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List-I Reaction	List-II Degree of dissociation 'α' (Assume $\alpha << 1$)
A. $2X_{(g)} \rightleftharpoons 3Y_{(g)} + Z_{(g)}$	a. $\alpha = \sqrt{\frac{K_c}{V}} \times 3$
B. $4X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$	b. $\alpha = [2K_cV]^{1/3}$
C. $2X_{(g)} \rightleftharpoons Y_{(g)} + 2Z_{(g)}$	c. $\alpha = \frac{4}{V}\sqrt{K_c}$
D. $3X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$	d. $\alpha = \left[\frac{16V^2K_c}{27}\right]^{1/4}$

2.

List-I	List-II $\Delta_o S$ in cal and $\Delta_r H$ in kcal respectively
A. $\ln K = 2 - \frac{1000}{T}$	a. 8, 2
B. $\ln K = \frac{1}{2} - \frac{500}{T}$	b. 4, 2
C. $\ln K = 4 - \frac{1000}{T}$	c. 1, 1
D. $\ln K = 3 - \frac{4000}{T}$	d. 6, 8

3.

List-A	List-B
(A) $A(g) + B(g) \rightleftharpoons AB(g)$	1. Addition of inert gas at constant P shows forward shift
(B) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$	2. Addition of inert gas at constant P shows backward shift
(C) $A(s) \rightleftharpoons B(g) + C(g)$	3. No effect on addition of inert gas at constant P or V
(D) $AB_3(g) \rightleftharpoons \frac{1}{2}A_2(g) + \frac{3}{2}B_2(g)$	4. No effect on addition of small amount of reactant

Type II : More Than One Match Are Possible

4.

List-A	List-B
(A) $\log_e K$ vs. $\frac{1}{T}$ plots	1. Slope $= -\frac{\Delta H^\circ}{R}$
(B) Exothermic reaction	2. Intercept $= \frac{\Delta S^\circ}{R}$
(C) Endothermic reaction	3. $K > 1$ if ΔH° is large and negative
	4. $K < 1$ if ΔH° is large and positive
	5. $K > 1$ if ΔS° is large and positive and $\Delta S^\circ > \Delta H^\circ$
	6. $K < 1$ if ΔH° is small and negative and ΔS° is large and negative

5.

List A	List B
(A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	1. High P
(B) $2SO_3 \rightleftharpoons 2SO_2 + O_2$	2. Low T
(C) Melting of ice	3. 88% yield at 200°C
(D) $N_2 + O_2 \rightleftharpoons 2NO$	4. 15% yield at 500°C
	5. High T
	6. Low P

6.

List-A	List-B
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$; ΔH = –ve	1. K increases with increase in T
(B) $N_2(g) + O_2(g) \rightleftharpoons 2NO_2$; ΔH = +ve	2. K decreases with increase in T
(C) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; ΔH = +ve	3. No effect of P on equilibrium
(D) $A(g) + B(g) \rightleftharpoons 2C(g) + D(g)$; ΔH = +ve	4. Addition of inert gas at constant P give more products

ANSWERS

1. A–d; B–c; C–b; D–a
2. A–b; B–c; C–a; D–d
3. A–2; B–3; C– 4; D–1
4. A– 1,2; B–3,6; C– 4,5;
5. A–1,2,3,4; B–5,6; C–1,5; D–5
6. A–2; B–1,3; C–1,4; D–1,4

13 Ionic Equilibrium

Ostwald dilution law : The dissociation of weak electrolyte obeys law of mass action. The application of law of mass action to weak electrolyte is known as Ostwald dilution law. **It is to be noted here, that either acids or bases are weak electrolytes but salts are usually strong electrolytes.**

Consider a weak electrolyte say HA (an acid)

$$HA \rightleftharpoons H^+ + A^-$$

Before dissociation	1	0	0
After dissociation	$1-\alpha$	α	α

Where α is degree of dissociation.

Let C be the concentration of HA in mol litre^{-1} before its dissociation then, $[HA]=C(1-\alpha)$; $[H^+]=C\alpha$; $[A^-]=C\alpha$

According to law of mass action

$$K_a=\frac{[H^+][A^-]}{[HA]}=\frac{(C\alpha\cdot C\alpha)}{C(1-\alpha)}=\frac{C\alpha^2}{1-\alpha}$$

If α is small, then $1-\alpha\approx 1$.

$$K_a=C\alpha^2 \quad ...(1)$$

or $$\alpha=\sqrt{\left(\frac{K_a}{C}\right)} \quad ...(2)$$

where K_a is dissociation constant of acid.

Similarly, for a weak base

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b=C\alpha^2 \quad ...(3)$$

$\therefore$ $$\alpha=\sqrt{\left(\frac{K_b}{C}\right)} \quad ...(4)$$

where K_b is dissociation constant of base.

Note: 1. K_a and K_b are just the equilibrium constants and hence depend only on temperature.

2. Greater are the values of K_a or K_b more is the strength of acid or base respectively.

3. Relations 1 to 4 are valid for mono basic acid and mono acid base.

4. Different expressions have to be derived for dibasic or tribasic acids and diacidic or triacidic base.

Acid and base

Arrhenius concept

(1) An acid furnishes H^+ ions in solution and a base furnishes OH^- ions in solutions

(2) The strength of acid depends upon its tendency to furnish H^+ ions.

Bronsted concept

(1) An acid is a proton donor; a base is a proton acceptor.

(2) The strength of an acid depends upon its tendency to donate proton. More is the tendency to donate proton, more is acidic nature.

(3) Water is amphoteric as it donates as well as accepts proton.

$$H_2O+H_2O \rightleftharpoons OH^- + H_3O^+$$

(4) Each cation is acid and each anion is base.

(5) A pair of acid and base which differ by a proton is known as conjugate pair of acid and base.

$$\text{Acid } (H_2S) \xrightarrow[\text{or } -H^+]{\text{Take out one proton}} \text{Conjugate base } (HS^-)$$

$$\text{Base } (NH_3) \xrightarrow[\text{or } +H^+]{\text{Add one proton}} \text{Conjugated base } (NH_4^+)$$

Lewis concept

(1) Acids are electron pair acceptor, *e.g.*, BF_3, $AlCl_3$.

(2) Bases are electron pair donor, *e.g.*, NH_3, PCl_3.

Relative strength of Acids and Bases :

For weak acids :

$$\text{Relative strength}=\frac{\text{Strength of I acid}}{\text{Strength II acid}}$$

$$=\frac{[H^+]\text{furnished by I acid}}{[H^+]\text{furnished by II acid}}=\frac{C_1\alpha_1}{C_2\alpha_2}$$

$$=\frac{C_1}{C_2}\times\sqrt{\left(\frac{K_{a_1}C_2}{K_{a_2}C_1}\right)}=\sqrt{\left(\frac{K_{a_1}C_1}{K_{a_2}C_2}\right)} \quad ...(5)$$

$$=\sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)}\ (\text{if } C_1=C_2) \quad ...(6)$$

For strong acids :

$$\text{Relative strength} = \frac{K_1}{K_2}$$

$$= \frac{\text{rate constant for a reaction catalysed by I acid}}{\text{rate constant for a reaction catalysed by II acid}}$$

Note : For rate constant of acid catalysed reactions, see ester hydrolysis and sugar hydrolysis in **chemical kinetics.**

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Ionic product of water : Pure water, a weak electrolyte dissociates as

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\therefore \quad K = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{(According to law of mass action)}$$

$$\text{or} \quad K_w = K[H_2O] = [H^+][OH^-] \quad \ldots(7)$$

$\because$ $[H_2O]$ is constant since only one molecule out of 550 million molecules of H_2O dissociates, *i.e.*, $\alpha_{H_2O} = \frac{1}{550 \times 10^6}$

$$\alpha_{H_2O} = 1.8 \times 10^{-9} = 1.8 \times 10^{-7}\%$$

here K_w is a characteristic constant for water, known as ionic product of water. The numerical value of K_w is 10^{-14} mol^2 $litre^{-2}$ at 25°C. The value of K_w however increases with increase in temperature.

pH and pOH values : Sorenson used a new term to express $[H^+]$ as pH defined as the negative power raised on 10 in order to express $[H^+]$.

i.e., $$[H^+] = 10^{-pH} \quad \ldots(8)$$

or $$pH = -\log[H^+] \quad \ldots(9)$$

(*i.e.*, negative logarithm of **magnitude of $[H^+]$**)

Thus, for pure water pH = 7 *i.e.*, Neutral solution
pH = 0 to 7 *i.e.*, Acidic solution
pH = 7 to 14 *i.e.*, Alkaline solution

Also $\because$ $[H^+][OH^-] = 10^{-14}$

$$\therefore \quad (-\log H^+) + (-\log OH^-) = 14$$

$$\therefore \quad \mathbf{pH + pOH = 14} \quad \ldots(10)$$

Common ion effect : The phenomenon in which degree of dissociation of a **weak electrolyte** is suppressed due to the presence of **common ion** present in it.

Consider a weak electrolyte along with common ion, *e.g.*,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$\text{For acetic acid } K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Thus, $[CH_3COO^-]$ in solution becomes more in presence of CH_3COONa. However K_a is constant. Thus, in order to have K_a constant, $[H^+]$ in solution must decrease or $[CH_3COOH]$, *i.e.*, undissociated acid must increase or in other words degree of dissociation of CH_3COOH decreases.

Note : In presence of a common ion (from strong electrolyte) present with weak electrolyte, the concentration of common ion is derived from strong electrolyte.

Buffer solutions : Solutions which possess reserve acidic nature or alkaline nature or solutions which resist change or do not show significant change in pH due to dilution or addition of small quantities of acid or alkali are known as buffer solutions.

Types of buffer solutions :

(1) Simple buffer : Salts of weak acid and weak base,
e.g., CH_3COONH_4, NH_4CN, etc.

(2) Mixed buffers : These are of two types.

(a) Acidic buffer mixtures : A weak acid + its salts or its conjugate base
e.g., $CH_3COOH + CH_3COONa$

(b) Basic buffer mixtures : A weak base + its salt or its conjugate acid
e.g., $NH_4OH + NH_4Cl$

Handerson equation for pH and pOH of mixed buffers

Acidic buffer mixtures : Consider a buffer mixture of weak acid + its conjugate base *i.e.*, $CH_3COOH + CH_3COONa$

Then $$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad \ldots(A)$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \ldots(B)$$

Applying law of mass action to Eq. (B)

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad \text{or} \quad [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

or $$-\log H^+ = -\log K_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

or $$pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} \quad \ldots(11)$$

$$pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} \quad \ldots(12)$$

Similarly for basic buffers *i.e.*, A weak base + its conjugate acid

$$pOH = -\log K_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]} \quad \ldots(13)$$

or $$pOH = pK_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]} \quad \ldots(14)$$

Addition of acid or base to a buffer : The anion of salt consumes H^+ given by acid and thus, [anion] in buffer decreases and [acid] in buffer increases and pH changes slightly.

$$H^+ + \text{Anion} \longrightarrow \text{Acid}$$

The undissociated acid consumes OH^- given by alkali and thus, [anion] in buffer increases and [acid] in buffer decreases which results a change in pH slightly.

$$OH^- + \text{Acid} \longrightarrow \text{Anion}$$

Similarly, acid or alkali addition brings in following changes in basic buffer solutions.

$$H^+ + \text{Base} \longrightarrow \text{Cation}$$

$$OH^- + \text{Cation} \longrightarrow \text{Base}$$

Note: No doubt pH of buffer solutions experimentally remains unchanged on addition of small amount of acid or base but it change theoretically to a very small extent which however cannot be detected by pH meters.

Buffer capacity : The property of a buffer solution to which it resist the change in pH on addition of acid or alkali. It is expressed as :

$$\phi = \frac{d(b)}{d\text{pH}} \qquad ...(15)$$

where b is no. of mole of acid or base added to one litre solution and dpH is change in pH.

e.g., suppose pH of buffer changes from 4.745 to 4.832 when 0.01 mole of KOH is added to 0.5 litre buffer.

$$\phi = \frac{0.01 \times 2}{0.087} = 0.230$$

pK_a and pK_b for a conjugate acid-base pair

$$pK_a + pK_b = pK_w = 14 \qquad ...(16)$$

Note : 1. Stronger is acid, weaker is its conjugate base.

2. Higher is the value of pK_a of an acid, lower is acid strength and higher is basic strength of its conjugate base.

Solubility product : Consider a sparingly soluble salts in water. Let solubility of it be s mol litre^{-1}.

$$A_xB_y(s) + aq. \rightleftharpoons A_xB_y(aq.)$$

$$\text{or } A_xB_y(s) + aq. \rightleftharpoons \underset{xs}{xA^{+y}} + \underset{ys}{yB^{-x}}$$

ions furnished after dissociation

According to law of mass action,

$$K = \frac{[A^{+y}]^x[B^{-x}]^y}{[A_xB_y]} \text{ or } K[A_xB_y] = [A^{+y}]^x[B^{-x}]^y$$

$$K_{sp} = [A^{+y}]^x[B^{-x}]^y \qquad ...(17)$$

where K_{sp} is a characteristic constant for a given solute known as solubility product and defined as the product of ionic concentrations with suitable powers. K_{sp} however changes with temperature.

Putting $[A^{+y}] = xs$ and $[B^{-x}] = ys$ in Eq. (17);

$$K_{sp} = (xs)^x(ys)^y = x^x \cdot y^y(s)^{x+y} \qquad ...(18)$$

e.g., For AgCl

$$\therefore AgCl(s) + aq. \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Cl^-};\ K_{sp} = s^2$$

For Ag_2CrO_4

$$\because Ag_2CrO_4(s) + aq. \rightleftharpoons \underset{2s}{2Ag} + \underset{s}{CrO_4^{2-}};\ K_{sp} = 4s^3$$

Now if

$[A^{+y}]^x[B^{-x}]^y > K_{sp}$; The solid A_xB_y will precipitate out

$[A^{+y}]^x[B^{-x}]^y < K_{sp}$; No precipitation

$[A^{+y}]^x[B^{-x}]^y = K_{sp}$; No precipitation upto this limit or precipitation will just start at this condition. This is a limiting case.

Effect of common ion on solubility

Consider saturated solution of AgCl. If a salt having either of the ion common to AgCl say KCl is added to it, then

$$AgCl(s) + aq. \rightleftharpoons Ag^+ + Cl^-$$

$$KCl + aq. \longrightarrow K^+ + Cl^-$$

For AgCl : $K_{sp} = [Ag^+][Cl^-]$

$[Cl^-]$ increases in solution due to presence of KCl and thus to have K_{sp} constant, $[Ag^+]$ will decrease or AgCl will precipitate out from solution, *i.e.*, solubility of AgCl will decrease with increasing concentration of KCl in solution.

Let 0.1 M KCl($aq.$) solution with AgCl($aq.$). If solubility of AgCl is s mol litre^{-1}, then

For AgCl : $K_{sp} = [Ag^+][Cl^-]$

$$K_{sp} = s(s + 0.1)$$

s being small in comparison to 0.1 and thus may be neglected therefore,

$$K_{sp} = s \times 0.1 \text{ or } s_{AgCl} = \frac{K_{sp}}{0.1}$$

where s is solubility of AgCl in presence of 0.1 M KCl($aq.$).

Note: 1. A solute on addition if undergoes complex formation with ions of sparingly soluble salt, the solubility of salt increases.

2. The solubility of sparingly soluble salt say AgCN is also influenced if the salt undergoes hydrolysis. Normally solubility of salts increases with hydrolysis.

Simultaneous solubility : The phenomenon when two or more sparingly soluble salts having one ion common (either cation AgCl and AgBr or anion $BaSO_4$ and $CaSO_4$) leads to simultaneous solubility equilibria. For example.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$AgBr \rightleftharpoons Ag^+ + Br^-$$

$$K_{sp}\ AgCl = [Ag^+][Cl^-]$$

$$K_{sp}\ AgBr = [Ag^+][Br^-]$$

Thus if both are present $[Ag^+]$ should be same

$$\text{or } \frac{K_{sp}AgCl}{K_{sp}AgBr} = \frac{[Cl^-]}{[Br^-]}$$

Hydrolysis : The phenomenon in which anion or cation furnished by a salt interacts with H_2O to produce acidic nature or alkaline nature is known as salt hydrolysis.

The nature of aqueous solution of salt to be acidic or alkaline depends upon the nature of salt.

Salts of strong acid and weak base : *e.g.*, NH_4Cl, NH_4NO_3, $CuSO_4$, $ZnCl_2$, $FeCl_3$, etc.

$$NH_4Cl + H_2O \rightleftharpoons \underset{\text{weak}}{NH_4OH} + \underset{\text{Strong electrolyte}}{HCl}$$

or $$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

or $$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

NH_4Cl on dissolution in water furnish NH_4^+ and Cl^- ion. Cl^- with H^+ gives HCl, a strong acid which returns back all the H^+ to solution. On the other hand NH_4^+ interacts with OH^- to give NH_4OH, a weak electrolyte having low degree of dissociation. Also due to common ion effect of unhydrolysed NH_4^+, the degree of dissociation of NH_4OH is further suppressed and thus in solution the $[H^+]$ becomes more and it acquires acidic character. It is thus suggested that acidic character of NH_4Cl solution is due to hydrolysis of NH_4^+ ion or the hydrolysis of weak component of salt.

Hydrolysis constant and degree of hydrolysis : Consider a salt say NH_4Cl in water. Let C mol litre^{-1} be the concentration of salt and h the degree of hydrolysis of salt.

	NH_4Cl	$+ H_2O \rightleftharpoons$	NH_4OH	$+ HCl$
Before hydrolysis	1	0	0	0
After hydrolysis	$(1-h)$	h	h	h

or $$\underset{(1-h)}{NH_4^+} + \underset{(1-h)}{Cl^-} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+} + \underset{h}{Cl^-}$$

or $$\underset{(1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$$

$\therefore$ According to law of mass action,

$$K = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]} \quad \text{or} \quad K[H_2O] = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

or $$K_H = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad ...(19)$$

Now for weak base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ...(20)$$

By Eqs. (19) and (20), $K_H \times K_b = [H^+][OH^-] = K_w$

or $$K_H = \frac{K_w}{K_b} \qquad ...(21)$$

Further, $$[NH_4^+] = C(1-h)$$

$$[NH_4OH] = Ch$$

$$[H^+] = Ch$$

$\therefore$ By Eqs. (19), $$K_H = \frac{Ch \cdot Ch}{C(1-h)} = \frac{Ch^2}{(1-h)} \qquad ...(22)$$

$\because$ h is small $\therefore$ $1 - h \approx 1$ or $K_H = Ch^2$

or $$h = \sqrt{\left(\frac{K_H}{C}\right)} \qquad ...(23)$$

Also pH is derived by $[H^+]$

$$[H^+] = Ch$$

By Eq. (23), $$[H^+] = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)} \qquad ...(24)$$

By Eqs. (21) and (24), $[H^+] = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)}$

$\therefore$ $$-\log H^+ = \frac{1}{2}[\log K_b - \log K_w - \log C]$$

$\therefore$ $$pH = \frac{1}{2}[\log K_b - \log K_w - \log C] \qquad ...(25)$$

Thus, following results can be written for case I and similar derivations can be made for case II and case III.

Case I : Salt of strong acid and weak base : *e.g.*, NH_4Cl

$$K_H = \frac{K_w}{K_h}; h = \sqrt{\left(\frac{K_H}{C}\right)} \text{ and } pH = \frac{1}{2}[\log K_b - \log K_w - \log C]$$

$$= \frac{1}{2}[pK_w - pK_b - \log C]$$

Case II : Salts of weak acid + Strong base : *e.g.*, CH_3COONa, KCN....., etc.

$$K_H = \frac{K_w}{K_a}; h = \sqrt{\left(\frac{K_H}{C}\right)} \text{ and } pOH = \frac{1}{2}[\log K_a - \log K_w - \log C]$$

$$= \frac{1}{2}[pK_w - pK_a - \log C]$$

Case III : Salts of weak acid + weak base : *e.g.*, CH_3COONH_4, NH_4CN,....., etc.

$$K_H = \frac{K_w}{K_a \cdot K_b}; h = \sqrt{K_H} \text{ (if } h \text{ is small) or } \frac{h}{1-h} = \sqrt{K_H}$$

$$pH = \frac{1}{2}[\log K_b - \log K_a - \log K_w] = \left[\frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b\right]$$

Case IV : Salts of strong acid + strong base : *e.g.*, NaCl, KNO_3,....., etc.

This category of salt does not undergo salt hydrolysis.

NOTE : (i) Eq. (21) and analogous equation for other category should be used only when the degree of hydrolysis is negligible.

(ii) All the derivations made for salt hydrolysis are for uni-univalent salts. For other types of salts (say uni-bivalent, *e.g.*, $Na_2C_2O_4$ or bi-bivalent CaC_2O_4, one should derive the similar equations following the same above methods). The term 'C' in the above equations however represents the concentration of ion that undergoes hydrolysis.

(iii) The pH of acidic salts of polyprotic acids in water say NaHS is given by : $pH = \frac{[pK_{a_1} = pK_{a_2}]}{2}$

NUMERICAL PROBLEMS

1. Calculate the amount of acetic acid present in one litre of its solution having $\alpha = 1\%$ and $K_a = 1.8 \times 10^{-5}$.
2. 0.16 g of N_2H_4 are dissolved in water and the total volume made upto 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_b for N_2H_4 is 4.0×10^{-6} M. **(Roorkee 1998)**
3. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution. **(Roorkee 1993)**
4. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSaC. 4×10^{-4} mole of saccharin is dissolved in 200 cm^3 water of pH 3. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium. **(Roorkee 1994)**
5. Acetyl salicylic acid, *i.e.*, aspirin ionises in water as :
$$HC_9H_7O_4 + H_2O \rightleftharpoons H_3O^+ + C_9H_7O_4^-; \quad K_a = 2.75 \times 10^{-9}$$
If two tablets of aspirin each of 0.32 g is dissolved in water to produce 250 mL solution, calculate $[H^+]$, $[OH^-]$ and $[C_9H_7O_4^-]$ in solution.
6. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} litre mol^{-1} sec^{-1}. Calculate the rate constant for proton transfer from water to NH_3. **(IIT 1996)**
7. Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid $= 2.6 \times 10^{-3}$.
8. An aqueous solution contains 10% ammonia by mass and has a density of 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for $NH_4^+ = 5.0 \times 10^{-10}$ M. **(Roorkee 1995)**
9. Liquid ammonia ionises to a slight extent. At −50°C, its ionisation constant, $K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-30}$. How many amide ions are present per cm^3 of pure liquid ammonia ? Assume $N = 6.0 \times 10^{23}$.
10. The ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22g/cm^3.
11. Calculate the dissociation constant of NH_4OH at 25°C, if $\Delta H°$ and $\Delta S°$ for the given changes are as follows :
$$NH_3 + H^+ \rightleftharpoons NH_4^+; \quad \Delta H° = -52.2 \text{ kJ mol}^{-1}$$
$$H_2O \rightleftharpoons H^+ + OH^-; \quad \Delta H° = 56.6 \text{ kJ mol}^{-1}$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-; \quad \Delta S° = -76.53 \text{ JK}^{-1} \text{ mol}^{-1}$$
12. Prove that degree of dissociation of a weak acid is given by:
$$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$
where K_a is its dissociation constant.
13. Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.
14. In the qualitative analysis, Bi^{3+} is detected by the appearance of the precipitates of bismuthyl hydroxide $[BiO(OH)_S]$. Calculate the pH when the following equilibrium exists K_b for $BiO(OH) = 4 \times 10^{-10}$.
15. Calculate the concentration of all species of significant concentrations present in 0.1 M H_3PO_4 solution. $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 3.6 \times 10^{-13}$. Also calculate pH of solution.
16. Calculate the $[OH^-]$ of $[NH_2 \cdot C_2H_4NH_3]^+$ and $[H_3N - C_2H_4NH_3]^{2+}$ in 0.15 M ethylene diamine (*aq.*); if
$$NH_2C_2H_4NH_2 + H_2O \rightleftharpoons NH_2C_2H_4NH_3^+ + OH^-; \quad K_1 = 8.5 \times 10^{-5}$$
$$NH_2C_2H_4NH_3^+ + H_2O \rightleftharpoons [NH_3C_2H_4NH_3]^{2+} + OH^-; \quad K_2 = 2.7 \times 10^{-8}$$
17. Calculate pH of (1) 10^{-3} N HNO_3, (2) 10^{-3} M H_2SO_4, (3) 10^{-3} N H_2SO_4, (4) 0.01 N HCl, (5) 10^{-8} N HCl, (6) 10^2 M HCl.
18. Calculate pH for acid solutions having $[H^+]$ as (a) $[H^+] = 0.05$ M, (b) $[H^+] = 5.0$ M, (c) $[H^+] = 10^{-8}$ M.
19. Calculate pH for.
(a) 0.001 N NaOH (b) 0.01 N $Ca(OH)_2$
(c) 0.01 M $Ca(OH)_2$ (d) 10^{-8} M NaOH
(e) 10^2 M NaOH (f) 0.0008 M $Mg(OH)_2$
Assume complete ionisation of each. **(Roorkee 1992)**
20. Calculate pH of basic solutions having $[OH^-]$ as
(a) $[OH^-] = 0.05$ M, (b) $[OH^-] = 5.0$ M,
(c) $[OH^-] = 10^{-8}$ M.
21. Calculate pH of (Given K_a $CH_3COOH = K_a$ $NH_4OH = 2.0 \times 10^{-3}$)
(a) 0.002 N acetic acid having 2.3% dissociation.
(b) 0.002 N NH_4OH having 2.3% dissociation.

22. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(IIT 2000)**

23. Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M HCl and 0.01 M in $CHCl_2COOH$. K_a for $CHCl_2COOH$ is 5×10^{-2}.

24. A solution contains 0.09 M $CHCl_2COOH$ and 0.1 M CH_3COOH. The pH of this solution is 1. If K_a for acetic acid is 10^{-5}, calculate K_a for $CHCl_2COOH$.

25. What is $[H^+]$ for a solution in which
(*i*) pH = 3 (*ii*) pH = 4.75 ?

26. The pH of 0.05 M aqueous solution of diethyl amine is 12.0. Calculate K_b. **(Roorkee 1993)**

27. The K_w for $2H_2O \rightleftharpoons H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. What is pH of water at 60°C? What happens to its neutrality?

28. Ionic product of water $(K_w) = 1\times10^{-14}$ at 25° C. What are dissociation constant of water and autoprotonation constant of water?

29. Will the pH of water be same at 4° C and 25° C? Explain. **(IIT 2003)**

30. The pH of pure water at 25°C and 35°C are 7 and 6 respectively. Calculate the heat of formation of water from H^+ and OH^-.

31. A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be pH of resulting solution?

32. 2.0 g of diborane (B_2H_6) reacts with water to produce 100 mL solution. If K_a for H_3BO_3 is 7.3×10^{-10}, calculate pH of solution.

33. 100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, V.P. of H_2O at 25° C is 23.7 mm.

34. Find the concentrations of H^+, HCO_3^- and CO_3^{2-} in a 0.01 M solution of carbonic acid if the pH of solution is 4.18. $K_1 = 4.45\times10^{-7}$, $K_2 = 4.69\times10^{-11}$.

35. Calculate the $[Cl^-]$, $[Na^+]$, $[H^+]$, $[OH^-]$ and pH of resulting solution obtained by mixing 50 mL of 0.6 N HCl and 50 mL of 0.3 N NaOH.

36. Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4.

37. What is the pH of 1 M solution of acetic acid? To what volume one litre of this solution be diluted so that pH of the resulting solution will be twice of the original value? $K_a = 1.8\times10^{-5}$. **(IIT 1990)**

38. Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

39. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0)? **(IIT 1998)**

40. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.
(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
(ii) If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing; K_a of acetic acid is 1.75×10^{-5} mol L^{-1}.] **(IIT 2002)**

41. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M? K_a for $C_6H_5NH_3^+$ is 2.4×10^{-5} M. **(Roorkee 1996)**

42. Calculate $[H^+]$ in a solution containing 0.1 M HCOOH and 0.1 M HOCN. K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}.

43. What is the concentration of acetic acid which has same pH as 0.5 M HCOOH solution. K_a HCOOH $= 2.4\times10^{-4}$ and K_a $CH_3COOH = 1.8\times10^{-5}$

44. What are $[H^+]$, $[A^-]$ and $[B^-]$ in a solution that is 0.03 M HA and 0.1 M HB ? K_a for HA and HB are 1.38×10^{-4} and 1.05×10^{-10} respectively.

45. Calculate $[H^+]$, pH, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in a solution containing 0.02 M CH_3COOH and 0.01 M C_6H_5COOH. $K_{CH_3COOH} = 1.8\times10^{-5}$ and $K_{C_6H_5COOH} = 6.4\times10^{-5}$.

46. What concentration of $HCOO^-$ is present in a solution of 0.015 M HCOOH and 0.02 M HCl. K_aHCOOH $= 1.8\times10^{-4}$

47. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively. **(Roorkee 1992)**

48. The K_a for formic acid and acetic acid are 2.1×10^{-4} and 1.1×10^{-5} respectively. Calculate relative strength of acids.

49. Calculate the pH of a solution of given mixtures:
(a) (2g CH_3COOH + 3g CH_3COONa) in 100 mL of mixture; $K_a = 1.8\times10^{-5}$
(b) 5 mL of 0.1 M NH_4OH + 250 mL of 0.1 M NH_4Cl; $K_b = 1.8\times10^{-5}$
(c) (0.25 mole of acid + 0.35 mole of salt) in 500 mL mixture; $K_a = 3.6\times10^{-4}$

50. Calculate the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1 *M* HCl. K_a for $HCO_3^- = 5.63 \times 10^{-11}$.

51. 0.15 mole of pyridinium chloride has been added into 500cm^3 of 0.2 *M* pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume.

(K_b for pyridine $= 1.5 \times 10^{-9}$ *M*) **(Roorkee 1995)**

52. Calculate the mass of $(NH_4)_2SO_4$ in g which must be added to 500 mL of 0.2 *M* NH_3 to yield a solution of pH = 9.35. K_b for $NH_3 = 1.78 \times 10^{-5}$.

53. What volume of 0.1 *M* sodium formate solution should be added to 50 mL of 0.05 *M* formic acid to produce a buffer solution of pH = 4.0 ; pK_a of formic acid = 3.80?

(Roorkee 1990)

54. How many mole of HCl will be required to prepare one litre of buffer solution (containing NaCN + HCl) of pH 8.5 using 0.01 g formula mass of NaCN ? $K_{HCN} = 4.1 \times 10^{-10}$.

55. A 40 mL solution of weak base BOH is titrated with 0.1*N* HCl solution. The pH of solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of acid respectively. Find out K_b for weak base.

(IIT 1991)

56. A weak acid H*A* after treatment with 12 mL of 0.1 *M* strong base *B*OH has a pH of 5. At the end point, the volume of same base required is 26.6 mL. Calculate K_a of acid.

57. A solution of weak acid was titrated with base NaOH. The equivalence point was reached when 36.12 mL of 0.1 *M* NaOH have been added. Now 18.06 mL 0.1 *M* HCl were added to titrated solution, the pH was found to be 4.92. What is K_a of acid?

58. Calculate $[H^+]$ in a 0.20 *M* solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.1 *M* sodium dichloroacetate. Neglect hydrolysis of sodium salt.

59. Calculate the change in pH of 1 litre buffer solution containing 0.1 mole each of NH_3 and NH_4Cl up on addition of :

(i) 0.02 mole of dissolved gaseous HCl.

(ii) 0.02 mole of dissolved NaOH. **(Roorkee 1992)**

Assume no change in volume. $K_{NH_3} = 1.8 \times 10^{-5}$

60. 20 mL of 0.2 *M* NaOH are added to 50 mL of 0.2 *M* acetic acid ($K_a = 1.8 \times 10^{-5}$).

(1) What is pH of solution ?

(2) Calculate volume of 0.2 *M* NaOH required to make the pH of solution 4.74.

61. Calculate the ratio of pH of a solution containing 1 mole of $CH_3COONa + 1$ mole of HCl per litre and of other solution containing 1 mole $CH_3COONa + 1$ mole of acetic acid per litre.

62. A 0.1 *M* solution of weak acid H*A* is 1% dissociated at 25°C. What is its K_a? If this solution is *w.r.t.* Na*A* 0.2 *M*, what will be the new degree of dissociation of H*A* and pH ?

63. The $[H^+]$ in 0.2 *M* solution of formic acid is 6.4×10^{-3} mol litre^{-1}. To this solution formate is added so as to adjust the conc. of sodium formate to one mol per litre. What will be pH of this solution? K_a for HCOOH is 2.4×10^{-4} and degree of dissociation of HCOONa is 0.75.

64. What is the pH of a solution when 0.20 mole of HCl is added to one litre solution containing.

(a) 1 *M* each of acetic acid and acetate ion ?

(b) 0.1 *M* each of acetic acid and acetate ion?

Given K_a for acetic acid is 1.8×10^{-5}.

65. Calculate the composition of an acidic buffer solution made up of H*A* and Na*A* of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.

66. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol litre^{-1}.

(Roorkee 1997)

67. Calculate the pH of a solution obtained by mixing 100 mL of 0.3 *M* HCl with 100 mL of 0.4 *M* NH_3. pK_a for $NH_4^+ = 9.2552$.

68. Calculate the pH of a solution obtained by mixing 50 mL of 0.2 *M* NH_4Cl and 75 mL of 0.1 *M* NaOH. pK_a for $NH_4^+ = 9.2552$.

69. A certain buffer solution contains equal concentration of X^- and H*X*. K_b for X^- is 10^{-10}. Calculate pH of buffer.

70. Two buffer, (*X*) and (*Y*) of pH 4.0 and 6.0 respectively are prepared from acid H*A* and the salt Na*A*. Both the buffers are 0.50 *M* in H*A*. What would be the pH of the solution obtained by mixing equal volumes of the two buffers ? ($K_{HA} = 1.0 \times 10^{-5}$) **(Roorkee 1999)**

71. A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.

(IIT 1991)

72. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 *M* $NaHCO_3$ solution, should be mixed with 10 mL sample of blood which is 2 *M* in H_2CO_3 in order to maintain a pH of 7.4 K_a for H_2CO_3 in blood is 7.8×10^{-7} ? **(IIT 1993)**

73. 0.1 M CH_3COOH solution is titrated against 0.05 M NaOH solution. Calculate pH at 1/4th and 3/4th stages of neutralization of acid. The pH for 0.1 M CH_3COOH is 3.

74. K_{sp} of AgCl is 1.5×10^{-10} at 25°C. Calculate solubility of AgCl in; (a) Pure water, (b) 0.1 M $AgNO_3$, (c) 0.1 M NaCl. **(Roorkee 1995)**

75. How many grams of potassium bromide (molar mass 120) can be added to 0.5 litre of 0.05 M solution of silver nitrate just to start the precipitation of silver bromide ? K_{sp} of AgBr is 5.0×10^{-13}.

76. The solubility of AgCl in water at 25°C is 1.79×10^{-3} g/litre. Calculate K_{sp} of AgCl at 25°C.

77. K_{sp} of AgBr is 4×10^{-13} and $[Ag^+]$ in a solution is 1×10^{-6} mol litre^{-1}. What is the $[Br^-]$ in that solution ?

78. The $[Ag^+]$ ion in a saturated solution of Ag_2CrO_4 at 25°C is 1.5×10^{-4} M. Determine K_{sp} of Ag_2CrO_4 at 25°C.

79. 25 mL of a sample of clear saturated solution of PbI_2 requires 10 mL of a certain $AgNO_3$ $(aq.)$ for its titration. What is the molarity of this $AgNO_3$ $(aq.)$? K_{sp} for $PbI_2 = 4\times10^{-9}$.

80. Equal volumes of 0.02 M $CaCl_2$ and 0.0004 M Na_2SO_4 are mixed. Will a precipitate form?
(K_{sp} of $CaSO_4 = 2.4\times10^{-5}$).

81. What (H_3O^+) must be maintained in a saturated H_2S solution to precipitate Pb^{2+}, but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01 M?
($K_{sp}H_2S = 1.1\times10^{-22}$; $K_{sp}ZnS = 1.0\times10^{-21}$)
(Roorkee 2000)

82. K_{sp} of $PbCl_2$ is 10^{-13}. What will be $[Pb^{2+}]$ in a solution prepared by mixing 100 mL of 0.1 M $Pb(NO_3)_2$ and 1 mL of 1 M HCl?

83. K_{sp} of $PbBr_2$ is 8×10^{-5}. If the salt is 80% dissociated in solution, calculate the solubility of salt in g per litre.

84. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. **(IIT 1999)**

85. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for C_6H_5COOAg is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 as compared to pure water.

86. Calculate the solubility of CaF_2 in a solution buffered at pH = 3.0. K_a for HF is 6.3×10^{-4} and K_{sp} of $CaF_2 = 3.45\times10^{-11}$.

87. Will a precipitate of $Mg(OH)_2$ be formed in a 0.001 M solution of $Mg(NO_3)_2$, if the pH of solution is adjusted to 9? K_{sp} of $Mg(OH)_2 = 8.9\times10^{-12}$.

88. Calculate pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{2+} ions. K_{sp} of $Mg(OH)_2 = 1\times10^{-11}$. **(Roorkee 1992)**

89. Calculate the $[OH^-]$ of a solution after 100 mL of 0.1 M $MgCl_2$ is added to 100 mL of 0.2 M NaOH. K_{sp} of $Mg(OH)_2$ is 1.2×10^{-11}

90. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl (K_{sp} $Ag_2CO_3 = 8.2\times10^{-12}$). **(IIT 1997)**

91. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water K_{sp} of AgBr $= 5\times10^{-13}$ and K_{sp} of AgCNS $= 1\times10^{-12}$. **(UPSEAT 1995)**

92. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What % of that metal ion is precipitated?
(K_{sp} of AgI $= 8.5\times10^{-17}$ and K_{sp} of $Hg_2I_2 = 2.5\times10^{-26}$)

93. 0.01 mole of $AgNO_3$ is added to 1 litre of a solution which is 0.1 M in Na_2CrO_4 and 0.005 M in $NaIO_3$. Calculate the mole of precipitate formed at equilibrium and the concentrations of Ag^+, IO_3^- and CrO_4^{2-}. (K_{sp} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively). **(Roorkee 2001)**

94. The K_{sp} of $Ca(OH)_2$ is 4.42×10^{-5} at 25°C. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in mg is precipitated? **(IIT 1992)**

95. A sample of hard water contains 0.005 mole of $CaCl_2$ per litre. What is the minimum concentration of Na_2SO_4 which must be added for removing Ca^{2+} ions from this water sample? K_{sp} for $CaSO_4$ is 2.4×10^{-5} at 25°C.

96. 1.75 g of solid NaOH are added to 0.25 dm^3 of 0.1 M $NiCl_2$ solution. Calculate :
(a) mass of $Ni(OH)_2$ formed; (b) pH of final solution
Given, K_{sp} of $Ni(OH)_2 = 1.6\times10^{-14}$

97. A mixture of water and AgCl is shaken until a saturated solution is obtained. Now the solution is filtered and 100 mL of clear solution of filtrate is mixed with 100 mL

of 0.03 M NaBr. Should a precipitate form ? K_{sp} of AgCl and AgBr are 1×10^{-10} and 5×10^{-13}.

98. Calculate pH of a saturated solution of $Mg(OH)_2$. K_{sp} for $Mg(OH)_2$ is 8.9×10^{-12}.

99. 0.1 mili mole of $CdSO_4$ are present in 10 mL acid solution of 0.08 N HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. What would be the pH of solution after filtering off precipitate, boiling of H_2S and making the solution 100 mL by adding H_2O ?

100. Zn salt is mixed with $(NH_4)_2S$ of molarity 0.021 M. What mass of Zn^{2+} will remain unprecipitated in 12 mL of the solution? K_{sp} of $ZnS = 4.51\times10^{-24}$.

101. Freshly precipitated Al and Mg hydroxides are stirred vigorously in a buffer solution containing 0.25 M of NH_4Cl and 0.05 M of NH_4OH.
Calculate $[Al^{3+}]$ and $[Mg^{2+}]$ in solution. K_b for $NH_4OH = 1.8\times10^{-5}$. K_{sp} of $Al(OH)_3 = 6\times10^{-32}$ and K_{sp} of $Mg(OH)_2 = 8.9\times10^{-12}$.

102. A solution has 0.05 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution. K_{sp} of $Mg(OH)_2 = 9.0\times10^{-12}$ and ionisation constant of NH_3 is 1.8×10^{-5}. **(Roorkee 1993)**

103. A particular water sample has 131 ppm $CaSO_4$. What fraction of the water must be evaporated in a container before solid $CaSO_4$ begins to deposit K_{sp} of $CaSO_4 = 9.0\times10^{-6}$?

104. To a solution of 0.1 M Mg^{2+} and 0.8 M NH_4Cl, an equal volume of NH_3 is added which just gives precipitate. Calculate $[NH_3]$ in solution. K_{sp} of $Mg(OH)_2 = 1.4\times10^{-11}$ and K_b of $NH_4OH = 1.8\times10^{-5}$.

105. 10 mL of 0.3 M Na_2SO_4 are mixed with 20 mL solution having initially 0.1 M Ca^{2+} and 0.1 M Sr^{2+} in it. What are the final concentrations of Ca^{2+}, Sr^{2+} and SO_4^{2-} in solution? Given K_{sp} of $SrSO_4 = 7.6\times10^{-7}$ and K_{sp} of $CaSO_4 = 2.4\times10^{-5}$.

106. The solubility of $CaCO_3$ is 7 mg/litre. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{2+} and Ba^{2+}, no precipitate is formed until 90% of Ba^{2+} has been precipitated as $BaCO_3$.

107. The solubility of $Mg(OH)_2$ is increased by the addition of NH_4^+ ion. Calculate.
(a) K_C for,
$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$$
K_{sp} of $Mg(OH)_2 = 6\times10^{-12}$, K_b of $NH_3 = 1.8\times10^{-5}$
(b) Find solubility of $Mg(OH)_2$ in a solution containing 0.5 M NH_4Cl before addition of $Mg(OH)_2$.

108. The K_{sp} of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3 L^{-3}. A solution of $K_2C_2O_4$ containing 0.152 mole in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the equilibrium is reached.
$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$
At equilibrium the solution contains 0.0358 mole of K_2CO_3. Assuming degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be same, calculate K_{sp} of Ag_2CO_3. **(IIT 1991)**

109. Calculate the solubility of AgCN in a buffer solution of pH = 3. Given K_{sp} of AgCN $= 1.2\times10^{-16}$ and K_a for HCN $= 4.8\times10^{-10}$.

110. Determine the concentration of NH_3 solution whose one litre can dissolve 0.10 mole AgCl. K_{sp} of AgCl and K_f of $Ag(NH_3)_2^+$ are 1.0×10^{-10} M^2 and 1.6×10^7 M^{-2} respectively. **(Roorkee 1999)**

111. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $K[Ag(CN)_2]^-$. Given $K_{\text{instability constant}}$ for $[Ag(CN)_2]^- = 4.0\times10^{-19}$ and K_{sp} AgCl $= 2.8\times10^{-10}$.

112. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_C = 6.2\times10^{-8}$ and K_{sp} of AgCl $= 1.8\times10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia. **(IIT 1998)**

113. Equal volumes of 0.02 M $AgNO_3$ and 0.02 M HCN are mixed. What is $[Ag^+]$ in solution after attaining equilibrium? Given K_a HCN $= 6.2\times10^{-10}$ and K_{sp} AgCN $= 2.2\times10^{-16}$.

114. Determine the mole of AgI which may be dissolved in 1.0 litre of 1.0 M CN^- solution. K_{sp} for AgI and K_C for $[Ag(CN)_2]^-$ are 1.2×10^{-17} M^2 and 7.1×10^{19} M^{-2} respectively. **(Roorkee 1998)**

115. 100.0 mL of a clear saturated solution of Ag_2SO_4 is added to 250.0 mL of a clear saturated solution of $PbCrO_4$. Will any precipitate form and if so what? Given, K_{sp} values for Ag_2SO_4, Ag_2CrO_4, $PbCrO_4$ and $PbSO_4$ are 1.4×10^{-5}, 2.4×10^{-12}, 2.8×10^{-13} and 1.6×10^{-8} respectively.

116. 2 M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2. Very little amount of $CaCO_3$ and

NaF are formed. If the solubility product of $CaCO_3$ is x and molar solubility of CaF_2 is y, find the molar concentration of F^- in the resulting solution after equilibrium is attained.

117. 25.0 mL clear saturated solution of $PbI_2(aq.)$ requires 13.3 mL of $AgNO_3(aq.)$ solution for complete precipitation. What is molarity of $AgNO_3$ solution? K_{sp} of PbI_2 is 7.1×10^{-9}.

118. 250.0 mL of saturated clear solution of $CaC_2O_4(aq.)$ requires 6.3 mL of 0.00102 M $KMnO_4(aq.)$ in acid medium for complete oxidation of $C_2O_4^{2-}$ ions. Calculate the K_{sp} of CaC_2O_4.

119. K_{sp} for $SrF_2 = 2.8\times10^{-9}$ at 25°C. How much NaF should be added to 100 mL of solution having 0.016 M in Sr^{2+} ions to reduce its concentration to 2.5×10^{-3} M?

120. An aqueous solution of a metal bromide MBr_2 (0.05M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? K_{sp} for $MS = 6.0\times10^{-21}$. Concentration of saturated $H_2S = 0.1\,M$; $K_1 = 10^{-7}$ and $K_2 = 1.3\times10^{-13}$ for H_2S. **(IIT 1993)**

121. H_2S is bubbled into a 0.02 M NaCN solution which is 0.02 M each in $Ag(CN)_2^-$ and $Cd(CN)_4^{-2}$. If K_{sp} of Ag_2S and K_{sp} of CdS are 1.0×10^{-50} and 7.1×10^{-28} and $K_{instability}$ for $[Ag(CN)_2^-]$ and $[Cd(CN)_4]^{2-}$ are 1.0×10^{-20} and 7.8×10^{-18}, which sulphide will precipitate first.

122. Calculate the pH at which an acid indicator with $K_a = 1\times10^{-5}$ changes colour when the indicator concentration is 1×10^{-3} M. Also report the pH at which coloured ion is 80% present.

123. An acid type indicator. HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0\times10^{-5}$)? **(IIT 1997)**

124. Bromophenol blue is an indicator with a value of $K_a = 5.84\times10^{-5}$. At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 4.84.

125. Calculate the percentage hydrolysis in 0.003 M aqueous solution of NaOCN. K_a for $HOCN = 3.33\times10^{-4}$. **(Roorkee 1996)**

126. What is the pH of a 0.5 M aqueous NaCN solution? pK_b of $CN^- = 4.70$. **(IIT 1996)**

127. Calculate degree of hydrolysis and pH of 0.2 M solution of NH_4Cl. Given K_b for NH_4OH is 1.8×10^{-5}.

128. Find out the mass of NH_4Cl dissolved in 500 mL to have pH = 4.5 K_b for NH_4OH is 1.8×10^{-5}.

129. (a) K_a for butyric acid is 2.0×10^{-5}. Calculate pH and hydroxyl ion concentration in 0.2 M aqueous solution of sodium butyrate. **(Roorkee 1994)**

(b) The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4}. Calculate the pH of 0.01 M solution of its sodium salt. **(IIT 2009)**

130. K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in an aqueous solution in which the concentration of Asc^- ions is 0.02 M. **(Roorkee 1997)**

131. Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for acid $= 1.9\times10^{-5}$. **(Roorkee 1990)**

132. 0.1 M NaOH is titrated with 0.1 M HA till the end point. K_a of HA is 5.6×10^{-6} and degree of dissociation is less compared to 1. Calculate the pH of the resulting solution at the end point. **(IIT 2004)**

133. Calcium lactate is a salt of weak acid and represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.13 mole of salt in 0.50 litre solution. The pOH of this is 5.60. Assuming complete dissociation of salt, calculate K_a of lactic acid. **(Roorkee 1991)**

134. Calculate the pH of 0.1 M K_3PO_4 solution. The third dissociation constant of orthophosphoric acid is 1.3×10^{-12}. Assume that the hydrolysis proceeds only in the first step.

135. Equilibrium constant for the acid ionisation of Fe^{3+} to $Fe(OH)^{2+}$ and H^+ is 6.5×10^{-3}. What is the maximum pH which could be used so that at least 95% of the total Fe^{3+} in a dilute solution exists as Fe^{3+}?

136. The acid ionisation constant for

$$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$$

is 1.0×10^{-9}. Calculate the pH of 0.0010 M solution of $ZnCl_2$. Also calculate basic dissociation constant of $Zn(OH)^+$.

137. The dissociation constants for aniline, acetic acid and water at 25°C are 3.83×10^{-10}, 1.75×10^{-5} and 1.008×10^{-14} respectively. Calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report the pH.

138. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8) **(IIT 1995)**

139. Calculate pH of the following mixtures. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$.

(a) 50 mL of 0.10 *M* NaOH + 50 mL of 0.05 *M* CH_3COOH.

(b) 50 mL of 0.05 *M* NaOH + 50 mL of 0.10 *M* CH_3COOH.

(c) 50 mL of 0.10 *M* NaOH + 50 mL of 0.10 *M* CH_3COOH.

(d) 50 mL of 0.10 *M* NH_4OH + 50 mL of 0.05 *M* HCl.

(e) 50 mL of 0.05 *M* NH_4OH + 50 mL of 0.10 *M* HCl.

(f) 50 mL of 0.10 *M* NH_4OH + 50 mL of 0.10 *M* HCl.

(g) 50 mL of 0.05 *M* NH_4OH + 50 mL of 0.05 *M* CH_3COOH.

140. The vapour pressure of 0.01 molal solution of weak base *B*OH in water at 20°C is 17.536 mm. Calculate K_b for base. Aqueous tension at 20°C is 17.540 mm. Assume molality and molarity same.

141. A 0.01 *M* aqueous solution of weak acid H*A* has an osmotic pressure 0.293 atm 25°C. Another 0.01 *M* aqueous solution of other weak acid H*B* has an osmotic pressure of 0.345 atm under the same conditions. Calculate equilibrium constants of two acids for their dissociation.

142. The salt $Zn(OH)_2$ is involved in the following two equilibria :

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq.) + 2OH^-(aq.) \qquad K_{sp} = 1.2 \times 10^{-17}$$

$$Zn(OH)_2(s) + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}(aq.) \quad K_f = 0.12$$

Calculate the $[OH^-]$ at which solubility of $Zn(OH)_2$ be a minimum. Also find the solubility of $Zn(OH)_2$ at this pH.

143. A 500 mL sample of an equilibrium mixture of gaseous N_2O_4 and NO_2 at 25°C and 753 mm of Hg was allowed to react with enough water to make 250.0 mL of solution at 25°C. Assume that all the dissolved N_2O_4 is converted to NO_2 which disproportionates in water yielding a solution of nitrous acid and nitric acid. Assume further that disproportionation reaction goes to completion and that none of the nitrous acid disproportionates. The equilibrium constant (K_p) for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.113 at 25°C. K_a for HNO_2 is 4.5×10^{-4} at 25°C.

(a) Write balanced equation for disproportionation.

(b) What is molar concentration of NO_2^- and pH of the solution?

(c) What is osmotic pressure of solution?

(d) How many grams of lime (CaO) would be required to neutralize the solution?

144. K_a for HCN and CH_3COOH are 4.9×10^{-10} and 1.8×10^{-5} respectively. Calculate the equilibrium constant for the reaction:

$$CH_3COOH + NaCN \rightleftharpoons CH_3COONa + HCN$$

145. It is found that 0.1 *M* solution of three sodium salts Na*X*, Na*Y* and Na*Z* have pH 7.0, 9.0 and 11.0 respectively. Arrange the acids (H*X*, H*Y* and H*Z*) in order of increasing acidic character. Where possible calculate dissociation constant of acid.

146. Calculate the pH of 0.05 *M* $KHC_8H_4O_4$

$$H_2C_8H_4O_4 + H_2O \rightleftharpoons H_3O^+ + HC_8H_4O_4^-; \quad pK_{a_1} = 2.94$$

$$HC_8H_4O_4^- + H_2O \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-}; \quad pK_{a_2} = 5.44$$

147. A buffer solution of 0.080 *M* Na_2HPO_4 and 0.020 *M* Na_3PO_4 is prepared. The electrolytic oxidation of 1.0 m mole *R*NHOH is carried out in 100 mL buffer to give.

$$RNHOH + H_2O \longrightarrow RNO_2 + 4H^+ + 4e$$

Calculate approximate pH of the solution after oxidation is complete. pK_{a_1}, pK_{a_2} and pK_{a_3} of H_3PO_4 are 2.12, 7.20 and 12.0 respectively.

148. Calculate the difference in pH for 1/3 and 2/3 stages of neutralisation of 0.10 *M* CH_3COOH and with 0.10 *M* NaOH.

149. The molar conductivity of a solution of a weak acid H*X* (0.01 *M*) is 10 times smaller than the molar conductivity of a solution of a weak acid H*Y* (0.1 *M*). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values $pK_a(HX) - pK_a(HY)$, is (consider degree of ionization of both acids to be << 1) **[JEE (Advanced II) 2015]**

SOLUTIONS (Numerical Problems)

1. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	1	0	0
	$1-\alpha$	α	α

where α is degree of dissociation of acid, if C mol/litre is concentration of acid, then

$[H^+] = C\alpha$; $[CH_3COO^-] = C\alpha$; $[CH_3COOH] = C(1-\alpha)$

Also $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \dfrac{C\alpha \cdot C\alpha}{C(1-\alpha)} = C\alpha^2$

[$\because K_a$ is small $\therefore \alpha$ will also be small and thus $1-\alpha \simeq 1$]

or $1.8\times10^{-5} = C\times\left(\dfrac{1}{100}\right)^2 \quad \therefore C = 0.18$

$\because$ 1 litre solution contains = 0.18 mole of CH_3COOH

$\therefore$ 1 litre solution contains = $0.18\times60 = \mathbf{10.8\ g\ CH_3COOH}$

2. $N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$

Before dissociation	1	0	0
After dissociation	$1-\alpha$	α	α

Also $K_b = \dfrac{C\alpha^2}{(1-\alpha)}$

Assuming $1-\alpha \simeq 1$

$K_b = C\alpha^2$

$[N_2H_4] = C = \dfrac{0.16\times1000}{32\times500} = 0.01$

Given $K_b = 4\times10^{-6}\,M \therefore \alpha^2 = \dfrac{4\times10^{-6}}{0.01} = 4\times10^{-4}$

$\alpha = 2\times10^{-2}$ *i.e.*, $\alpha = \mathbf{0.02\ or\ 2\%}$

3. Given, $HNiC \rightleftharpoons H^+ + NiC^-$

	1	0	0
	$(1-\alpha)$	α	α

Also, $C = \dfrac{0.1}{2} = 5\times10^{-2}$ mol litre^{-1}; $K_a = 1.4\times10^{-5}$

$\therefore \quad K_a = \dfrac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad (\because 1-\alpha \simeq 1)$

$\therefore \quad \alpha = \sqrt{\left(\dfrac{K_a}{C}\right)} = \sqrt{\left(\dfrac{1.4\times10^{-5}}{5\times10^{-2}}\right)}$

$= \mathbf{1.67\times10^{-2}}$ or **1.67%**

4. $[HSaC] = \dfrac{\text{mole}}{\text{litre}} = \dfrac{4\times10^{-4}}{200/1000} = 2\times10^{-3}\,M$

The dissociation of HSaC takes place in presence of $[H^+] = 10^{-3}$

$HSaC \rightleftharpoons H^+ + SaC^-$

Conc. before dissociation 2×10^{-3} 10^{-3} 0

In presence of H^+ the dissociation of HSaC is almost negligible because of common ion effect. Thus, at equilibrium

$[HSaC] = 2\times10^{-3}$; $[H^+] = 10^{-3}$

$\because \quad K_a = \dfrac{[H^+][SaC^-]}{[HSaC]} \qquad \therefore 2\times10^{-12} = \dfrac{[10^{-3}][SaC^-]}{2\times10^{-3}}$

$\therefore \quad \mathbf{[SaC^-] = 4\times10^{-12}\,M}$

5. $[HC_9H_7O_4] = \dfrac{0.32\times2\times1000}{180\times250} = \mathbf{0.014\,M}$

$\because \quad \alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{2.75\times10^{-9}}{0.014}} = 4.43\times10^{-4}$

$\therefore \quad [H^+] = C\cdot\alpha = 0.014\times4.43\times10^{-4} = \mathbf{6.21\times10^{-6}\,M}$

$[C_9H_7O_4^-] = C\cdot\alpha = \mathbf{6.21\times10^{-9}\,M}$

$[OH^-] = \dfrac{10^{-14}}{[H^+]} = \dfrac{10^{-14}}{6.21\times10^{-6}} = \mathbf{1.61\times10^{-9}\,M}$

6. $NH_3 + H_2O \underset{K_b}{\overset{K_f}{\rightleftharpoons}} NH_4^+ + OH^-$; $\quad K_b = 3.4\times10^{10}$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$; $\quad K_a = 5.6\times10^{-10}$

$K_{(\text{base})NH_3} = \dfrac{K_f}{K_b} = \dfrac{K_w}{K_{\text{acid}\,(NH_4^+)}} \quad (\because K_{\text{acid}} \times K_{\text{base}} = K_w)$

or $\dfrac{K_f}{3.4\times10^{10}} = \dfrac{10^{-14}}{5.6\times10^{-10}} \quad \therefore \mathbf{K_f = 6.07\times10^5}$

7. $CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$

Mole before dissociation	1	0	0
Mole after dissociation	$(1-\alpha)$	α	α

Given, $[H^+] = C\cdot\alpha = 1.5\times10^{-3}$ mole litre^{-1}

$\because \quad K_a = \dfrac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$

$2.6\times10^{-3} = \dfrac{1.5\times10^{-3}\times\alpha}{(1-\alpha)} \quad \therefore \alpha = 0.634$

Now, $C\cdot\alpha = 1.50\times10^{-3}$

$\therefore \quad C = \dfrac{1.50\times10^{-3}}{0.634} = \mathbf{2.37\times10^{-3}\,M}$

Note : Since K_a is of the order of $10^{-3}\,M$ and thus it is not advisable to use $K_a = C\alpha^2$. Because $(1-\alpha)$ is not equal to 1 since α is not small.

8. Given, $\dfrac{\text{mass of } NH_3}{\text{mass of solution}} = \dfrac{10}{100}$

$\because$ 100 g solution contains 10 g NH_3

$\therefore \quad M_{NH_3} = (10\times1000)/[(17\times(100/0.99)] = 5.82$

$(\because V = \text{mass / density})$

Now $NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore \quad [OH^-] = C\cdot\alpha = C\sqrt{(K_b/C)} = \sqrt{(K_b\cdot C)}$

$[\because C = 5.82M$ and $K_b = K_w / K_a$

$= 10^{-14}/(5\times10^{-10}) = 2\times10^{-5}]$

$\therefore \quad [OH^-] = \sqrt{[2\times10^{-5}\times5.82]} = 1.07\times10^{-2}\,M$

$\therefore \quad [H^+] = 10^{-14}/1.07\times10^{-2} = 0.9268\times10^{-12}\,M$

$\therefore \quad \text{pH} = -\log[H^+] = -\log 0.9268\times10^{-12} = \mathbf{12.0330}$

9. $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (self ionisation)

and $K = [NH_4^+][NH_2^-]$ $\therefore$ $[NH_4^+] = [NH_2^-]$

$\therefore$ $[NH_2^-] = \sqrt{K} = \sqrt{10^{-30}} = 10^{-15}\ M$

Number of amide ions in 10^3 cm^3 $= 10^{-15} \times 6 \times 10^{23}$

$\therefore$ Number of amide ions in one cm^3

$$= \frac{10^{-15} \times 6 \times 10^{23}}{10^3} = \mathbf{6 \times 10^5}\ \textbf{ions}$$

10. Given density of formic acid $= 1.22\ g/cm^3$

$\therefore$ Mass of formic acid in 1 litre solution $= 1.22 \times 10^3$ g

Thus, $$[HCOOH] = \frac{1.22 \times 10^3}{46} = 26.5M$$

Since in case of auto ionisation $[HCOOH_2^+] = [HCOO^-]$

and $[HCOO^-][HCOOH_2^+] = 10^{-6}$ $\therefore$ $[HCOO^-] = 10^{-3}$

Now % dissociation of

$$HCOOH = \frac{[HCOO^-] \times 100}{[HCOOH]} = \frac{10^{-3}}{26.5} \times 100$$

$$\left[\alpha = \frac{C\alpha}{C(1-\alpha)}\right] \qquad = \mathbf{0.004\%}$$

11. $NH_3 + H^+ \rightleftharpoons NH_4^+$; $\Delta H° = -52.2$

Adding, $H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H° = 56.6$

$\therefore$ $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$: $\Delta H° = 4.4$ kJ mol^{-1}

Similarly, $\Delta S°$ for the change $= -76.53$ JK^{-1} mol^{-1}

or for the change :

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$; $\Delta H° = 4.4$ kJ mol^{-1}

and $\Delta S° = -76.53$ JK^{-1} mol^{-1}

Now we have $\Delta G° = \Delta H° - T\Delta S°$

$\therefore$ $\Delta G° = 4.4 - (-76.53 \times 10^{-3}) \times 298 = 27.21$ KJ mol^{-1}

Also, $\Delta G° = -2.303RT \log K_b$

$27.21 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_b$

$\therefore$ $K_b = \mathbf{1.7 \times 10^{-5}}$

12. For a weak monoprotic acid

$$HA \rightleftharpoons H^+ + A^-$$

Before dissociation	1	0	0
After dissociation	$1-\alpha$	α	α

$$[H^+] = C\alpha \qquad ...(i)$$

and $$K_a = \frac{C\alpha^2}{(1-\alpha)} \qquad ...(ii)$$

By substituting value of C from Eq. (ii) in Eq. (i)

$$[H^+] = \frac{K_a \cdot (1-\alpha) \cdot \alpha}{\alpha^2} = \frac{K_a(1-\alpha)}{\alpha} \qquad ...(iii)$$

Thus, $-\log[H^+] = -[\log K_a + \log(1-\alpha) - \log \alpha]$

or $$pH = \log \frac{1}{K_a} + \log \frac{\alpha}{(1-\alpha)} \qquad ...(iv)$$

Also, $pH = pK_a - \log\left[\frac{1-\alpha}{\alpha}\right]$ or $\log \frac{1-\alpha}{\alpha} = [pK_a - pH]$

$$\frac{1-\alpha}{\alpha} = 10^{(pK_a - pH)} \quad \text{or} \quad \frac{1}{\alpha} - 1 = 10^{(pK_a - pH)}$$

or $$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$

13. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

	1	0	0
	$(1-\alpha)$	α	α

Given, $pH = 11$

$\therefore$ $[H^+] = 10^{-11}$ $\therefore$ $[OH^-] = 10^{-3} = C\alpha$

Since, $C = 0.05$

$\therefore$ $\alpha = \frac{10^{-3}}{C} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2}$ or **2%**

14. $[OH^-] \times [BiO^+] = 4 \times 10^{-10}$

$\therefore$ $[OH^-]^2 = 4 \times 10^{-10}$ $\therefore$ $[OH^-] = 2 \times 10^{-5}$

$\therefore$ $pOH = 4.6989$

$\therefore$ $pH = \mathbf{9.3010}$

15. **I Step** $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = 7.5 \times 10^{-3}$

II Step $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = 6.2 \times 10^{-8}$

III Step $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = 3.6 \times 10^{-13}$

For I Step : $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

	0.1	0	0
	$0.1-C$	C	C

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{C \cdot C}{(0.1-C)}$$

$$7.5 \times 10^{-3} = \frac{C^3}{(0.1-C)} \quad \therefore \quad C = 0.024$$

$\therefore$ $[H^+] = \mathbf{0.024}\ M$ $\therefore$ $pH = \mathbf{1.6198}$

$[H_2PO_4^-] = \mathbf{0.024}\ M$

$[H_3PO_4] = 0.1 - 0.024 = \mathbf{0.076}\ M$

The value of K_1 is much larger than K_2 and K_3. Also dissociation of II and III steps occurs in presence of H^+ furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.

For II step : $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

	0.024	0.024	0
	$(0.024 - y)$	$(0.024 + y)$	y

The dissociation of $H_2PO_4^-$ occurs in presence of $[H^+]$ furnished in step I.

Thus, $K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$ or $6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$

$\because$ y is small $\therefore$ $0.024 - y \approx 0.024$ and neglecting y^2.

$\therefore$ $6.2 \times 10^{-8} = \frac{0.024\,y}{0.024}$ $\therefore$ $y = 6.2 \times 10^{-8}$

or $[HPO_4^{2-}] = K_2 = \mathbf{6.2 \times 10^{-8}}$ **(Insignificant)**

For III Step : $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

	$(6.2 \times 10^{-8} - x)$	$(0.024 + x)$	x

$$\therefore \quad K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.024+x)\cdot x}{(6.2\times10^{-8}-x)}$$

Again neglecting x^2 and assuming, $6.2\times10^{-8}-x = 6.2\times10^{-8}$

$$\therefore \quad 3.6\times10^{-13} = \frac{0.024\,x}{6.2\times10^{-8}}$$

$$\therefore \quad x = \frac{3.6\times10^{-13}\times6.2\times10^{-8}}{0.024} = \mathbf{9.3\times10^{-19}}$$

(Insignificant)

Note: For weak polyprotic acid having no other electrolyte, the anion concentration produced in II step of dissociation is always equal to K_2 if concentration is reasonable.

16. Case I: $[OH^-] = [NH_2C_2H_4NH_3]^+$

$$= C\times\sqrt{\frac{K_{b_1}}{C}} = \sqrt{0.15\times8.5\times10^{-5}}$$

$$= \mathbf{3.57\times10^{-3}}\ M$$

Case II: $NH_2C_2H_4NH_3^+ + H_2O \rightleftharpoons$

	$[NH_3C_2H_4NH_3]^{2+}$	+ OH^-
	3.57×10^{-3}	3.57×10^{-3}
	$[3.57\times10^{-3}-X]$	X $(X+3.57\times10^{-3})$

$$\therefore \quad 2.7\times10^{-8} = \frac{X\cdot(X+3.57\times10^{-3})}{(3.57\times10^{-3}-X)}$$

Neglecting X^2, also $3.57\times10^{-3}-X = 3.57\times10^{-3}$;

(X is very small)

$$2.7\times10^{-8} = \frac{3.57\times10^{-3}\cdot X}{3.57\times10^{-3}}$$

$$\therefore \quad X = 2.7\times10^{-8}$$

$$\therefore \quad [NH_2C_2H_4NH_3]^{2+} = \mathbf{2.7\times10^{-8}}\ M = K_{b_2}$$

17. Strong acids ionise completely at normal dilutions.

(1) $10^{-3}\ N\ HNO_3$: $HNO_3 \longrightarrow H^+ + NO_3^-$

Conc. before ionisation	$10^{-3}N$	0	0
Conc. after ionisation	0	10^{-3}	10^{-3}

$\therefore \quad [H^+] = 10^{-3}$ mol/litre or Eq./litre ($\because H^+$ is monovalent)

$$\therefore \quad pH = -\log[H^+] = -\log 10^{-3}$$

$$pH = 3$$

(2) $10^{-3}\ M\ H_2SO_4$: $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

Conc. before ionisation	$10^{-3}M$	0	0
Conc. after ionisation	0	2×10^{-3}	10^{-3}

$\because$ Mole ratio of $H_2SO_4 : H^+ : SO_4^{2-} :: 1 : 2 : 1$

$$\therefore \quad [H^+] = 2\times10^{-3}\ M$$

$$\because \quad pH = -\log[H^+] = -\log 2\times10^{-3}$$

$$\therefore \quad pH = \mathbf{2.6989}$$

(3) $10^{-3}\ N\ H_2SO_4$: $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

Conc. before ionisation	$10^{-3}N$	0	0
Conc. after ionisation	0	10^{-3}	10^{-3}

$\because$ Equal equivalent of a substance gives equal equivalent of its components.

$$\therefore \quad [H^+] = 10^{-3}\ M$$

$$\because \quad pH = -\log[H^+] \quad \therefore \quad pH = 3$$

(4) $0.01\ N$ HCl: $HCl \longrightarrow H^+ + Cl^-$

Conc. before ionisation	$10^{-2}N$	0	0
Conc. after ionisation	0	10^{-2}	10^{-2}

$$\therefore \quad [H^+] = 10^{-2}\ M$$

$$\because \quad pH = -\log[H^+] \quad \therefore \quad pH = 2$$

(5) $10^{-8}\ N$ HCl:

Solution 1: $HCl \longrightarrow H^+ + Cl^-$

Conc. before ionisation	$10^{-8}N$	0	0
Conc. after ionisation	0	10^{-8}	10^{-8}

$\therefore \quad [H^+] = 10^{-8}\ M$ but pH = 8 is not possible because it is acid. Now $[H^+] = 10^{-7}\ M$ are already present in solution and since $10^{-8} < 10^{-7}$ and thus, it should not be neglected.

$$\therefore \quad [H^+] = 10^{-8} + 10^{-7} = 10^{-7}(1.1)M = 1.1\times10^{-7}\ M$$

$$\therefore \quad pH = \mathbf{6.9586}$$

Solution II The above solution lacks with discrepancy that dissociation of H_2O, a weak electrolyte is also suppressed in presence of HCl due to common ion effect and thus, $[H^+]_{H_2O} \neq 10^{-7}$ but will be lesser than this.

Therefore, dissociation of H_2O in presence of 10^{-8} H^+.

$$H_2O \rightleftharpoons \underset{(10^{-8}+a)}{H^+} + \underset{a}{OH^-}$$

$$\therefore \quad K_w = (10^{-8}+a)a \quad \therefore \quad a = 0.95\times10^{-7}$$

$$\therefore \quad [H^+] = 10^{-8} + 0.95\times10^{-7} = 10^{-7}\times1.05 = 1.05\times10^{-7}$$

$$\therefore \quad pH = \mathbf{6.9788}$$

(6) $10^2\ M$ HCl: $HCl \longrightarrow H^+ + Cl^-$

Conc. before dissociation	10^2	0	0
Conc. after dissociation	0	10^2	10^2

$$\therefore \quad [H^+] = 10^2\ M \quad \therefore \quad pH = -2$$

Students are often under the illusion that it is impossible to have a negative pH. There is no theoretical basis for this. A negative pH only means that the hydrogen ion concentration is greater than 1 M. However in actual practice, a negative pH is uncommon because of two reasons. First, even strong acids (say 100% H_2SO_4) becomes partially dissociated at high concentrations. The second reason has to do with activity.

Sorensons originally intended pH to be related to $[H^+]$, but his fundamental method of measurement—the hydrogen electrode—is now known to depend on thermodynamics activities rather than $[H^+]$, *i.e.*, on a_{H^+} and $a_{H^+} = [H^+]f_{H^+}$. In dilute solutions activity coefficient, f_{H^+} is near enough to unity and thus, $a_{H^+} = [H^+]$. At high concentrations, the activity coefficient is less than unity. Thus, pH defined by

$-\log[H^+]$ is not only of little theoretical significance, but in fact cannot be measured directly. It has therefore, come to be accepted that $pH = -\log_{10} a_{H^+}$ (this is what a pH meter reading is a measure of), *i.e.*, pH of 10^2 *M* HCl cannot be calculated until f_{H^+} is known. Nevertheless, there is mathematically no basis for not having a negative pH.

18. (a) $[H^+] = 0.05 = 5\times10^{-2}$

$\therefore$ $pH = -\log[H^+] = -\log 5\times10^{-2}$

$pH = \mathbf{1.3010}$

(b) $[H^+] = 5.0M$ but $pH \neq -\log 5 \neq -0.6989$

See Problem 17 part 6.

(c) $[H^+] = 10^{-8}$ $\therefore$ $pH \neq -\log 10^{-8} \neq 8$

See Problem 17 part 5.

19. **(a) 0.001 *N* NaOH :**

$$\begin{array}{ccccc} NaOH & \longrightarrow & Na^+ & + & OH^- \\ 10^{-3}N & & 0 & & 0 \\ 0 & & 10^{-3} & & 10^{-3} \end{array}$$

$\therefore$ $[OH^-] = 10^{-3}M$ $(\because N_{NaOH} = M_{NaOH})$

$\therefore$ $pOH = -\log[OH^-] = -\log 10^{-3} = 3$

$\therefore$ $pH = 14 - pOH = 14 - 3 = 11$ $\therefore$ $pH = \mathbf{11}$

(b) 0.01 *N* $Ca(OH)_2$:

$$\begin{array}{ccccc} Ca(OH)_2 & \rightarrow & Ca^{2+} & + & 2OH^- \\ 10^{-2}N & & 0 & & 0 \\ 0 & & 10^{-2} & & 10^{-2} \end{array}$$

$\therefore$ Equivalent litre^{-1} are given equation ratio $Ca(OH)_2 : Ca^{2+} : OH^- :: 1:1:1$

$\therefore$ $[OH^-] = 10^{-2}M$ $\therefore$ $pOH = 2$ $\therefore$ $pH = \mathbf{12}$

(c) 0.01 *M* $Ca(OH)_2$:

$$\begin{array}{ccccc} Ca(OH)_2 & \rightarrow & Ca^{2+} & + & 2OH^- \\ 10^{-2}M & & 0 & & 0 \\ 0 & & 10^{-2} & & 2\times10^{-2} \end{array}$$

$\therefore$ Mole ratio of $Ca(OH)_2$ $Ca^{2+} : OH^- :: 1:1:2$

$\therefore$ $[OH^-] = 2\times10^{-2}M$ $\therefore$ $pOH = 1.6989$

$\therefore$ $pH = 14 - 1.6989 = \mathbf{12.3010}$

(d) 10^{-8} *M* NaOH:

$$\begin{array}{ccccc} NaOH & \longrightarrow & Na^+ & + & OH^- \\ 10^{-8}N & & 0 & & 0 \\ 0 & & 10^{-8} & & 10^{-8} \end{array}$$

$\therefore$ $[OH^-] = 10^{-8}M$

Now proceed for OH^- as in problem 17 part 5.

(e) 10^2 *M* NaOH:

$$\begin{array}{ccccc} NaOH & \longrightarrow & Na^+ & + & OH^- \\ 10^2M & & 0 & & 0 \\ 0 & & 10^2 & & 10^2 \end{array}$$

$[OH^-] = 10^2M$

Now proceed as in problem 17 part 6.

(f) 0.0008 *M* $Mg(OH)_2$:

$$\begin{array}{ccccc} Mg(OH)_2 & \longrightarrow & Mg^{2+} & + & 2OH^- \\ 8\times10^{-4}M & & 0 & & 0 \\ 0 & & 8\times10^{-4} & & 2\times8\times10^{-4} \end{array}$$

$\therefore$ $[OH^-] = 16\times10^{-4}M$ $\therefore$ $pOH = 2.7958$

$\therefore$ $pH = \mathbf{11.2041}$

20. (a) $[OH^-] = 0.05M = 5\times10^{-2}$

$\therefore$ $pOH = -\log[OH^-]$ $\therefore$ $pOH = 1.3010$

$\therefore$ $pH = \mathbf{12.6989}$

(b) $[OH^-] = 5$

Proceed as in problem 17 part 6.

(c) $[OH^-] = 10^{-8}$

Proceed as in problem 17 part 5.

21. **(a) 0.002 *N* CH_3COOH:** Acetic acid is weak electrolyte and partially dissociated.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Conc. before dissociation	1	0	0
Conc. after dissociation	$1-\alpha$	α	α

$\therefore$ $[H^+] = C\alpha = 2\times10^{-3}\times\dfrac{2.3}{100} = 4.6\times10^{-5}M$

$\therefore$ $pH = -\log[H^+] = -\log 4.6\times10^{-5}$

$pH = \mathbf{4.3372}$

(b) 0.002 *N* NH_4OH: NH_4OH is weak base and partially dissociated.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Conc. before dissociation	1	0	0
Conc. after dissociation	$1-\alpha$	α	α

$\therefore$ $[OH^-] = C\alpha = 2\times10^{-3}\times\dfrac{2.3}{100} = 4.6\times10^{-5}M$

$\because$ $pOH = -\log[OH^-] = -\log 4.6\times10^{-5}$

$\therefore$ $pOH = 4.3372$ $\therefore$ $pH = 14 - 4.3372$

$pH = \mathbf{9.6628}$

22. Concentration of SO_2 in air is 10 ppm or 10 mole in 10^6 mole air or 10^{-5} mole SO_2 per mole of air. The concentration of SO_2 in air being substantial and since rain water is falling from enormously great height so, each drop of rain water will get saturated with SO_2 before it reaches earth.

Now the given concentration or solubility of SO_2 at 298 K is 1.3653 *M*. This value of solubility corresponds when $P_{SO_2} = 1$ atm.

Thus according to Henry's law.

$[SO_2]$ dissolved in water $\propto P_{SO_2}$ in gas phase

Thus solubility of SO_2 at the condition of P_{SO_2} of 10^{-5} atm as $P \propto$ mole and therefore since solubility is reported at 1 atm

$\therefore [SO_2]$ dissolved at pressure 1 atm = 1.3653 *M*

$\therefore [SO_2]_2$ dissolved at pressure 10^{-5} atm

$= 1.3653\times10^{-5}M = C$

i.e., $[H_2SO_3] = [SO_2] = 1.3653\times10^{-5}M$

Now, $SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$

	1	0	0
	$(1-\alpha)$	α	α

$\therefore$ $K_a = \dfrac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$

or $0.012 = \frac{1.3653\times10^{-5}\times\alpha^2}{(1-\alpha)}$

($\because pK_b = 1.92$ and thus $K_b = 0.012$)

$1.3653\times10^{-5}\alpha^2 + 0.012\alpha - 0.012 = 0$

$\alpha = \frac{-0.012 \pm \sqrt{1.44\times10^{-5} + 4\times1.44\times10^{-5}}}{2}$

$= 1$

$\therefore \quad [H^+] = C\times\alpha = 1.3653\times10^{-5}$

$\therefore \quad pH = \mathbf{4.8648}$

23. $CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$

	C	0	0.01
	$C(1-\alpha)$	$C\alpha$	$C\alpha + 0.01$

$\therefore \quad K_a = \frac{C\alpha\times(C\alpha+0.01)}{C(1-\alpha)} = \frac{\alpha(0.01\alpha+0.01)}{(1-\alpha)} = 5\times10^{-2}$

or $\frac{0.01\alpha(1+\alpha)}{(1-\alpha)} = 5\times10^{-2}$ or $\alpha^2 + 6\alpha - 5 = 0$

$\therefore \quad \alpha = 0.7416$

$\therefore \quad [CHCl_2COO^-] = 0.01\times0.7416 = \mathbf{7.416\times10^{-3}}\ M$

$[H^+] = 7.416\times10^{-3} + 0.01 = \mathbf{0.0174}\ M$

24. pH will be decided by $[H^+]$ furnished by HCl and $CHCl_2COOH$.

$CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$

Initial conc.	0.09	0	0.09 (From HCl)
Final conc.	$(0.09 - x)$	x	$(0.09 + x)$

$\therefore \quad [H^+] = 0.09 + x;$

but $pH = 1, \quad \therefore \quad [H^+] = 10^{-1} = 0.1$

$\therefore \quad 0.09 + x = 0.1 \quad \therefore \quad x = 0.01$

K_a for $CHCl_2COOH$ can be given as

$K_a = \frac{[H^+][CHCl_2COO^-]}{[CHCl_2COOH]} = \frac{0.1\times0.01}{(0.09-0.01)} = \mathbf{1.25\times10^{-2}}$

25. (i) $pH = 3$ or $-\log[H^+] = 3 \quad \therefore \quad [H^+] = \mathbf{10^{-3}}\ M$

(ii) $pH = 4.75 \quad \therefore \quad -\log[H^+] = 4.75$

$\therefore \quad [H^+] = \mathbf{1.7782\times10^{-5}}\ M$

26. Diethyl amine is base and give OH^- as,

$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

Initial conc.	1	0	0
Equilibrium	$(1-\alpha)$	α	α

$\therefore \quad [OH^-] = C\alpha$

where C is conc. of base and $C = 0.05\ M$

$\because \quad pH = 12 \quad \therefore \quad pOH = 2$

or $[OH^-] = 10^{-2}\ M \quad \therefore \quad C\alpha = 10^{-2}$

or $0.05\times\alpha = 10^{-2} \quad (\because C = 0.05)$

$\therefore \quad \alpha = 0.2$

Now for a base, $K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.05\times(0.2)^2}{(1-0.2)}$

$= \frac{0.05\times0.04}{0.8} = \mathbf{2.5\times10^{-3}}$

Note : Do not use $K_b = C\alpha^2$ since $\alpha = 0.2$ and $1-\alpha = 0.8$.

27. K_w for H_2O at 25° C $= 10^{-14}$

$\therefore \quad [H^+][OH^-] = 10^{-14} \quad (\because K_w = [H^+][OH^-])$

$\therefore \quad [H^+] = 10^{-7}\ M \quad \therefore\ pH = 7$

Now K_w for H_2O at 60°C $= 9.62\times10^{-14}$

$\therefore \quad [H^+][OH^-] = 9.62\times10^{-14}$

For pure water $[H^+] = [OH^-]$

$\therefore \quad [H^+]^2 = 9.62\times10^{-14}$

$\therefore \quad [H^+] = \sqrt{(9.62\times10^{-14})} = 3.10\times10^{-7}\ M$

$\therefore \quad pH = -\log H^+ = -\log 3.10\times10^{-7}$

$pH = \mathbf{6.51}$

Thus, pH of water becomes 6.51 at 60°C but the nature is neutral since calculation for pure water has been made, *i.e.* **pH scale at 60°C becomes in between 0 to 13.02.**

28. $H_2O \rightleftharpoons H^+ + OH^-$ (molarity of water = 55.6 M)

$\therefore \quad K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.6} = \mathbf{1.8\times10^{-16}}$

Also, $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$K_{a\cdot p} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = \frac{K_w}{[H_2O]^2}$

$= \frac{10^{-14}}{(55.6)^2} = \mathbf{3.24\times10^{-18}}$

29. At 25°C, K_w for $H_2O = 10^{-14}$. Thus $[H^+] = [OH^-] = 10^{-7}$ or pH of water = 7. Also as the temperature decreases K_w for H_2O decrease (*i.e.*, $K_w < 10^{-14}$) because of low dissociation of water ($H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = +ve$) following Le Chatelier's principle. This leads to lower concentrations of H^+ and OH^- ions. Thus pH of water is more at 4°C than at 25°C, however H_2O remains neutral.

30. At 25°C; $[H^+] = 10^{-7} \quad \therefore \quad K_w = 10^{-14}$

At 35°C; $[H^+] = 10^{-6} \quad \therefore \quad K_w = 10^{-12}$

Now using $2.303\log_{10}\frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1\times T_2}\right]$

$2.303\log_{10}\frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2}\left[\frac{10}{298\times308}\right]$

$\therefore \quad \Delta H = 84551.4\ \text{cal/mol} = \mathbf{84.551\ kcal/mol}$

Thus, $H_2O \rightleftharpoons H^+ + OH^-; \quad \Delta H = 84.551\ \text{kcal/mol}$

$\therefore \quad H^+ + OH^- \rightleftharpoons H_2O; \quad \Delta H = -84.551\ \text{kcal/mol}$

31. $HCl_I = 10^{-5}\ M$ since pH = 5

Meq. of HCl_I in 1 mL $= 10^{-5}\times1$

Meq. of HCl_{II} in 1000 mL $= N\times1000$

Since II is prepared by diluting I and Meq. does not change on dilution.

i.e., Meq. of HCl (concentrated) = Meq. of HCl (dilute)

$\therefore\ 10^{-5}\times 1 = N\times 1000 \quad \therefore\ N_{HCl_{II}} = 10^{-8}$

Now, proceed as in problem 17 part 5.

$\therefore$ pH = **6.9788**

32. $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2$

1 mole (=27.6 g) of B_2H_6 = 2 mole H_3BO_3

$\therefore$ 2.0 g of $B_2H_6 = \frac{2\times 2}{27.6} = 0.145$ mole H_3BO_3

$\therefore\ [H_3BO_3] = \frac{0.145\times 1000}{100} = 1.45M$

Now $H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$

$$K_a = \frac{C\alpha^2}{1-\alpha} \qquad (\because 1-\alpha \simeq 1)$$

or $7.3\times 10^{-10} = 1.45\times\alpha^2 \quad \therefore\ \alpha = 2.24\times 10^{-5}$

$\therefore\ [H^+] = C\alpha = 1.45\times 2.24\times 10^{-5} = 3.25\times 10^{-5}$

$\therefore$ pH = **4.4881**

33. For HCl gas $PV = nRT$

$\because\ P_{HCl_{dry}} = \frac{740-23.7}{760}$ atm $\quad V = \frac{100}{1000}$ litre

$T = 25+273 = 298$ K

$\therefore$ Mole of HCl, *i.e.*, $n_{HCl} = \frac{PV}{RT}$

$$= \frac{(740-23.7)\times 100}{760\times 1000\times 0.0821\times 298}$$

$\therefore\ n = 3.85\times 10^{-3}$

Now, Molarity of HCl $= \frac{n}{V_{solution}} = \frac{3.85\times 10^{-3}}{1}$ (V in litre)

$\therefore\ [H^+] = 3.85\times 10^{-3}\ M$

$\therefore\ pH = -\log H^+ = -\log 3.85\times 10^{-3}$

pH = **2.4142**

34. Given, $pH = 4.18 = -\log[H^+]$

$\therefore\ [H^+] = \mathbf{6.61\times 10^{-5}}$ **mol litre^{-1}**

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

or $4.45\times 10^{-7} = \frac{[6.61\times 10^{-5}][HCO_3^-]}{[0.01]}$

or $[HCO_3^-] = \mathbf{6.73\times 10^{-5}}$ **mol litre^{-1}**

Again for dissociation of HCO_3^-, we have

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

or $4.69\times 10^{-11} = \frac{[6.61\times 10^{-5}][CO_3^{2-}]}{[6.73\times 10^{-5}]}$

$\therefore\ [CO_3^{2-}] = \mathbf{4.78\times 10^{-11}}$ **mol litre^{-1}**

35. $HCl + NaOH \longrightarrow NaCl + H_2O$

Meq. before reaction	50×0.6 = 30	50×0.3 = 15	0	0
Meq. after reaction	15	0	15	15

For monovalent electrolytes

$$\text{Molarity} = \text{Normality} = \frac{\text{milli equivalent}}{\text{total volume}}$$

$\therefore\ [Cl^-] = \frac{15+15}{100} = \mathbf{0.3}\ M$ (Cl^- proved by HCl and NaCl)

$[Na^+] = \frac{15}{100} = \mathbf{0.15}\ M$

$[H^+] = \frac{15}{100} = \mathbf{0.15}\ M$

$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{0.15} = \mathbf{6.6\times 10^{-14}}\ M$

Also $pH = -\log[H^+] = -\log 0.15$

pH = **0.8239**

36. Milli equivalent of H^+ from HCl = 10×0.1 = 1

Milli equivalent of H^+ from $H_2SO_4 = 40\times 0.2\times 2 = 16$

$\therefore$ Total Meq. of H^+ in solution = 1+16 = 17

$\therefore\ [H^+] = \frac{17}{50} = 3.4\times 10^{-1} \qquad \left(\because [H^+] = \frac{\text{Meq.}}{V_{\text{in mL}}}\right)$

$\therefore\ pH = -\log[H^+] = -\log 0.34$

pH = **0.4685**

37. **Case I :** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Conc. before dissociation	1	0	0
Conc. after dissociation	1−α	α	α

$$[H^+] = C\alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_aC)} = \sqrt{(1.8\times 10^{-5}\times 1)}$$

$$= \sqrt{(18\times 10^{-6})} = 4.24\times 10^{-3}\ M$$

$\therefore\ pH = -\log H^+ = -\log(4.24\times 10^{-3})$

pH = 2.3724

Case II : New pH is given as = 2.3724×2 = 4.7448

Let new conc. be C_1 and degree of dissociation be α_1

$\therefore\ -\log[H^+] = 4.7448 \quad \therefore\ [H^+] = 1.8\times 10^{-5}$

or $C_1\alpha_1 = 1.8\times 10^{-5}$

Now again $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

$$K_a = \frac{C_1\alpha_1\times C_1\alpha_1}{C_1(1-\alpha_1)} = \frac{C_1\alpha_1\cdot\alpha_1}{(1-\alpha_1)}$$

$\therefore\ 1.8\times 10^{-5} = \frac{1.8\times 10^{-5}\times\alpha_1}{(1-\alpha_1)}$

$\alpha_1 = 0.5$

Now $C_1\alpha_1 = 1.8\times 10^{-5}$

$\therefore\ C_1 = \frac{1.8\times 10^{-5}}{\alpha_1} = \frac{1.8\times 10^{-5}}{0.5} = 3.6\times 10^{-5}\ M$

Let 1 litre of conc. solution be diluted to V litre.

Eq. of dilute solution = Eq. of concentration solution

$3.6\times10^{-5}\times V = 1\times1$

$\therefore \quad V = \dfrac{1}{3.6\times10^{-5}} = \mathbf{2.77\times10^{4}}$ **litre**

Note : In II case α_1 comes 0.5 by $K_a = \dfrac{C_1\alpha_1^2}{(1-\alpha_1)}$ and thus, it is not advisable to assume $(1-\alpha_1)\approx 1$.

38.

	$HCl + NaOH \longrightarrow NaCl + H_2O$			
Meq. before reaction	$100\times0.1 = 10$	$9.9\times1 = 9.9$	0	0
Meq. after reaction	0.1	0	9.9	9.9

$\therefore$ $[H^+]$ left from $HCl = \dfrac{0.1}{109.9} = 9.099\times10^{-4}\ M$

$\therefore \quad pH = -\log H^+ = -\log 9.099\times10^{-4}$

$pH = \mathbf{3.0409}$

39. pH of HCl = 2 $\quad\therefore\quad [HCl] = 10^{-2}\ M$

pH of NaOH = 12 $\quad\therefore\quad [NaOH] = 10^{-2}\ M$

	$HCl + NaOH \longrightarrow NaCl + H_2O$			
Meq. before reaction	$200\times10^{-2} = 2$	$300\times10^{-2} = 3$	0	0
Meq. after reaction	0	1	2	2

$\therefore$ $[OH^-]$ left from $NaOH = \dfrac{1}{500} = 2\times10^{-3}\ M$

$\therefore \quad pOH = -\log OH^- = -\log 2\times10^{-3}$

$\therefore \quad pOH = 2.6989 \quad\therefore\quad pH = \mathbf{11.3010}$

40. (i) Meq. of $CH_3COOH = 500\times0.2 = 100$

Meq. of $HCl = 500\times0.2 = 100$

$\therefore \quad [HCl] = \dfrac{100}{1000} = 0.1; [CH_3COOH] = \dfrac{100}{1000} = 0.1$

For CH_3COOH : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Before dissociation	0.1	0	0.1 (from HCl)
After dissociation	$(0.1-x)$	x	$(0.1+x)$

$\therefore \quad K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \dfrac{x(0.1+x)}{(0.1-x)}$

Due to common ion effect dissociation of CH_3COOH is very small in presence of HCl. Therefore, $(0.1+x) = 0.1$ and $(0.1-x) = 0.1$.

$\therefore \quad K_a = \dfrac{x\times0.1}{0.1} \quad\therefore\quad x = K_a = 1.75\times10^{-5}$

Thus, degree of dissociation

$\alpha = \dfrac{x}{0.1} = \dfrac{1.75\times10^{-5}}{0.1} = 1.75\times10^{-4} = \mathbf{0.000175 = 0.0175\%}$

Also, $[H^+] = 0.1+x = 0.1 \quad (x << 0.1)$

$\therefore \quad pH = -\log[H^+] = -\log[0.1] = \mathbf{1}$

(ii) Eq. of NaOH or mole of NaOH added $= \dfrac{6}{40} = 0.15$

Therefore, new equilibrium will have

CH_3COOH	$+ HCl$	$+ NaOH \rightarrow$	CH_3COONa	$+ NaCl$	$+ H_2O$
0.1	0.1	0.15	0	0	0
0.05	0	0	0.05	0	0

Thus, the solution will act as acidic buffer having $[CH_3COOH] = \dfrac{0.05}{1000}$ and $[CH_3COONa] = \dfrac{0.05}{1000}$

Thus, $\quad pH = -\log K_a + \log\dfrac{[\text{Conjugate base}]}{[\text{Acid}]}$

$= -\log 1.75\times10^{-5} + \log\dfrac{[0.05/1000]}{[0.05/1000]}$

$pH = \mathbf{4.757}$

41. $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

Thus, $\quad K_b = \dfrac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} \quad ...(1)$

Also K_b for $C_6H_5NH_2 = \dfrac{K_w}{K_a \text{ for } C_6H_5NH_3^+}$

$= \dfrac{1\times10^{-14}}{2.4\times10^{-5}} \quad ...(2)$

Since dissociation of $C_6H_5NH_2$ occurs in presence of NaOH and thus dissociation of $C_6H_5NH_2$ will suppress.

Thus, $\quad [OH^-] = ?; \quad [C_6H_5NH_2] = 0.24;$

$[C_6H_5NH_3^+] = 10^{-8}$

Therefore, $\quad \dfrac{1\times10^{-14}}{2.4\times10^{-5}} = \dfrac{10^{-8}\times[OH^-]}{0.24}$

$\therefore \quad [OH^-] = \dfrac{0.24\times10^{-14}}{2.4\times10^{-5}\times10^{-8}} = 0.01$

$\therefore \quad [NaOH] = \mathbf{0.01\ M}$

42. In this problem both the acids contribute for $[H^+]$ due to appreciable dissociation. Thus,

$$HCOOH \rightleftharpoons \underset{x+y}{H^+} + \underset{x}{HCOO^-}$$

$$HOCN \rightleftharpoons \underset{x+y}{H^+} + \underset{y}{OCN^-}$$

Because $[H^+]$ will remain common in solution. Thus,

$K_{HCOOH} = \dfrac{[H^+][HCOO^-]}{[HCOOH]} = 1.8\times10^{-4} \quad ...(1)$

$K_{HOCN} = \dfrac{[H^+][OCN^-]}{[HOCN]} = 3.3\times10^{-4} \quad ...(2)$

or $\quad K_{HCOOH} = \dfrac{(x+y)x}{0.1} = 1.8\times10^{-4} \quad ...(3)$

$K_{HOCN} = \dfrac{(x+y)y}{0.1} = 3.3\times10^{-4} \quad ...(4)$

Thus, by Eqs. (3) and (4) $\dfrac{x}{y} = \dfrac{1.8}{3.3}$

or $\quad y = 1.83x \quad ...(5)$

From Eq. (3) $(x+1.83x)\cdot x = 1.8\times10^{-5} \quad\therefore\quad x = 2.52\times10^{-3}$

Therefore, $\quad y = 4.61\times10^{-3}$

Thus, $\quad [H^+] = x+y = 2.52\times10^{-3} + 4.61\times10^{-3}$

$= \mathbf{7.13\times10^{-3}\ M}$

43. $HCOOH \rightleftharpoons H^+ + HCOO^-$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Since both have same pH and therefore.

$[H^+]$ by $HCOOH = [H^+]$ by CH_3COOH

$$C_1\alpha_1 = C_2\alpha_2$$

$$\sqrt{K_{a_1}C_1} = \sqrt{(K_{a_2}C_2)}$$

$$\therefore \sqrt{(2.4\times10^{-4}\times0.5)} = \sqrt{(1.8\times10^{-5}\times C)}$$

$$\therefore C_{CH_3COOH} = \mathbf{6.666\ M}$$

44. $HA \rightleftharpoons H^+ + A^-; \quad K_a = 1.38\times10^{-4}$

$HB \rightleftharpoons H^+ + B^-; \quad K_a = 1.05\times10^{-10}$

It is thus evident on account of low K_a values for HB, $[H^+]$ from HB is appreciably small in comparison to $[H^+]$ from HA and thus may be neglected.

For HA: $$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$1.38\times10^{-4} = \frac{[H^+]^2}{[HA]}$$

$$[H^+]^2 = 1.38\times10^{-4}\times[HA]$$

$$= 1.38\times10^{-4}\times0.03$$

Therefore, $[H^+] = [A^-] = \mathbf{2.04\times10^{-3}\ M}$

Now for HB: $$K_a = \frac{[H^+][B^-]}{[HB]}$$

$$1.05\times10^{-10} = \frac{2.04\times10^{-3}\times[B^-]}{0.1}$$

(Since $[H^+]$ is provided by acid HA and HB is almost undissociated)

or $$[B^-] = \mathbf{5.15\times10^{-9}\ M}$$

45. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$

$$[H^+] = \sqrt{K_{a_1}\cdot C_1 + K_{a_2}\cdot C_2}$$

$$= \sqrt{1.8\times10^{-5}\times0.02 + 6.4\times10^{-5}\times0.01} = 1\times10^{-3}$$

$$\therefore \mathbf{pH = 3}$$

Also $$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\therefore 1.8\times10^{-5} = \frac{[CH_3COO^-][1\times10^{-3}]}{0.02}$$

$$\therefore [CH_3COO^-] = \mathbf{3.6\times10^{-4}}$$

Similarly, $[C_6H_5COO^-] = \mathbf{6.4\times10^{-4}}$

46. Given, $[HCOOH] = 0.015M$

$[HCl] = 0.02M$

$\therefore$ $[H^+]$ in solution $= 0.02\ M$

The dissociation of HCOOH is suppressed due to common ion effect in presence of HCl. The $[H^+]$ is provided by HCl in solution.

$HCOOH \rightleftharpoons HCOO^- + H^+$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$1.8\times10^{-4} = \frac{[0.02][HCOO^-]}{[0.015]}$$

$$\therefore [HCOO^-] = \mathbf{1.35\times10^{-4}\ M}$$

47. $H_2S \rightleftharpoons H^+ + HS^-; \quad K_{a_1} = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}; \quad K_{a_2} = 1.3\times10^{-13}$

$HCl \longrightarrow H^+ + Cl^-$

Due to common ion effect the dissociation of H_2S is suppressed and the $[H^+]$ in solution is due to HCl.

$$\therefore K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$10^{-7} = \frac{[0.3][HS^-]}{[0.1]} \quad [\because [H^+] \text{ from HCl} = 0.3]$$

$$\therefore [HS^-] = \frac{10^{-7}\times0.1}{0.3} = \mathbf{3.3\times10^{-8}\ M}$$

Further $$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$1.3\times10^{-13} = \frac{[0.3][S^{2-}]}{3.3\times10^{-8}}$$

$$\therefore [S^{2-}] = \frac{1.3\times10^{-13}\times3.3\times10^{-8}}{0.3} = \mathbf{1.43\times10^{-20}\ M}$$

48. $\because$ Relative strength of weak acids $= \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\times\frac{C_1}{C_2}\right)}$

Assume C_1 and C_2 are same (Although not given)

$$\therefore \text{Relative strength} = \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)} = \sqrt{\left(\frac{2.1\times10^{-4}}{1.1\times10^{-5}}\right)}$$

Relative strength for HCOOH to $CH_3COOH = \mathbf{4.36:1}$

49. (a) We have $pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$

$\because$ $[\text{Conjugate base}] = \frac{3\times1000}{82\times100}M$ and $[\text{Acid}] = \frac{2\times1000}{60\times100}M$

$$\therefore pH = -\log 1.8\times10^{-5} + \log\frac{\frac{3\times1000}{82\times100}}{\frac{2\times1000}{60\times100}} \quad \therefore \mathbf{pH = 4.7851}$$

(b) $pOH = -\log K_b + \log\frac{[\text{Conjugate acid}]}{[\text{Base}]}$

$\because$ Total volume after mixing $= 250 + 5 = 255$ mL

Meq. of conjugate acid $= 250\times0.1 = 25$

Meq. of base $= 5\times0.1 = 0.5$

$$\therefore [\text{Conjugate acid}] = \frac{25}{255} \text{ and } [\text{Base}] = \frac{0.5}{255}$$

$$\therefore pOH = -\log 1.8\times10^{-5} + \log\frac{25/225}{0.5/255}$$

$pOH = 6.4437$ $\therefore$ $pH = 14 - pOH = \mathbf{7.5563}$

(c) $pH = -\log K_a + \log \frac{[Anion]}{[Acid]}$

$= -\log 3.6\times10^{-4} + \log \frac{0.35/500}{0.25/500}$

$pH = \mathbf{3.5898}$

50.

	$Na_2CO_3 + HCl \longrightarrow NaCl + NaHCO_3$			
Meq. before reaction	$\frac{30}{106}\times1000$	150×1		
	$= 283$	$= 150$	0	0
Meq. after reaction	133	0	150	150

The solution contains Na_2CO_3 and HCO_3^- and thus, acts as buffer.

$\therefore\ pH = -\log K_a + \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$

$pH = -\log K_a + \log \frac{133}{150} = -\log 5.63\times10^{-11} + \log \frac{133}{150}$

$= 10.249 - 0.052$

$pH = \mathbf{10.197}$

51. [Pyridinium chloride] $= (0.15/500)\times1000 = 0.3\ M$

[Pyridine] $= 0.2\ M$

$\therefore$ A mixture of pyridine and its salt pyridinium chloride forms a basic buffer and therefore,

$pOH = -\log K_b + \log$ [Conjugate acid]/[Base]

or $pOH = -\log 1.5\times10^{-9} + \log(0.30/0.20)$

$= -\log 1.5 + 9\log 10 + \log 1.5 = 9$

$\therefore\ [OH^-] = 10^{-9}$

and $[H^+] = 10^{-5}$ So $pH = \mathbf{5}$

52. $pOH = -\log K_b + \log \frac{[Conjugate\ acid]}{[Base]}$

or $pOH = -\log K_b + \log \frac{[NH_4^+]}{[NH_4OH]}$

$\because\ [NH_4^+]$ is obtained from salt $(NH_4)_2SO_4$

$\because\ pH = 9.35\ \ \therefore\ \ pOH = 14 - 9.35 = 4.65$

$\therefore$ Millimole of NH_4OH in solution $= 0.2\times500 = 100$

Let millimole of NH_4^+ added in solution $= a$

$\therefore\ [NH_4^+] = \frac{a}{500};\ \ [NH_4OH] = \frac{100}{500}$

$4.65 = -\log 1.78\times10^{-5} + \log \frac{a/500}{100/500}$

$4.65 = 4.7496 + \log \frac{a}{100}\ \ \therefore\ \ a = 79.51$

$\therefore$ Millimole of $(NH_4)_2SO_4$ added $= \frac{a}{2} = \frac{79.51}{2} = 39.755$

$\therefore\ \frac{w}{132}\times1000 = 39.755\ \ \therefore\ \ w_{(NH_4)_2SO_4} = \mathbf{5.248\ g}$

53. Let V mL of 0.1 M HCOONa be mixed to 50 mL of 0.05 M HCOOH.

$\because\ [Molarity] = \frac{Total\ millimole}{Total\ volume}$

$\therefore$ In mixture $[HCOONa] = \frac{0.1\times V}{(V+50)}$

$[HCOOH] = \frac{50\times0.05}{V+50}$

$\because\ pH = -\log K_a + \log \frac{[Conjugate\ base]}{[Acid]}$

$\therefore\ 4.0 = 3.80 + \log \frac{(0.1\times V)/(V+50)}{2.5/(V+50)}$

$\therefore\ V = \mathbf{39.62\ mL}$

54. NaCN + HCl is not a buffer but if HCl is in less mass then, it gives a buffer as it produces HCN.

	$NaCN + HCl \longrightarrow NaCl + HCN$			
Mole added	0.01	a	0	0
Mole after reaction	$(0.01 - a)$	0	a	a

This is buffer of HCN + NaCN

Let a mole of HCl be used for this purpose

$\therefore\ pH = -\log K_a + \log \frac{0.01-a}{a}$

$8.5 = -\log 4.1\times10^{-10} + \log \frac{0.01-a}{a}$

$\therefore\ a = \mathbf{8.85\times10^{-3}\ mol\ of\ HCl}$

55. **Case I :**

	$BOH + HCl \longrightarrow BCl + H_2O$			
Millimole before reaction	a	$1.0\times5 = 0.5$	0	0
Millimole after reaction	$(a - 0.5)$	0	0.5	0.5

$\because\ pH = 10.04\ \ \therefore\ pOH = -\log K_b + \log \frac{[B^+]}{[BOH]}$ ...(1)

$\therefore\ pOH = 3.96\ \ \therefore\ 3.96 = -\log K_b + \log \frac{0.5}{(a-0.5)}$ ...(2)

Case II :

	$BOH + HCl \longrightarrow BCl + H_2O$			
Millimole before reaction	a	$0.1\times20 = 2$		
Millimole after reaction	$(a - 0.2)$	0	2	2

$\because\ pH = 9.14\ \ \therefore\ pOH = -\log K_b + \log \frac{[B^+]}{[BOH]}$ ...(3)

$\therefore\ pOH = 4.86\ \ \therefore\ 4.86 = -\log K_b + \log \frac{2}{a-2}$ ...(4)

Solving Eqs. (2) and (4), $K_b = \mathbf{1.81\times10^{-5}}$

56. For neutralization :

Total Meq. of acid = Meq. of base $= 26.6\times0.1 = 2.66$

Now for partial neutralization of acid

	$HA + BOH \longrightarrow BA + H_2O$			
Meq. before reaction	2.66	1.2	0	0
Meq. after reaction	1.46	0	1.2	1.2

The resultant mixture acts as a buffer and $[HA]$ and $[BA]$ may be placed in terms of Meq. since volume of mixture is constant.

$\therefore\ pH = -\log K_a + \log \frac{[Conjugate\ base]}{[Acid]}$

or $5 = -\log K_a + \log \frac{[1.2]}{[1.46]}$

$K_a = \mathbf{8.219\times10^{-6}}$

57. For complete neutralization,

Meq. of acid = Meq. of NaOH $= 36.12\times0.1 = 3.612$

$\therefore$

	$HA + NaOH \longrightarrow NaA + H_2O$			
	3.612	3.612	0	0
	0	0	3.612	3.612

Now 1.806 Meq. of HCl (18.06×0.1) are added to this solution containing 3.612 Meq. of NaA.

$$NaA + HCl \longrightarrow NaCl + HA$$

Meq. before reaction	3.612	1.806	0	0
Meq. after reaction	1.806	0	1.806	1.806

The solution has HA and NaA and thus,acts as buffer

$$\therefore \quad pH = -\log K_a + \log \frac{1.806}{1.806}$$

$$4.92 = -\log K_a$$

$$\therefore \quad K_a = \mathbf{1.2\times10^{-5}}$$

58.

$$CHCl_2\cdot COOH \rightleftharpoons CHCl_2\cdot COO^- + H^+$$

Before dissociation	0.2	–	–
After dissociation	$(0.2-x)$	x	x

$$CHCl_2\cdot COONa \longrightarrow CHCl_2COO^- + Na^+$$

$$0.1 \qquad 0.1$$

For the dissociation of acid

$$K_a = 5\times10^{-2} = \frac{[CHCl_2COO^-][H^+]}{[CHCl_2\cdot COOH]}$$

or $$0.05 = \frac{[0.1+x][x]}{[0.2-x]}$$

$$\therefore \quad x = 0.05 \quad \text{or} \quad [H^+] = \mathbf{0.05}$$

59. Initial pH of solution when,

$$[NH_3] = \frac{0.1}{1} \text{ and } [NH_4Cl] = \frac{0.1}{1}$$

$$pOH = -\log 1.8\times10^{-5} + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

$$= -\log 1.8\times10^{-5} + \log \frac{0.1}{0.1}$$

$$pOH = 4.7447 \quad \therefore \quad pH = \mathbf{9.2553}$$

(i) Now 0.02 mole of HCl are added, then

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

Mole before reaction	0.02	0.1	0.1
Mole after reaction	0	0.08	(0.1 + 0.02)

$\because$ Volume = 1 litre

$$\therefore \quad [NH_4OH] = \frac{0.08}{1} \quad \text{and} \quad [NH_4Cl] = \frac{0.12}{1}$$

$$\therefore \quad pOH_I = -\log 1.8\times10^{-5} + \log \frac{0.12}{0.08}$$

$$\therefore \quad pOH_I = 4.9208 \quad \therefore \quad pH_I = \mathbf{9.0792}$$

Change in pH = pH – pH_I = 9.2553 – 9.0792 = +0.1761

$\therefore$ Change in pH = **0.1761 unit, *i.e.*, pH decreases**

(ii) Now 0.02 mole of NaOH are added

$$NaOH + NH_4Cl \longrightarrow NaCl + NH_4OH$$

Mole before reaction	0.02	0.1	0	0.1
Mole after reaction	0	0.08	0.02	0.12

$$\therefore \quad pOH_2 = -\log 1.8\times10^{-5} + \log \frac{0.08}{0.12}$$

$$pOH_2 = 4.5686 \quad \therefore \quad pH_2 = \mathbf{9.4314}$$

Change in pH = pH – pH_2 = 9.2553 – 9.4314 = –0.1761

$\therefore$ Change in pH = **0.1761 unit, *i.e.*, pH increases**

60. (1)

$$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$$

Millimole added	20×0.2 = 4	50×0.2 = 10	0	0
Millimole after reaction	0	6	4	4

$\because$ $$[\text{Molarity}] = \frac{\text{Millimole}}{\text{Total volume}}$$

$$\therefore \quad [CH_3COOH] = \frac{6}{70} \quad [CH_3COONa] = \frac{4}{70}$$

$$\therefore \quad pH = -\log 1.8\times10^{-5} + \log \frac{4/70}{6/70}$$

$$pH = \mathbf{4.5686}$$

(2) Let V mL of 0.2 M NaOH is required to make pH 4.74 then,

$$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$$

Millimole added	$0.2\times V$ = 0.2V	50×0.2 = 10	0	0
Millimole after reaction	0	$(10-0.2V)$	0.2V	0.2V

$$\therefore \quad [\text{Acid}] = \frac{10-0.2V}{50+V}; \quad [\text{Conjugate base}] = \frac{0.2V}{50+V}$$

$$\therefore \quad 4.74 = -\log 1.8\times10^{-5} + \log \frac{(0.2V)/(50+V)}{(10-0.2V)/(50+V)}$$

(take $\log 1.8\times10^{-5} = 4.7447 = 4.74$)

$$\therefore \quad V = \mathbf{25\ mL}$$

61. **Case I :** pH when 1 mole CH_3COONa and 1 mole HCl are present.

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$$

Before reaction	1	1	0	0
After reaction	0	0	1	1

$$\therefore \quad [CH_3COOH] = 1M$$

$$\therefore \quad [H^+] = C\cdot\alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a\cdot C)} = \sqrt{(K_a)} \because C = 1$$

$$\therefore \quad pH_I = \frac{1}{2}\log K_a$$

Case II : pH when 1 mole CH_3COONa and 1 mole of CH_3COOH; a buffer solution

$$\therefore \quad pH_2 = -\log K_a + \log \frac{\left[\begin{matrix}\text{Conjugate}\\ \text{base}\end{matrix}\right]}{[\text{Acid}]}$$

$\because$ [Salt] = [Anion] = 1 M

$\because$ [Acid] = 1 M

$$pH_2 = -\log K_a$$

$$\therefore \quad \frac{pH_I}{pH_2} = \frac{1}{2}$$

62. For weak acid HA : $\alpha_{HA} = \frac{1}{100} = 0.01, [HA] = 0.1M$

$$\therefore \quad K_a = C\alpha^2 = 0.1\times(0.01)^2 = 10^{-5}$$

Now 0.2 M NaA, a salt of HA, is added to it resulting a buffer solution of [HA] = 0.1 M and [NaA] = 0.2 M

$$\therefore \quad pH = -\log 10^{-5} + \log \frac{0.2}{0.1}$$

$$pH = \mathbf{5.3010}$$

Also

$$HA \rightleftharpoons H^+ + A^-$$

$$1 \qquad 0 \qquad 0$$

$$(1-\alpha) \qquad \alpha \qquad \alpha$$

$\because$ $[A^-]$ is provided by NaA since dissociation of HA in presence of NaA is suppressed due to a common ion effect

$$\therefore \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(C\cdot\alpha)\times0.2}{C(1-\alpha)} = 10^{-5}$$

$$\therefore \quad \alpha = \mathbf{5\times10^{-5}}$$

63. In 0.2 M HCOOH $[H^+] = 6.4\times10^{-3}$

$$C\alpha = 6.4\times10^{-3} \quad \therefore \quad \alpha = 3.2\times10^{-2}$$

Now sodium formate is added and the dissociation will further be suppressed and therefore, new degree of dissociation (α_1) for HCOOH in presence of HCOONa is so small that it may be neglected, *i.e.*,

$\therefore$ [HCOOH] after dissociation = [HCOOH] before dissociation

$\therefore$ $[HCOOH] = 0.2$

$$HCOONa \rightleftharpoons HCOO^- + Na^+$$

Conc. before dissociation	1	0	0
Conc. after dissociation	(1 – 0.75)	0.75	0.75

So $[HCOOH] = 0.2 \therefore [HCOO^-] = 0.75$

$$\therefore \quad pH = -\log 2.4\times10^{-4} + \log\frac{0.75}{0.2} = \mathbf{4.19}$$

64. (a) Initially [Acetic acid] = 1 M

[Acetate] = 1 M

Now 0.2 mole of HCl are added to it.

$$HCl + CH_3COO^- \longrightarrow CH_3COOH + Cl^-$$

Mole before reaction	0.2	1	1	0
Mole after reaction	0	0.8	1.2	0.2

$\therefore$ Now $[CH_3COOH] = 1.2; [CH_3COO^-] = 0.8$

$$\therefore \quad pH = -\log 1.8\times10^{-5} + \log\frac{0.8}{1.2} = \mathbf{4.5686}$$

(b) In II case initially [Acetic acid] = 0.1 M

[Acetate] = 0.1 M

Now 0.2 mole of HCl are added to it

$$HCl + CH_3COO^- \rightarrow CH_3COOH + Cl^-$$

Mole of before reaction	0.2	0.1	0.1	0
Mole after reaction	0.1	0	0.2	0.1

$\therefore$ $[H^+]$ from free HCl $= 0.1 = 10^{-1} \quad \therefore \quad pH = \mathbf{1}$

Note : CH_3COOH no doubt gives H^+ but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H^+ from CH_3COOH may be neglected.

65.
$$pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Let a mol litre^{-1} be concentration of salt, then concentration of acid $= (0.29 - a)$.

$$4.4 = -\log 1.8\times10^{-5} + \log\frac{a}{(0.29-a)} \quad \therefore \quad a = 0.09$$

$\therefore$ [Salt] = $\mathbf{0.09\ M}$

[Acid] $= 0.29 - 0.09 = \mathbf{0.20\ M}$

66.
$$pOH = -\log K_b + \log\frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

$$5 = 4.7 + \log\frac{a}{b}$$

$$\frac{a}{b} = 2 \quad \therefore \quad a = 2b$$

Given $a + b = 0.6$

$2b + b = 0.6$

$\therefore$ $3b = 0.6$

or $b = 0.2$ mole or $0.2\times17 = \mathbf{3.4\ g/L}$

$\therefore$ $a = 0.4$ mole or $0.4\times53.5 = \mathbf{21.4\ g/L}$

Thus, [Salt] = $\mathbf{0.4\ M}$ and [Base] = $\mathbf{0.2\ M}$

67.
$$HCl + NH_3 \longrightarrow NH_4Cl$$

mm at $t = 0$	30	40	0
mm after reaction	0	10	30

$$\therefore \quad pOH = pK_b + \log\frac{[NH_4^+]}{[NH_3]} \qquad (pK_a + pK_b = 14)$$

$$= 4.7448 + \log\frac{30}{10} = 5.2218$$

$\therefore$ $pH = 14 - 5.2218 = \mathbf{8.7782}$

68.
$$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl$$

50×0.2 = 10	75×0.1 = 7.5	0	0
2.5	0	7.5	7.5

$$(pK_a + pK_b = 14)$$

$$\therefore \quad pOH = 4.7448 + \log\frac{2.5}{7.5} = 4.2676$$

$\therefore$ $pH = \mathbf{9.7324}$

69.
$$K_{b(x^{-1})} = 10^{-10}$$

Also for conjugate acid – base pair

$$K_{a_{(HX)}} \times K_{b(x^{-1})} = 10^{-14} \quad \therefore \quad K_{a(HX)} = 10^{-4}$$

Now $[HX] = [X^-]$
(acid) (anion)

$$\therefore \quad pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]} = -\log 10^{-4}$$

$pH = 4$

70. pH of buffer is given by:

$$pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Case I : $$4 = -\log 1.0\times10^{-5} + \log\frac{[\text{Conjugate base}]}{(0.5)}$$

$$\therefore \quad \log\frac{[\text{Conjugate base}]}{0.5} = -1$$

[Conjugate base] $= 0.1\times0.5 = 0.05\ M$

Case II : $$6 = -\log 1.0\times10^{-5} + \log\frac{[\text{Conjugate base}]}{0.5}$$

$$\therefore \quad \log\frac{[\text{Conjugate base}]}{0.5} = 1$$

$\therefore$ [Conjugate base] = [Salt] $= 10\times0.5 = 5M$

Now the two buffer [(I. NaA = 0.05 M and HA = 0.5 M) and (II. NaA = 5 M and HA = 0.5 M)] are mixed in equal proportion.

Thus, new conc. of NaA is mixed buffer

$$= \frac{0.05\times V + 5\times V}{2V} = \frac{5.05}{2}$$

New conc. of HA in mixed buffer $= \dfrac{0.5\times V + 0.5\times V}{2V} = 0.5M$

Thus, $$pH = -\log 1.0\times10^{-5} + \log\frac{[5.05/2]}{[0.5]}$$

$pH = 5 + 0.7033 = \mathbf{5.7033}$

71. $\underset{\text{Weak}}{HA} + \underset{\text{Strong}}{BOH} \rightleftharpoons BA + H_2O$

$\therefore\ HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$

or $HA + OH^- \rightleftharpoons A^- + H_2O$

$\therefore\ K = \dfrac{[A^-]}{[HA][OH^-]}$ ...(1)

Also for weak acid HA : $HA \rightleftharpoons H^+ + A^-$

$K_a = \dfrac{[H^+][A^-]}{[HA]}$ ...(2)

By Eqs. (2) and (1), $\dfrac{K_a}{K} = K_w$

$\therefore\ K = \dfrac{K_a}{K_w} = \dfrac{10^{-4}}{10^{-14}} = \mathbf{10^{10}}$

72. $[H_2CO_3]$ in blood $= 2M$

Volume of blood $= 10$ mL

$[NaHCO_3] = 5M$

Let volume of $NaHCO_3$ used $= V$ mL

$\therefore\ [H_2CO_3]$ in mixture $= \dfrac{2\times 10}{(V+10)}$

$[NaHCO_3]$ in mixture $= \dfrac{(5\times V)}{(V+10)}$

$\therefore\ pH = pK_a + \log\dfrac{[\text{Conjugate base}]}{[\text{Acid}]}$

$7.4 = -\log 7.8\times 10^{-7} + \log\dfrac{(5\times V)/(V+10)}{(2\times 10)/(V+10)}$

$\therefore\ V = \mathbf{78.36\ mL}$

73. K_a for CH_3COOH can be derived by $[H^+] = 10^{-3}$

$C\alpha = 10^{-3}\quad \therefore\ \alpha = \dfrac{10^{-3}}{0.1} = 10^{-2}$

Now $K_a = C\alpha^2 = 0.1\times(10^{-2})^2 = 10^{-5}$

Case I : $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Before addition NaOH 0.1

After addition of NaOH $0.1\times\frac{3}{4}$ $0.1\times\frac{1}{4}$

when $\frac{1}{4}$ acid neutralizes

$\because\ pH = -\log K_a + \log\dfrac{[\text{Conjugate base}]}{[\text{Acid}]}$

$pH = -\log 10^{-5} + \log\dfrac{0.1/4}{0.3/4}\quad \therefore\ pH = \mathbf{4.5228}$

Case II : $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

After addition of NaOH $0.1\times 1/4$ $0.1\times 3/4$

For 3/4 neutralization

$\therefore\ pH = -\log 10^{-5} + \log\dfrac{0.3/4}{0.1/4}\quad \therefore\ pH = \mathbf{5.4771}$

74. (a) In pure water :

Let solubility of AgCl be s mol litre^{-1}

For $AgCl(s) \rightleftharpoons Ag^+(aq.) + Cl^-(aq.)$

$K_{sp} = [Ag^+][Cl^-] = s\times s$

$\therefore\ s = \sqrt{(K_{sp})} = \sqrt{(1.5\times 10^{-10})}$

$= \mathbf{1.224\times 10^{-5}\ mol\ litre^{-1}}$

(b) In 0.1 M $AgNO_3$:

$AgCl(s) \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Cl^-}$

$AgNO_3 \longrightarrow \underset{0.1}{Ag^+} + \underset{0.1}{NO_3^-}$

$\therefore\ K_{sp} = [Ag^+][Cl^-] = (0.1+s)(s)$

($\because s <<< 0.1$, presence of common ion decreases solubility)

$\therefore\ s(0.1) = 1.5\times 10^{-10}$

$\therefore\ s = \mathbf{1.5\times 10^{-9}\ mol\ litre^{-1}}$

(c) Solubility of AgCl is more in ($aq.$) NaCl than $AgNO_3$ due to complex formation.

$AgCl(s) + NaCl \rightleftharpoons [AgCl_2]^- + Na^+$

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-(aq.)$

In saturated solution $K_{sp} = [Ag^+][Cl^-]$ ... (i)

$Ag^+ + 2Cl^- \rightleftharpoons [AgCl_2]^-$

In NaCl($aq.$) $K_f = \dfrac{[AgCl_2]^-}{[Ag^+][Cl^-]^2}$ ... (ii)

By (i) and (ii) $K_{sp}\times K_f = \dfrac{[AgCl_2]^-}{[Cl^-]}$ ... (iii)

Solubility of AgCl in pure water :

$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2$

$\therefore\ [Ag^+] = \sqrt{K_{SP}} = \sqrt{1.0\times 10^{-10}}$

$= 10^{-5}$ M

In 0.01 M NaCl : By (iii)

$[AgCl_2]^- = K_{sp}\times K_f\times Cl^-$

$= 1\times 10^{-10}\times 3\times 10^{+5}\times 0.01$

$= 3\times 10^{-7}$ M

75. $KBr + AgNO_3 \longrightarrow AgBr + KNO_3$

Let a mole of KBr be added into 1 litre of 0.05 M $AgNO_3$ to bring in precipitation.

Thus, $[KBr] = \frac{a}{1}$; $[AgNO_3] = 0.05$

or $[Br^-] = a$ and $[Ag^+] = 0.05$

$\therefore\ [Ag^+][Br^-] = K_{sp}$

$0.05\times a = 5.0\times 10^{-13}$

$\therefore\ a = 5\times 10^{-11}\,M = 5\times 10^{-11}\times 120$

$= \mathbf{6.00\times 10^{-9}\ g/1000\ mL}$

Thus, mass of KBr needed for precipitation of AgBr from 500 mL 0.05 M are $\mathbf{3.0\times 10^{-9}\ g}$

76. Solubility (s) of $AgCl = 1.79\times 10^{-3}$ g / litre

$= \dfrac{1.79\times 10^{-3}}{143.5}$ mol litre^{-1}

$= 1.247\times 10^{-5}$ mol litre^{-1}

$\therefore \quad K_{sp} = [Ag^+][Cl^-] = s \times s$

$= [1.247\times10^{-5}][1.247\times10^{-5}]$

$K_{sp} = \mathbf{1.55\times10^{-10}\ mol^2\ litre^{-2}}$

77. $AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq.)$

$K_{sp} = [Ag^+][Br^-]$

$4\times10^{-13} = [1\times10^{-6}][Br^-]$

$\therefore \quad [Br^-] = \dfrac{4\times10^{-13}}{1\times10^{-6}} = \mathbf{4\times10^{-7}\ mol\ litre^{-1}}$

78. For saturated solution of Ag_2CrO_4, if solubility is s mol litre^{-1}. Then,

$$\underset{2s}{Ag_2CrO_4}(s) \rightleftharpoons 2\underset{2s}{Ag^+}(aq.) + \underset{s}{CrO_4^{2-}}(aq.)$$

$K_{sp} = (2s)^2(s) = 4s^3 \qquad [\because [Ag^+] = 2s = 1.5\times10^{-4}$

$= 4\times(0.75\times10^{-4})^3 \qquad \therefore s = 0.75\times10^{-4}]$

$K_{sp} = \mathbf{1.688\times10^{-12}\ mol^3\ litre^{-3}}$

79. For PbI_2, $\underset{s}{PbI_2} \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2I^-}$

where s is solubility of PbI_2

$\therefore \quad K_{sp} = 4s^3 \qquad \therefore \ s^3 = \dfrac{K_{sp}}{4}$

or $\quad s = \sqrt[3]{\dfrac{K_{sp}}{4}} = \sqrt[3]{\dfrac{4\times10^{-9}}{4}} = 10^{-3}$

$\therefore \quad [I^-] = 2s = 2\times10^{-3}$ mol/litre

Now, for $\quad Ag^+ + I^- \longrightarrow AgI$

Meq. of Ag^+ = Meq. of I^-

$N\times10 = 2\times10^{-3}\times25$

$\therefore \quad N$ or M of $AgNO_3 = \mathbf{5\times10^{-3}}$

80. $\underset{\text{Millimole added}}{\underset{0.02V}{CaCl_2} + \underset{0.0004\times V}{Na_2SO_4}} \longrightarrow \underset{0}{CaSO_4} + \underset{0}{2NaCl}$

Suppose V mL of both are mixed

$\therefore \quad [Ca^{2+}] = \dfrac{0.02V}{2V} \qquad [SO_4^{2-}] = \dfrac{0.0004V}{2V}$

Thus, $[Ca^{2+}][SO_4^{2-}]$ in solution $< K_{sp}$

$2\times10^{-6} < 2.4\times10^{-5}$

$\therefore$ **$CaSO_4$ will not precipitate.**

81. For ZnS not to be precipitated from a solution of Zn^{2+} and Pb^{2+}

$[Zn^{2+}][S^{2-}] < K_{sp}$ of ZnS

$[10^{-2}][S^{2-}] < 1.0\times10^{-21}$

or the maximum $[S^{2-}] = 10^{-19}$ at which ZnS will begin to precipitate or upto this concentration, no precipitation will occur.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$\therefore \quad [H^+]^2[S^{2-}] = 1.1\times10^{-22}$

$\therefore \quad [H^+]^2[10^{-19}] = 1.1\times10^{-22}$

$\therefore \quad [H^+]^2 = 11\times10^{-4} \quad \therefore \ [H^+] = \mathbf{3.3\times10^{-2}\ M}$

Thus, if $[H^+] = 3.3\times10^{-2}$ or slightly higher, the precipitation of ZnS will not take place and only PbS will precipitate.

82. $Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$

Millimole added	$100\times0.1 = 10$	$1\times1 = 1$	0	0
Millimole left	9.5	0	0.5	1

$\because$ Concentration in $M = \dfrac{m\text{mole}}{\text{Total volume}}$

$\therefore \quad [Pb^{2+}] = \dfrac{9.5+0.5}{101}$

Now if $PbCl_2$ is precipitated, then contribution 0.5 of $[Pb^{2+}]$ from $PbCl_2$ should be left.

To see precipitation, ionic concentration product $> K_{sp}$

Ionic conc. product

$= [Pb^{2+}][Cl^-]^2 = \left[\dfrac{10}{101}\right]\left[\dfrac{1}{101}\right]^2 = 9.70\times10^{-6}$

which is greater than K_{sp} of $PbCl_2$ and thus, precipitation of $PbCl_2$ occurs.

$\therefore \quad [Pb^{2+}] = \dfrac{9.5}{101} = \mathbf{9.4\times10^{-2}\ mol\ litre^{-1}}$

83. Let solubility of $PbBr_2$ be s mol litre^{-1}

$$PbBr_2(s) \rightleftharpoons PbBr_2(aq.) \rightleftharpoons \underset{\frac{s\times80}{100}}{Pb^{2+}} + \underset{\frac{2s\times80}{100}}{2Br^-}$$

$\because$ Ionisation of $PbBr_2(s) = 80\%$

$\therefore \quad K_{sp} = [Pb^{2+}][Br^-]^2$

$8\times10^{-5} = \left[\dfrac{s\times80}{100}\right]\left[\dfrac{2s\times80}{100}\right]^2$

$\therefore \quad s = 0.034$ mol litre^{-1} ($\because$ M. mass of $PbBr_2 = 367$)

$s = 0.034\times367$ litre^{-1}

$s = \mathbf{12.48\ g\ litre^{-1}}$

84. K_{sp} of $Pb(OH)_2 = 4s^3 = 4\times(6.7\times10^{-6})^3 = 1.203\times10^{-15}$

The buffer contains pH = 8 $\therefore$ pOH = 6 or $[OH^-] = 10^{-6}$

Now left solubility of $Pb(OH)_2$ be s mol litre^{-1} in it.

Thus, $\quad [Pb^{2+}][OH^-]^2 = K_{sp}$

$[Pb^{2+}][10^{-6}]^2 = 1.203\times10^{-15}$

$\left[\begin{array}{l}\text{Buffer has pH = 8; } \therefore \text{pOH} = 6\\ \text{and } [OH^-] = 10^{-6}\end{array}\right]$

$\therefore \quad [Pb^{2+}] = \dfrac{1203\times10^{-15}}{10^{-12}} = \mathbf{1.203\times10^{-3}\ mol\ litre^{-1}}$

85. K_{sp} of $C_6H_5COOAg = [C_6H_5COO^-][Ag^+]$

$= 2.5\times10^{-13}$

In pure water $\quad S^2 = 25\times10^{-14}$

$S = 5\times10^{-7}$

In pH = 3.19 ; pOH = 10.81 or $[OH^-]=1.55\times10^{-11}$, $C_6H_5COO^-$ undergoes hydrolysis to form C_6H_5COOH

$$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$$

$$\therefore \quad K_H = \frac{K_w}{K_a} = \frac{[C_6H_5COOH]OH^-}{[C_6H_5COO^-]}$$

$$\therefore \quad \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{K_w}{K_a[OH^-]}$$

$$= \frac{10^{-14}}{6.46\times10^{-5}\times1.55\times10^{-11}} = 10$$

$[Ag^+]$ dissolved in pH 3.19 = $[C_6H_5COO^-]$ left after hydrolysis + $[C_6H_5COOH]$ formed due to hydrolysis

$= [C_6H_5COO^-] + 10[C_6H_5COO^-] = 11[C_6H_5COO^-]$

$$\therefore \quad [C_6H_5COO^-] = \frac{[Ag^+]}{11}$$

$$[Ag^+][C_6H_5COO^-] = [Ag^+]\frac{[Ag^+]}{11} = 2.5\times10^{-13}$$

$$\therefore \quad [Ag^+] = 1.658\times10^{-6}$$

i.e., solubility is $\frac{1.658\times10^{-6}}{5\times10^{-7}} = \mathbf{3.316}$ times greater then pure water.

86. $[Ca^{2+}][F^-]^2 = 3.45\times10^{-11}$

The F^- reacts with H^+ (pH = 3.0) to produce HF

$$K_{a_{HF}} = \frac{[H^+][F^-]}{[HF]}$$

or $$6.3\times10^{-4} = \frac{10^{-3}\times[F^-]}{[HF]}$$

$$\therefore \quad HF = 1.58\times[F^-]$$

Also the solution contains $[HF]+[F^-] = 2\times[Ca^{2+}]$

or $1.58\times[F^-]+[F^-] = 2\times[Ca^{2+}]$

$$\therefore \quad [F^-] = \frac{2}{2.58}\times[Ca^{2+}] = 0.775[Ca^{2+}]$$

Let solubility of CaF_2 be S mol litre^{-1} $\therefore$ $[Ca^{2+}] = S$

$$\therefore \quad [F^-] = 0.775\times S$$

Thus $S\times(0.775\times S)^2 = 3.45\times10^{-11}$

$$\therefore \quad S = \mathbf{3.86\times10^{-4}}\ M$$

87. pH = 9 $\therefore$ $[H^+] = 10^{-9}\ M$ or $[OH^-] = 10^{-5}\ M$

Now if $Mg(NO_3)_2$ is present in a solution of $[OH^-] = 10^{-5}\ M$, then,

Product of ionic conc.

$= [Mg^{2+}][OH^-]^2 = [0.001][10^{-5}]^2$

$= 10^{-13}$ lesser than K_{sp} of $Mg(OH)_2$ *i.e.*, 8.9×10^{-12}

$\therefore$ **$Mg(OH)_2$ will not precipitate.**

88. When $Mg(OH)_2$ starts precipitation, then,

$[Mg^{2+}][OH^-]^2 = K_{sp}$ of $Mg(OH)_2$

$$[0.1][OH^-]^2 = 1\times10^{-11}$$

$\therefore$ $[OH^-] = 10^{-5}\ M$ $\therefore$ pOH = 5

$\therefore$ pH = 14 − pOH $\therefore$ pH = 14 − 5 = **9**

89.

	$MgCl_2$	+ 2NaOH	⟶ $Mg(OH)_2$	+ 2NaCl
mm before reaction	10	20	0	0
	0	0	10	20

Thus, 10 *m* mole of $Mg(OH)_2$ are formed. The product of $[Mg^{2+}][OH^-]^2$ is therefore $\left[\frac{10}{200}\right]\times\left[\frac{20}{200}\right]^2 = 5\times10^{-4}$ which is more than K_{sp} of $Mg(OH)_2$. Now solubility (s) of $Mg(OH)_2$ can be derived by

$$K_{sp} = 4s^3$$

$$\therefore \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2\times10^{-11}}{4}} = 1.4\times10^{-4}$$

$$\therefore \quad [OH^-] = 2s = \mathbf{2.8\times10^{-4}}$$

90.

	Na_2CO_3	+ 2AgCl	⇌ 2NaCl	+ Ag_2CO_3
mm added	7.5	excess	0	0
mm left	(7.5 − *a*)	excess	2*a*	*a*

Given $[Cl^-] = \frac{0.0026}{35.5} = 7.32\times10^{-5}$

Also, conc. of Cl^- formed = $\frac{\text{Millimole}}{\text{Volume in mL}} = \frac{2a}{5}$

$\therefore$ $\frac{2a}{5} = \frac{0.0026}{35.5}$ $\therefore$ $a = 1.83\times10^{-4}$ millimole

$\therefore$ *m* mole of Na_2CO_3 left in 5 mL = $7.5 - 1.83\times10^{-4} = 7.5$

or $$[CO_3^{2-}] = \frac{7.5}{5}$$

Now $K_{sp_{Ag_2CO_3}} = [Ag^+]^2[CO_3^{2-}]$

$$\therefore \quad [Ag^+]^2 = \frac{8.2\times10^{-12}}{7.5/5} = 5.46\times10^{-12}$$

$$\therefore \quad [Ag^+] = 2.34\times10^{-6}$$

$$\therefore \quad K_{sp} \text{ of AgCl} = [Ag^+][Cl^-] = 2.34\times10^{-6}\times\frac{0.0026}{35.5}$$

$$K_{sp} = \mathbf{1.71\times10^{-19}}$$

91. Let solubility of AgCNS and AgBr in a solution be *a* and *b* mol litre^{-1} respectively.

$$AgCNS(s) \rightleftharpoons Ag^+ + CNS^-$$

[Ion] furnished on dissolution $\quad a \quad a$

$$AgBr(s) \rightleftharpoons Ag^+ + Br^-$$

[Ion] furnished on dissolution $\quad b \quad b$

$\therefore$ $[Ag^+] = a+b$; $[CNS^-] = a$; $[Br^-] = b$

$\therefore$ For AgCNS $K_{sp_{AgCNS}} = [Ag^+][CNS^-]$

$$1\times10^{-12} = (a+b)(a) \qquad ...(1)$$

For AgBr $K_{sp_{AgBr}} = [Ag^+][Br^-]$

$$5\times10^{-13} = (a+b)(b) \qquad ...(2)$$

By Eqs. (1) and (2),

$$\therefore \quad \frac{a}{b} = \frac{10^{-12}}{5\times10^{-13}} = 2 \quad \text{or} \quad a = 2b$$

$\therefore$ By Eq. (1), $(2b+b)(2b)=1\times10^{-12}$ $\therefore$ $6b^2=1\times10^{-12}$

$b=\mathbf{4\times10^{-7}\ mol\ litre^{-1}}$

By Eq. (1), $(a+a/2)(a)=1\times10^{-12}$

$\therefore$ $a=\mathbf{8.16\times10^{-7}\ mol\ litre^{-1}}$

92. The $[I^-]$ needed for precipitation of Ag^+ and Hg_2^{2+} are derived as:

For AgI: $[Ag^+][I^-]=K_{sp_{AgI}}$

$(0.1)[I^-]=8.5\times10^{-17}$

$\therefore$ $[I^-]=8.5\times10^{-16}\ M$ ...(1)

For Hg_2I_2: $[Hg_2^{2+}][I^-]^2=2.5\times10^{-26}$

$(0.1)[I^-]^2=2.5\times10^{-26}$

$\therefore$ $[I^-]=5\times10^{-13}\ M$ ...(2)

Since, $[I^-]$ required for precipitation of AgI is less and thus AgI begins **to precipitate first.** Also it will continue upto addition of $[I^-]=5\times10^{-13}$ when Hg_2I_2 begins to precipitate and thus,

Maximum $[I^-]$ for AgI precipitation $=\mathbf{5\times10^{-13}}M$

Now at this concentration of I^-, $[Ag^+]$ left in solution is

$[Ag^+]_{left}[I^-]=K_{sp_{AgI}}$

$\therefore$ $[Ag^+]_{left}=\dfrac{8.5\times10^{-17}}{5.0\times10^{-13}}=\mathbf{1.7\times10^{-4}}\ M$

$\because$ $0.1M\ Ag^+$ will be left $=1.7\times10^{-4}\ M\ Ag^+$ in solution

$\therefore$ 100 " " $=\mathbf{0.17\%}\ M\ Ag^+$

$\therefore$ % of Ag precipitated $=\mathbf{99.83\%}$

93. The K_{sp} values of Ag_2CrO_4 and $AgIO_3$ reveals that CrO_4^{2-} and IO_3^- will be precipitated on addition of $AgNO_3$ as:

$[Ag^+][IO_3^-]=10^{-13}$

$[Ag^+]_{needed}=\dfrac{10^{-13}}{[0.005]}=2\times10^{-11}$

$[Ag^+]^2[CrO_4^{2-}]=10^{-8}$

$[Ag^+]_{needed}=\sqrt{\dfrac{10^{-8}}{0.1}}=3.16\times10^{-4}$

Thus, $AgIO_3$ will be precipitated first.

Now, in order to precipitate $AgIO_3$, one can show:

$$\underset{0.01}{AgNO_3}+\underset{0.005}{NaIO_3}\longrightarrow\underset{0}{AgIO_3}+\underset{0}{NaNO_3}$$

$$\underset{0.005}{}\quad\underset{0}{}\quad\underset{0.005}{}\quad\underset{0.005}{}$$

The left mole of $AgNO_3$ are now used to precipitate Ag_2CrO_4

$$\underset{0.005}{2AgNO_3}+\underset{0.1}{Na_2CrO_4}\longrightarrow\underset{0}{Ag_2CrO_4}+\underset{0}{2NaNO_3}$$

$$\underset{0}{}\quad\underset{0.0975}{}\quad\underset{0.0025}{}\quad\underset{0.005}{}$$

Thus, $[CrO_4^{2-}]$ left in solution $=\mathbf{0.0975}$

Now, solution has $\underset{0.005}{AgIO_3}(s)+\underset{0.0025}{Ag_2CrO_4}(s)+\underset{0.0975}{CrO_4^{2-}}$ ions

$\therefore$ $[Ag^+]_{left}=\dfrac{K_{sp}Ag_2CrO_4}{[CrO_4^{2-}]}=\sqrt{\dfrac{10^{-8}}{0.0975}}=\mathbf{3.2\times10^{-4}}\ M$

$\therefore$ $[IO_3^-]_{left}=\dfrac{K_{sp}AgIO_3}{[Ag^+]}=\dfrac{10^{-13}}{3.2\times10^{-4}}=\mathbf{3.2\times10^{-10}}\ M$

94. 500 mL of 0.4 M NaOH are mixed with 500 mL of $Ca(OH)_2$, a saturated solution having $Ca(OH)_2$ solubility as $s\,M$.

For $Ca(OH)_2\rightleftharpoons Ca^{2+}+2OH^-$

$K_{sp}=s\times(2s)^2=4s^3$

Then, $4s^3=4.42\times10^{-5}$

$\therefore$ $s=\sqrt[3]{\left(\dfrac{4.42\times10^{-5}}{4}\right)}=0.0223M$

Now $Ca(OH)_2$ + NaOH are mixed

$\therefore$ Solution has Ca^{2+} and OH^- out of which some Ca^{2+} are precipitated

On mixing, $[Ca^{2+}]=\dfrac{0.0223\times500}{1000}$

$=0.01115=111.5\times10^{-4}\ M$

$[OH^-]=\underset{\text{(from Ca(OH)}_2\text{)}}{\dfrac{0.0223\times2\times500}{1000}}+\underset{\text{(from NaOH)}}{\dfrac{500\times0.4}{1000}}$

$=0.2223\ M$

$\therefore$ $[Ca^{2+}][OH^-]^2=K_{sp}$

$[Ca^{2+}]_{left}[0.2223]^2=4.42\times10^{-5}$

$[Ca^{2+}]_{left}=\dfrac{4.42\times10^{-5}}{[0.2223]^2}=8.94\times10^{-4}$ mol litre^{-1}

$\because$ Mole of $Ca(OH)_2$ precipitated = Mole of $[Ca^{2+}]$ precipitated

$=111.5\times10^{-4}-8.94\times10^{-4}=102.46\times10^{-4}$

$\therefore$ Mass of $Ca(OH)_2$ precipitated from $Ca(OH)_2$ solution

$=102.46\times10^{-4}\times74=7582.04\times10^{-4}$ g $=\mathbf{758.2\ mg}$

95. For $CaSO_4\rightleftharpoons Ca^{2+}+SO_4^{2-}$

$[Ca^{2+}][SO_4^{2-}]=K_{sp}$

Let $[SO_4^{2-}]=a$, just sufficient to precipitate $CaSO_4$ from a solution having $[Ca^{2+}]=0.005\ M$

Then, $[0.005][a]=2.4\times10^{-5}$ $\therefore$ $a=\dfrac{2.4\times10^{-5}}{0.005}$

$[SO_4^{2-}]=\mathbf{4.8\times10^{-3}}$ **mol litre^{-1}**

96. (a) $2NaOH + NiCl_2 \longrightarrow Ni(OH)_2 + 2NaCl$

Mole before reaction	$\frac{1.75}{40}$	0.25×0.1		
	$=0.0438$	$=0.025$		
Mole left	0	$\left(0.025-\frac{0.0438}{2}\right)$	$\frac{0.0438}{2}$	0.0438

$\therefore$ Mole of $Ni(OH)_2$ formed $= \frac{0.0438}{2}$

$\therefore$ mass of $Ni(OH)_2$ formed $= \frac{0.0438}{2} \times 92.6 = 2.0279\,g$

(b) Also for $Ni(OH)_2$ solution, $Ni(OH)_2 \rightleftharpoons Ni + 2OH^-$

$$[Ni^{2+}][OH^-]^2 = K_{sp}$$

$$\left[\frac{0.025 - \frac{0.0438}{2}}{0.25}\right][OH^-]^2 = 1.6 \times 10^{-14}$$

$\therefore [OH^-] = 11.35 \times 10^{-7}$ $\therefore$ pOH $= 5.94$ $\therefore$ pH $= \mathbf{8.06}$

Note: $Ni(OH)_2$ formed will be precipitated out since maximum solubility of $Ni(OH)_2$ is $1.58 \times 10^{-5}\,M$.

97. $[Ag^+]$ in solution $= \sqrt{K_{sp_{AgCl}}} = \sqrt{1 \times 10^{-10}} = 10^{-5}\,M$

Now the solution after mixing with NaBr has $[Ag^+] = \frac{10^{-5} \times 100}{200}$

and $[Br^-] = \frac{100 \times 0.03}{200}$

Thus, $[Ag^+][Br^-] = \left[\frac{10^{-5} \times 100}{200}\right] \times \left[\frac{100 \times 0.03}{200}\right]$

$$= \mathbf{7.5 \times 10^{-8}}$$

The product of ionic concentration is greater than K_{sp} and thus AgBr will be precipitated.

98. Let solubility of $Mg(OH)_2$ be s mol litre^{-1}

$$Mg(OH)_2 \rightleftharpoons \underset{s}{Mg^{2+}} + \underset{2s}{2OH^-}$$

$\therefore$ $[Mg^{2+}][OH^-]^2 = K_{sp}$

$$4s^3 = 8.9 \times 10^{-12}$$

$\therefore$ $s = 1.305 \times 10^{-4}\,M$; $OH^- = 2 \times 1.305 \times 10^{-4}\,M$

$\therefore$ pOH $= 3.5832$

pH $= \mathbf{10.4168}$

99.

$$CdSO_4 + HCl + H_2S \longrightarrow CdS + H_2SO_4$$

Millimole added	0.1	$10 \times 0.08 = 0.8$			
Millimole after reaction	0	0.8		0.1	0.1

$\therefore$ Millimole of H^+ left $= \underset{\text{(from HCl)}}{0.8} + \underset{\text{(from } H_2SO_4\text{)}}{0.1 \times 2} = 1.0$

Total volume $= 100$ mL

$\therefore$ $[H^+] = \frac{1}{100} = 10^{-2}\,M$

$\therefore$ pH $= 2$

100. $[(NH_4)_2S] = 0.021M$

$\therefore$ $[S^{2-}] = 0.021M$

$\therefore$ At equilibrium, $[Zn^{2+}][S^{2-}] = K_{sp}$ of ZnS

$\therefore$ $[Zn^{2+}] = \frac{4.51 \times 10^{-24}}{0.021} = 2.15 \times 10^{-22}\,M$

$\therefore$ $[Zn^{2+}]$ left in solution $= 2.15 \times 10^{-22} \times 65\,g$ / litre

$$= \frac{2.15 \times 10^{-22} \times 65 \times 12}{1000}\,g / 12\,mL$$

$$= \mathbf{1.677 \times 10^{-22}\ g / 12\ mL}$$

101. For buffer solution,

$NH_4Cl = 0.25M$ and $NH_4OH = 0.05M$

$$pOH = -\log K_b + \log \frac{[Salt]}{[Base]}$$

$\therefore$ $pOH = -\log 18 \times 10^{-5} + \log \frac{0.25}{0.05}$

$\therefore$ $[OH^-] = 3.6 \times 10^{-6}\,M$

Now $Al(OH)_3$ and $Mg(OH)_2$ are stirred vigorously in it,

$\therefore$ $[Al^{3+}][OH^-]^3 = K_{sp}$ of $Al[OH]_3$

$[Al^{3+}][3.6 \times 10^{-6}]^3 = 6 \times 10^{-32}$

$\therefore$ $[Al^{3+}] = \mathbf{1.28 \times 10^{-15}}\,M$

Also $[Mg^{2+}][OH^-]^2 = K_{sp}$ $Mg(OH)_2$

$[Mg^{2+}][3.6 \times 10^{-6}]^2 = 8.9 \times 10^{-12}$

$\therefore$ $[Mg^{2+}] = \mathbf{0.686}\,M$

102. The minimum $[OH^-]$ at which there will be no precipitation of $Mg(OH)_2$ can be obtained by

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$9.0 \times 10^{-12} = [0.05][OH^-]^2$$

$\therefore$ $[OH^-] = 1.34 \times 10^{-5}\,M$

Thus, a solution having $[OH^-] = 1.34 \times 10^{-5}\,M$ will not show precipitation of $Mg(OH)_2$ in $0.05\,M$ Mg^{2+} solution. These hydroxyl ions are to be derived by a buffer of NH_4Cl and NH_4OH, *i.e.*,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

For NH_4OH $\quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

In presence of NH_4Cl; all the $[NH_4^+]$ are provided by NH_4Cl since common ion effect decreases dissociation of NH_4OH.

$\therefore$ $1.8 \times 10^{-5} = \frac{[NH_4^+][1.34 \times 10^{-5}]}{[0.05]}$

$\therefore$ $[NH_4^+] = 0.067M$ or $[NH_4Cl] = \mathbf{0.067}\,M$

103. Maximum solubility of $CaSO_4$ in water

$$S = \sqrt{K_{sp}} = 3 \times 10^{-3} \text{ mol litre}^{-1}$$

Let V litre of sample is taken, then $CaSO_4$ present

$$= \frac{131 \times V \times 10^{-3}}{10^6}\,g$$

[$\because$ ppm = g of $CaSO_4$ in 10^6 g of sample]

$$= 131 \times 10^{-3} V\,g = \frac{131 \times 10^{-3} \times V}{136} \text{ mole in } V \text{ litre}$$

if water is evaporated on heating so that just deposition of $CaSO_4$ occurs. Let V_1 litre of water is left, then

$\frac{131\times10^{-3}\times V}{136}$ mole are present in V_1 litre solution are equal to $3\times10^{-3}\times V_1$ mole.

$\therefore \quad \frac{131\times10^{-3}\times V}{136} = 3\times10^{-3}\times V_1 \qquad \therefore \quad V_1 = 0.32V$

Thus, volume evaporated $= V - 0.32V =$ **0.68 V or 68% of water should be evaporated.**

104. Suppose V mL of solution contains 0.1 M Mg^{2+} and 0.8 M NH_4Cl

Now V mL of 'a' molarity NH_3 is added which just gives precipitate of $Mg(OH)_2$, then

$$[Mg^{2+}][OH^-]^2 = K_{sp}\ Mg(OH)_2$$

$$\left[\frac{0.1V}{2V}\right][OH^-]^2 = 1.4\times10^{-11}$$

$$\left([Mg^{2+}] = \frac{\text{Millimole}}{\text{Total volume}}\right)$$

$$\therefore \quad [OH^-] = 1.67\times10^{-5}\ M$$

Now if the $[OH^-] = 1.67\times10^{-5}$, on addition of NH_3 in NH_4Cl, then $Mg(OH)_2$ will precipitate. For buffer solution of NH_3 and NH_4Cl.

$$\therefore \quad -\log[OH^-] = -\log K_b + \log\frac{[NH_4Cl]}{[NH_3]}$$

$$-\log 1.67\times10^{-5} = -\log 1.8\times10^{-5} + \log\frac{(0.8\times V)/2V}{(a\times V)/2V}$$

$$\therefore \quad a = 0.7421M$$

$$\therefore \quad [NH_3] \text{ in solution} = \frac{0.7421\times V}{2V} = \mathbf{0.3710\ M}$$

105. $[Ca^{2+}][SO_4^{2-}] = 2.4\times10^{-5}$

$[Sr^{2+}][SO_4^{2-}] = 7.6\times10^{-7}$

$$\therefore \quad \frac{[Sr^{2+}]}{[Ca^{2+}]} = 0.03167$$

Initial conc. of $SO_4^{2-} = \frac{10\times0.3}{30} = 0.1M$

Initial conc. of Sr^{2+} = Initial conc. of Ca^{2+} $= \frac{0.1\times20}{30} = 0.0667M$

Let final conc. of $Ca^{2+} = X$, $\therefore$ $[Sr^{2+}] = 0.03167X$

$\therefore$ Change in conc. of SO_4^{2-} = change in conc. of Ca^{2+} and Sr^{2+}

$$= 0.0667 - X + 0.0667 - 0.03167X$$
$$= 0.1334 - 1.03167X$$

$$\therefore \quad \text{Final } [SO_4^{2-}] = 0.1 - [0.1334 - 1.03167X]$$

[Using $[Ca^{2+}][SO_4^{2-}] = K_{sp}$ at equilibrium]

$$\therefore \quad X\cdot[0.1 - (0.1334 - 1.03167X)] = 2.4\times10^{-5}$$

$$\therefore \quad 1.03167X^2 - 0.0334X = 2.4\times10^{-5}$$

$$\therefore \quad X = \mathbf{3.3\times10^{-2}\ M} \text{ or } [Ca^{2+}] = \mathbf{3.3\times10^{-2}\ M}$$

$$\therefore \quad [Sr^{2+}] = \mathbf{1.05\times10^{-3}\ M} \quad \therefore \quad [SO_4^{2-}] = \mathbf{7.17\times10^{-4}\ M}$$

106. K_{sp} of $CaCO_3 = \left(\frac{7\times10^{-3}}{100}\right)^2 = 49\times10^{-10}$

When only Ba^{2+} is 90% precipitated then only $CaCO_3$ starts precipitation then if solution contains a mol litre^{-1} of Ca^{2+} and Ba^{2+} each,

$$[Ca^{2+}][CO_3^{2-}] = 49\times10^{-10}$$

$$[CO_3^{2-}] = \frac{49\times10^{-10}}{a}$$

Now for $BaCO_3$;

$$K_{sp} = [Ba^{2+}][CO_3^{2-}] = \frac{a\times10}{100}\times\frac{49\times10^{-10}}{a}$$
$$= \mathbf{4.9\times10^{-10}}$$

107. (a) For $Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$

$$\therefore \quad K_C = \frac{[NH_3]^2[Mg^{2+}]}{[NH_4^+]^2} = \frac{[NH_4OH]^2[Mg^{2+}]}{[NH_4^+]^2} \qquad ...(1)$$

Also $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ...(2)$$

$$\therefore \quad K_C \times K_b^2 = [Mg^{2+}][OH^-]^2 = K_{sp} \text{ of } Mg(OH)_2$$

$$\therefore \quad K_C = \frac{K_{sp}}{K_b^2} = \frac{6\times10^{-12}}{(1.8\times10^{-5})^2} = \mathbf{1.85\times10^{-2}}$$

(b) Let a mol litre^{-1} of $Mg(OH)_2$ be dissolved in presence of 0.5 M NH_4Cl

$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$$

Mole before reaction	0.5	0	0
Mole after reaction	$(0.5-2a)$	$2a$	a

$$\therefore \quad K_C = \frac{a\times(2a)^2}{(0.5-2a)^2}$$

$$1.85\times10^{-2} = \frac{4a^3}{(0.5-2a)^2} \qquad ...(3)$$

Solving cubic equation,

$$\therefore \quad a = \mathbf{0.081\ M}$$

Note : Eq. (3) is cubic equation and its solution is not included in our subject. However if $2a$ is neglected in comparison to 0.5, then 'a' comes equal to 0.1049 M.

108. $Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$

Mole before reaction	excess	0.1520	
Mole at equilibrium	$(0.1520 - 0.0358) = 0.1162$	0.0358	0.0358

At equilibrium,

$$\therefore \quad [C_2O_4^{2-}] = \frac{0.1162}{0.5} = 0.2324\ M; \qquad [CO_3^{2-}] = \frac{0.0358}{0.5} = 0.0716M$$

$\because [Ag^+]^2[C_2O_4^{2-}] = \left[\frac{2\times 0.0358}{0.5}\right]^2\left[\frac{0.1520}{0.5}\right] = 6.23\times10^{-3}$

Thus, $[Ag^+]^2[C_2O_4^{2-}] > K_{sp}$ of $Ag_2C_2O_4$ (1.29×10^{-11})

$\therefore$ $Ag_2C_2O_4$ will precipitate out.

$\because$ Ag_2CO_3 is solid and $Ag_2C_2O_4$ is almost precipitated out. For $Ag_2C_2O_4$ precipitation.

$$[Ag^+]^2[C_2O_4^{2-}] = K_{sp_{Ag_2C_2O_4}}$$

$$[Ag^+]^2[0.2324] = 1.29\times10^{-11}$$

$$\therefore \quad [Ag^+]^2 = \frac{1.29\times10^{-11}}{0.2324} = 5.55\times10^{-11}$$

Now for Ag_2CO_3

$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = [5.55\times10^{-11}][0.0716]$$

$$= \mathbf{3.97\times10^{-12}\ mol^3\ litre^{-3}}$$

109. Let solubility of AgCN be a mol litre^{-1}

$$AgCN \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{CN^-} \quad \text{(After reaction)}$$

However the CN^- formed will react with H^+ to form HCN

$$CN^- + H^+ \longrightarrow HCN$$

a	10^{-3}		(Before reaction)
0	10^{-3} (buffer)	a	(After reaction)

$\therefore$ $[Ag^+] = a$ and $[HCN] = a$

Since HCN is weak acid and has low degree of dissociation. Also its dissociation is suppressed in presence of $[H^+]$. Thus

Now $$HCN \rightleftharpoons H^+ + CN^-$$

$$\therefore \quad \frac{[CN^-][H^+]}{[HCN]} = K_a$$

or $$[CN^-] = \frac{K_a[HCN]}{[H^+]} = \frac{a\times(4.8\times10^{-10})}{10^{-3}}$$

Now for $AgCN(s) + aq. \rightleftharpoons Ag^+ + CN^-$

$$K_{sp} = [Ag^+][CN^-]$$

$$1.2\times10^{-16} = \frac{a\times a\times4.8\times10^{-10}}{10^{-3}}$$

$$\therefore \quad a^2 = \frac{1.2\times10^{-16}\times10^{-3}}{4.8\times10^{-10}}$$

$$\therefore \quad a = \mathbf{1.58\times10^{-5}\ mol\ litre^{-1}}$$

110. $$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-] \quad ...(1)$$

Given $$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \quad ...(2)$$

By Eqs. (1) and (2), $K_{sp}\times K_f = \dfrac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$

or $$1\times10^{-10}\times1.6\times10^{7} = \frac{a\times a}{[NH_3]^2}$$

Given solubility of AgCl = $0.1M$

$\therefore$ $a = 0.1M$ for $Ag(NH_3)_2^+$ and Cl^-

$$\therefore \quad [NH_3]^2 = \frac{0.1\times0.1}{1.6\times10^{-3}} = 6.25 \quad \therefore \quad [NH_3] = \mathbf{2.5\ M}$$

Also $0.2M$ NH_3 is needed to dissolve $0.1\ M$ Ag^+ ions, thus

$$[NH_3] = 2.5\times+0.2 = \mathbf{2.7\ M}$$

111. $$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} = 4\times10^{-19} \quad ...(1)$$

$$K_{sp}\,AgCl = [Ag^+][Cl^-] = 2.8\times10^{-10} \quad ...(2)$$

By Eq. (1) $4\times10^{-19} = \dfrac{x\cdot4x^2}{0.05}$

$\therefore$ $x = [Ag^+] = 1.70\times10^{-7}$

$\therefore$ $[Ag^+][Cl^-] = 1.70\times10^{-7}\times0.02 = 3.41\times10^{-9} > K_{sp}$

Thus, precipitation of AgCl will take place.

112. $Ag(NH_3)_2^+\,(aq.) \rightleftharpoons \underset{a+b}{Ag^+}\,(aq.) + \underset{2a}{2NH_3}\,(aq.)$;

$$K_C = \frac{[NH_3]^2[Ag^+]}{[Ag(NH_3)_2^+]} \quad ...(1)$$

$AgCl(s) \rightleftharpoons \underset{a+b}{Ag^+}\,(aq.) + \underset{b}{Cl^-}\,(aq.)$;

$$K_{sp} = [Ag^+][Cl^-] \quad ...(2)$$

In case of simultaneous solubility Ag^+ remains same in solution.

Given $[NH_3] = 2a = 1M$; also $[Ag(NH_3)_2^+] = [Cl^-] = b$ because Ag^+ obtained from AgCl passes in $[Ag(NH_3)_2^+]$ state.

Thus, by Eqs. (1) and (2)

$$\frac{K_C}{K_{sp}} = \frac{[NH_3]^2}{[Cl^-][Ag(NH_3)_2^+]} = \frac{1}{b^2}$$

or $$b^2 = \frac{1.8\times10^{-10}}{62\times10^{-8}} = 0.29\times10^{-2}$$

$\therefore$ $$b = 0.539\times10^{-1} = \mathbf{0.0539}$$

or $$[Ag(NH_3)_2^+] = \mathbf{0.0539}$$

113.

Ag^+	+ HCN	$\longrightarrow$ AgCN	+ H^+	
$\frac{0.02\times V}{2V}$	$\frac{0.02\times V}{2V}$	0	0	
0	0	0.01	0.01	$\therefore [H^+] = 10^{-2}$

$$AgCN \rightleftharpoons Ag^+ + CN^-$$

$$\therefore K_{sp} = 2.2\times10^{-16} = [Ag^+][CN^-]$$

$HCN \rightleftharpoons H^+ + CN^-$ $K_a = 6.2\times10^{-10} = \dfrac{[H^+][CN^-]}{[HCN]}$

Now, soluble CN^- formed will hydrolyse as

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$\therefore$ $[Ag^+]$ of soluble $AgCN = CN^-$ left after hydrolysis + HCN formed after hydrolysis.

$$\therefore \quad \left[\frac{2.2\times10^{-16}}{[CN^-]}\right] = [CN^-] + \frac{[H^+][CN^-]}{6.2\times10^{-10}}$$

$$= [CN^-] + \frac{10^{-2}[CN^-]}{6.2\times10^{-10}} \quad \left[\because CN^- <<< \frac{10^{-2}[CN^-]}{6.2\times10^{-10}}\right]$$

$$\text{or} \quad [CN^-]^2 = \frac{2.2\times10^{-16}\times6.2\times10^{-10}}{10^{-2}}$$

$$\therefore \quad [CN^-] = 3.7\times10^{-12}$$

$$\therefore \quad [Ag^+] = \frac{K_{sp}}{[CN^-]} = \frac{2.2\times10^{-16}}{3.7\times10^{-12}} = \mathbf{5.96\times10^{-5}\ M}$$

114. Given, $AgI(s) \rightleftharpoons Ag^+(aq.) + I^-(aq.)$;

$$K_{sp} = [Ag^+][I^-] = 1.2\times10^{-17} \qquad ...(1)$$

$$Ag^+(aq.) + 2CN^-(aq.) \rightleftharpoons [Ag(CN)_2]^-(aq.);$$

$$K_f = \frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2} = 7.1\times10^{19} \qquad ...(2)$$

Let x mole of AgI be dissolved in CN^- solution then,

Now,

	$AgI(s) + 2CN^-$	$\rightleftharpoons [Ag(CN)_2]^-$	$+ I^-$
Mole before reaction	1	0	0
Mole after reaction	$(1-2x)$	x	x

By Eqs. (1) and (2), $K_{eq.} = K_{sp} \times K_f$

$$K_{eq.} = \frac{[Ag(CN)_2^-][I^-]}{[CN^-]^2} = 1.2\times10^{-17}\times7.1\times10^{19}$$

$$K_{eq.} = 8.52\times10^2 \qquad ...(3)$$

$$\therefore \quad K_{eq.} = 8.52\times10^2 = \frac{x\cdot x}{(1-2x)^2} = \frac{x^2}{(1-2x)^2}$$

$$\text{or} \quad \frac{x}{1-2x} = 29.2$$

Thus, $x = 29.2 - 58.4x$ or $x = \mathbf{0.49\ mol}$

115. For $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

$$K_{sp} = 4s^3 \quad \text{or} \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.4\times10^{-5}}{4}} = 1.52\times10^{-2}\ M$$

($2s$, s)

For $PbCrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{2-}$

$$K_{sp} = s_1^2 \quad \text{or} \quad s_1 = \sqrt{K_{sp}} = \sqrt{2.8\times10^{-13}} = 5.29\times10^{-7} M$$

In solution, conc. of each ion can be given as :

$$\text{Thus,} \quad [Ag^+] = \frac{2s\times100}{350} = \frac{2\times1.52\times100}{350} = 0.869\times10^{-2}\ M$$

$$[SO_4^{2-}] = \frac{s\times100}{350} = \frac{1.52\times10^{-2}\times100}{350} = 0.43\times10^{-2}$$

$$[Pb^{2+}] = \frac{s_1\times250}{350} = \frac{5.29\times10^{-7}\times250}{350} = 3.78\times10^{-7}$$

$$[CrO_4^{2-}] = \frac{s_1\times250}{350} = \frac{5.29\times10^{-7}\times250}{350} = 3.78\times10^{-7}$$

It is thus evident that

$$[Ag^+]^2[CrO_4^{2-}] = (0.869\times10^{-2})^2\times(3.78\times10^{-7})$$

$$= \mathbf{2.85\times10^{-11}} > K_{sp}\ Ag_2CrO_4$$

The product is greater than K_{sp} of Ag_2CrO_4 and thus Ag_2CrO_4 will ppt.

116.

	$Na_2CO_3 + CaF_2(s)$	$\longrightarrow CaCO_3$	$+ 2NaF$
Mole taken	2	0	0
Mole left	$(2-a)$	a	$2a$

where a is very-very small and thus assume that $CaCO_3$ is in soluble form

Now, K_{sp} of $CaCO_3 = x = [Ca^{2+}][CO_3^{2-}]$

Also $[CO_3^{2-}] = 2 - a + a = 2 \quad \therefore \quad [Ca^{2+}] = \dfrac{x}{2}$

For $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$ (y, $2y$)

$$K_{sp_{CaF_2}} = [Ca^{2+}][F^-]^2$$

$$K_{sp_{CaF_2}} = [y][2y]^2 = 4y^3$$

Further for $[F^-]$, we can have

$$[F^-] = [F^-] \text{ from } CaF_2 + [F^-] \text{ from NaF}$$

$$[F^-] = \sqrt{\frac{K_{sp_{CaF_2}}}{[Ca^{2+}]}} + \text{Negligible value}$$

$$\therefore \quad [F^-] = \sqrt{\frac{4y^3}{x/2}} = \sqrt{\frac{\mathbf{8}y^3}{x}}$$

117. For PbI_2 saturated solution,

$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$ (s, $2s$)

$$\therefore \quad K_{sp} = 4s^3$$

$$\text{or} \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\left[\frac{7.1\times10^{-9}}{4}\right]} = 1.21\times10^{-3}\ M$$

$\therefore$ $[I^-]$ in solution $= 2\times1.21\times10^{-3}\ M = 2.42\times10^{-3}\ M$

Now, if $AgNO_3$ is used to neutralise these I^- ions

Then, Meq. of $AgNO_3$ = Meq. of I^-

$$13.3\times N = 2.42\times10^{-3}\times25$$

$$\therefore \quad N_{AgNO_3} = \mathbf{4.55\times10^{-3}} = M_{AgNO_3}$$

For $AgNO_3$ normality = molarity

118. Meq. of $C_2O_4^{2-}$ = Meq. of $KMnO_4$

$$= 0.00102\times6.3\times5(Mn^{7+} + 5e \rightarrow Mn^{2+}) = 0.032$$

$$\therefore \text{ Molarity of } C_2O_4^{2-} = \frac{\text{Meq.}}{\text{Volume in mL}\times\text{Valence factor}}$$

$$\text{or} \quad s = \frac{0.032}{250\times2}M = 6.4\times10^{-5}\ M \qquad (C_2^{3+} \rightarrow 2C^{4+} + 2e)$$

$\therefore$ K_{sp} of $CaC_2O_4 = s^2 = (6.4\times10^{-5})^2$

$= 4.09\times10^{-9}$

119. Initial $[Sr^{2+}] = 16\times10^{-3}\ M$

Left $[Sr^{2+}] = 2.5\times10^{-3}\ M$

$\therefore$ $[Sr^{2+}]$ precipitated $= (16-2.5)\times10^{-3} = 13.5\times10^{-3}\ M$

$\therefore$ $[F^-]$ needed for this precipitation $= 2\times13.5\times10^{-3}\ M$

$= 27.0\times10^{-3}\ M$

$(\because Sr^{2+} + 2F^- \longrightarrow SrF_2)$

Also $[Sr^{2+}][F^-]^2 = K_{sp_{SrF_2}} = 2.8\times10^{-9}$

$\therefore$ $[F^-]^2 = \dfrac{2.8\times10^{-9}}{2.5\times10^{-3}}$

$\therefore$ $[F^-] = 1.058\times10^{-3}\ M$, *i.e.*, the concentration of F^- which will also appear in solution state.

Thus, $[F^-]$ needed $= [27.0+1.058]\times10^{-3}\ M$

$= 28.058\times10^{-3}\ M$

$\therefore$ NaF needed for 1 litre $= 28.058\times10^{-3}\times42$g

$\therefore$ NaF needed for 100 mL $= \dfrac{28.058\times10^{-3}\times42}{10}$g

$= \mathbf{0.1178\ g}$

120. Given, $MBr_2(g) \rightleftharpoons MBr_2(aq.) \longrightarrow M^{2+} + 2Br^-$

$MBr_2 + H_2S \longrightarrow MS + 2HBr$

K_{sp} of $MS = [M^{2+}][S^{2-}]$

$6\times10^{-21} = [0.05][S^{2-}]$

$\therefore$ $[S^{2-}] = 1.2\times10^{-19}\ M$

Thus, MS will be precipitated if H_2S provides $1.2\times10^{-19}\ M$ ions of S^{2-}.

Now for H_2S $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_1\times K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$10^{-7}\times1.3\times10^{-13} = \frac{[H^+]^2[1.2\times10^{-19}]}{[0.1]}$$

$\therefore$ $[H^+] = 1.04\times10^{-1}$ and $pH = \mathbf{0.9826}$

121. $H_2S \rightleftharpoons 2H^+ + S^{-2}$

$NaCN \longrightarrow Na^+ + CN^-$

0.2 0 0

0 0.2 0.2

Also $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} = \frac{[Ag^+]\times(0.2)^2}{0.02} = 1.0\times10^{-20}$$

$[Ag^+] = 5\times10^{-21}\ M$

For $Cd(CN)_4^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$

$$K = \frac{[Cd^{2+}][CN^-]^4}{[Cd(CN)_4]^{2-}}$$

$$7.8\times10^{-18} = \frac{[Cd^{2+}]\times(0.2)^4}{0.02}$$

$\therefore$ $[Cd^{2+}] = 9.75\times10^{-17}$

Now, $[Ag^+]^2\times[S^{2-}] = 1.0\times10^{-50}$

$\therefore$ $[S^{2-}]$ needed to precipitate $Ag_2S = \dfrac{1.0\times10^{-50}}{(5\times10^{-21})^2}$

$= 4\times10^{-10}\ M$

$[S^{2-}]$ needed to precipitate $CdS = \dfrac{7.1\times10^{-28}}{9.75\times10^{-17}}$

$= 7.28\times10^{-12}\ M$

Therefore, CdS will be precipitated first.

122. For indicator dissociation equilibrium; being an acid

$$\underset{\text{Colour } A}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour } B}{In^-}$$

$\therefore$ $K_{In} = \dfrac{[H^+][In^-]}{[HIn]}$

The midpoint of the colour range of an indicator HIn is the point at which $[In^-] = [HIn]$.

$\therefore$ $K_{In} = [H^+] = 1\times10^{-5}$

$\therefore$ $[H^+] = 1\times10^{-5}$ or $pH = 5$

Thus, at pH = 5 of the solution, the indicator will change its colour.

Again $K_{In} = \dfrac{[H^+][In^-]}{[HIn]}$

$$1\times10^{-5} = \frac{[H^+]\times80\times100}{100\times20}$$

$\therefore$ $[H^+] = 0.25\times10^{-5}$ $\therefore$ $pH = \mathbf{5.6020}$

123. The two conditions when colour of indicator will be visible are derived by

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

(i) $pH = 5 + \log 10 = 6$

(ii) $pH = 5 + \log 0.1 = 4$

Thus, minimum change in pH = **2**

124. $HBPh \rightleftharpoons H^+ + BPh^-$

$K_a = \dfrac{[H^+][BPh^-]}{[HBPh]}$, when $BPh^- = HBPh$, indicator will work. Thus

$[H^+] = 5.84\times10^{-5}$ $\therefore$ $pH = 4.2336$

Also if $pH = 4.84$ or $[H^+] = 1.44\times10^{-5}$, then

$K_a = \dfrac{[H^+][BPh^-]}{[HBPh]}$ or $5.84\times10^{-5} = \dfrac{1.44\times10^{-5}\cdot C\alpha}{C(1-\alpha)}$

$\alpha = \mathbf{0.8}$ or $\mathbf{80\%}$

125. $NaOCN + H_2O \rightleftharpoons NaOH + HCN$

$$h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w}{K_aC}\right)} = \sqrt{\frac{10^{-14}}{3.33\times10^{-4}\times0.003}}$$

$h = 10^{-4}$

$\therefore$ % hydrolysis $= 10^{-4} \times 100 = 10^{-2}$

126. pK_a for HCN $= 14 - 4.70 = 9.30$

$$\underset{1-h}{NaCN} + H_2O \rightleftharpoons \underset{h}{NaOH} + \underset{h}{HCN}$$

$$\therefore \quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{K_H \cdot C} = \sqrt{\left(\frac{K_w \cdot C}{K_a}\right)}$$

or $\quad pOH = \frac{1}{2}[pK_w - \log C - pK_a]$

$$= \frac{1}{2}[14 + 0.3010 - 9.30] = 2.5$$

$\therefore \quad pH = 14 - 2.5 = \mathbf{11.5}$

127.

	$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$		
Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

where h is degree of hydrolysis

$$h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot C}\right)}$$

$$= \sqrt{\frac{10^{-14}}{1.8\times10^{-5} \times 0.2}} = 5.27\times10^{-5}$$

From HCl, a strong acid

$$\therefore \quad [H^+] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.2}{1.8\times10^{-5}}\right)} = 1.054\times10^{-5}$$

$$\therefore \quad pH = -\log[H^+] = -\log 1.054\times10^{-5} = \mathbf{4.9771}$$

Let conc. of NH_4Cl be C mol litre^{-1}

128.

	$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$		
Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

$$\therefore \quad [H^+] = \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)} = \sqrt{\left(\frac{10^{-14} \times C}{1.8\times10^{-5}}\right)}$$

$$10^{-4.5} = \sqrt{\left(\frac{10^{-14} \times C}{1.8\times10^{-5}}\right)} \quad \therefore \quad C = 1.8 \text{ mol litre}^{-1}$$

$\therefore$ Mass of $NH_4Cl = 1.8\times53.5$ g / litre^{-1}

$$= 1.8\times53.5\times\frac{1}{2} \text{g} / 500 \text{ mL} = \mathbf{48.15\ g}$$

129. (a)

	$NaBu + H_2O \rightleftharpoons NaOH + BuH$		
Conc. before hydrolysis	1	0	0
Conc. after hydrolysis	$1-h$	h	h

$$\therefore [OH^-] = C \cdot h = C \cdot \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w}{K_a} \cdot C\right)}$$

$$[OH^-] = \frac{10^{-14} \times 0.2}{2\times10^{-5}} = \sqrt{10^{-10}} = 10^{-5}$$

$\therefore \quad pOH = 5$

Also $\quad pH + pOH = 14 \quad \therefore \quad pH = 14 - 5 = 9$

(b) **[Ans : 8]**

130. $Asc^- + H_2O \rightleftharpoons HAsc + OH^-$

$$\therefore \quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{K_H \cdot C} = \sqrt{\left(\frac{K_w}{K_a} \cdot C\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.02}{5\times10^{-5}}\right)} = 2\times10^{-6}$$

$$\therefore \quad [H^+] = \frac{1\times10^{-14}}{2\times10^{-6}} = 5\times10^{-9}$$

Also $\quad h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w}{K_a \times C}\right)}$

$$= \sqrt{\left(\frac{10^{-14}}{5\times10^{-5} \times 0.02}\right)} = 10^{-4} \quad \text{or} \quad \mathbf{0.01\%}$$

131. Let V mL of acid and V mL of NaOH be used. Conc. of both acid and NaOH are same.

$\therefore \quad CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Conc. before reaction	$\frac{0.1\times V}{2V}$	$\frac{0.1\times V}{2V}$	0	0
Conc. after reaction	0	0	$\frac{0.1\times V}{2V}$	$\frac{0.1\times V}{2V}$

$$\therefore \quad [CH_3COONa] = \frac{0.1}{2} = 0.05\ M$$

Now calculate pH by hydrolysis of CH_3COONa

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$[OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w \times C}{K_a}\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.05}{1.9\times10^{-5}}\right)} = 5.12\times10^{-6}$$

$\therefore \quad pOH = 5.29 \quad \therefore \quad pH = \mathbf{8.71}$

132. **[Ans : 8.975]**

133. $Ca(LaC)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HLaC$

or $\quad 2LaC^- + 2H_2O \rightleftharpoons 2OH^- + 2HLaC$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

$$\therefore \quad [Ca(LaC)_2] = \frac{0.13}{0.5} = 0.26\ M$$

$$\therefore \quad [LaC^-] = 0.26\times2 = 0.52\ M$$

$\because$ 1 mole $Ca(LaC)_2$ gives 2 moles (LaC)

Now $\quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)}$

$$= \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w \times C}{K_a}\right)}$$

where C is conc. of anion which undergoes hydrolysis

$$\therefore \quad 10^{-5.60} = \sqrt{\left(\frac{10^{-14} \times 0.52}{K_a}\right)} \quad \therefore \quad K_a = 8.25\times10^{-4}$$

134. $K_3PO_4 + H_2O \rightleftharpoons K_2HPO_4 + KOH$

or $\quad PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$

Since hydrolysis proceeds only in 1 step

$$\therefore \quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_w}{K_a \cdot C}\right)} = \sqrt{\left(\frac{K_w \cdot C}{K_a}\right)}$$

K_a is III dissociation constant of acid H_3PO_4

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_1$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_2$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad K_3 = K_a = 1.3\times10^{-12}$$

$$\therefore \quad [OH^-] = \sqrt{\left(\frac{10^{-14}\times 0.1}{1.3\times10^{-12}}\right)} \quad \therefore \quad pOH = 1.5634$$

$$\therefore \quad pH = \mathbf{12.4366}$$

135. $\underset{(1-h)}{Fe^{3+}} + H_2O \rightleftharpoons \underset{h}{Fe(OH)^{2+}} + \underset{h}{H^+}; \quad K_H = 6.5\times10^{-3}$

$$[H^+] = Ch$$

and $$K_H = \frac{C\cdot h^2}{1-h} \quad \text{and} \quad h = \frac{5}{100}$$

Thus, $$6.5\times10^{-3} = \frac{C\times5\times5\times100}{100\times100\times95}$$

$$\therefore \quad C = 2.47M \quad \therefore \quad [H^+] = 2.47\times\frac{5}{100} \quad \therefore \quad pH = \mathbf{0.9083}$$

136. $$Zn^{2+} + H_2O \rightleftharpoons [Zn(OH)]^+ + H^+ \qquad K_H = 1.0\times10^{-9}$$

$$\therefore \quad [H^+] = C\cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)}$$

$$= \sqrt{10^{-9}\times0.001} = 10^{-6} \quad \therefore \quad pH = 6$$

137. $\because$ $Aniline^+ + Acetate^- + H_2O \rightleftharpoons Aniline + Acetic\ acid$

Before hydrolysis	1	1	0	0
After hydrolysis	$1-h$	$1-h$	h	h

Let concentration of salt be C mol litre^{-1}

$$\therefore \quad K_H = \frac{[Aniline]\,[Acetic\ acid]}{[Aniline]^+\,[Acetate]^-} = \frac{C\cdot h\cdot C\cdot h}{C\cdot(1-h)\cdot C\cdot(1-h)}$$

$$\therefore \quad K_H = \frac{h^2}{(1-h)^2} \quad \therefore \quad \frac{h}{1-h} = \sqrt{(K_H)}$$

$$\frac{h}{1-h} = \sqrt{\left(\frac{K_w}{K_a\cdot K_b}\right)} = \sqrt{\left(\frac{1.008\times10^{-14}}{1.75\times10^{-5}\times3.83\times10^{-10}}\right)}$$

$$\therefore \quad h = \mathbf{54.95\%}$$

Note: If $K_H = h^2$ is used assuming $1-h \approx 1$ the value of h comes greater than 1 which is not possible and thus, it is always advised in all such cases, not to assume $1-h \approx 1$ when h values are higher. Also the term dissociation constant of water is used here for ionic product of water. See the value.

138. The pH of salt $HCOONH_4$ (a salt of weak acid + weak base) is given by :

$$HCOONH_4 + H_2O \rightleftharpoons HCOOH + NH_4OH$$

$$pH = \frac{1}{2}[\log K_b - \log K_a - \log K_w]$$

$$\therefore \quad pH = \frac{1}{2}[pK_a + pK_w - pK_b]$$

$$pH = \frac{1}{2}[3.8 + 14 - 4.8] = \mathbf{6.5}$$

139. (a) $$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$$

mM before reaction	50×0.1	50×0.05		
	$=5$	$=2.5$	0	0
mM after reaction	2.5	0	2.5	2.5

$\because$ Strong alkali is left free and thus, it will decide pH of solution.

$$\therefore \quad [NaOH] = \frac{2.5}{100} = 2.5\times10^{-2}M$$

$$\therefore \quad [OH^-] = 2.5\times10^{-2}M \quad \therefore \quad pOH = 1.6021$$

$$\therefore \quad pH = \mathbf{12.3979}$$

(b) $$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$$

mM before reaction	50×0.05	50×0.1		
	$=2.5$	$=2.5$	0	0
mM after reaction	0	2.5	2.5	2.5

The solution consists CH_3COOH and CH_3COONa and thus, is a buffer

$$\therefore \quad pH = -\log K_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$\because$ $$[CH_3COOH] = \frac{2.5}{100}M; \quad [CH_3COONa] = \frac{2.5}{100}M$$

$$\therefore \quad pH = -\log 1.8\times10^{-5} + \log\frac{2.5/100}{2.5/100} \quad \therefore \quad pH = \mathbf{4.7447}$$

(c) $$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$$

mM before reaction	50×0.1	50×0.1		
	$=5$	$=5$	0	0
mM after reaction	0	0	5	5

$\because$ CH_3COONa is left with concentration $= \frac{5}{100}M$ and thus, pH is decided by salt hydrolysis

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

Before hydrolysis	1	0	0
After hydrolysis	$1-h$	h	h

$$\therefore \quad [OH^-] = Ch = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w\cdot C}{K_a}\right)}$$

$$= \sqrt{\left(\frac{10^{-14}}{1.8\times10^{-5}}\times\frac{5}{100}\right)}$$

$$= 5.27\times10^{-6}M$$

$$\therefore \quad pH = \mathbf{8.7218}$$

(d) $$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

mM before reaction	50×0.1	50×0.05		
	$=5$	$=2.5$	0	0
mM after reaction	2.5	0	2.5	2.5

The solution contains NH_4OH and NH_4Cl and thus, acts as buffer

Thus, $$pOH = -\log K_b + \log\frac{[NH_4Cl]}{[NH_4OH]}$$

$\because$ $$[NH_4Cl] = \frac{2.5}{100}M; \quad [NH_4OH] = \frac{2.5}{100}$$

$$\therefore \quad pOH = -\log 1.8\times10^{-5} + \log\frac{2.5/100}{2.5/100}$$

$$pOH = 4.7447 \quad \therefore \quad pH = \mathbf{9.2553}$$

(e) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

mM before reaction	50×0.05	50×0.1		
	$=2.5$	$=5$	0	0
mM after reaction	0	2.5	2.5	2.5

$\because$ Strong acid is left and therefore, pH is decided by HCl.

$$[HCl] = [H^+] = \frac{2.5}{100}M \quad \therefore \quad pH = \mathbf{1.6021}$$

(f) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

mM before reaction	50×0.1	50×0.1		
	$=5$	$=5$		
mM after reaction	0	0	5	5

$\because$ Salt is left and thus, pH will be decided by salt hydrolysis.

$$[NH_4Cl] = \frac{5}{100} = 5\times10^{-2}M$$

Since NH_4Cl is salt of strong acid and weak base and therefore,

$$pH = \frac{1}{2}[\log K_b - \log C - \log K_w]$$

$$= \frac{1}{2}[\log 1.8\times10^{-5} - \log 5\times10^{-2} - \log 1\times10^{-14}]$$

$\therefore$ $\mathbf{pH = 5.2782}$

(g) $NH_4OH + CH_3COOH \rightarrow CH_3COONH_4 + H_2O$

mM before reaction	50×0.05	50×0.05		
	$=2.5$	$=2.5$	0	0
mM after reaction	0	0	2.5	2.5

$\because$ Salt is left and thus, pH will be decided by salt hydrolysis.

$$[CH_3COONH_4] = \frac{2.5}{100} = 2.5\times10^{-2}M$$

Now $CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

$$CH_3COOH = Ch$$

Now for dissociation of CH_3COOH

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$\therefore \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$\because$ α is small and thus, $[CH_3COOH] = Ch$

Also $[CH_3COO^-]$ is provided from CH_3COONH_4 left unhydrolysed in solution, *i.e.*, $[CH_3COO^-] = C(1-h)$

$$\therefore \quad K_a = \frac{C(1-h)[H^+]}{Ch} \qquad \because \ h \ll 1$$

or $[H^+] = hK_a \qquad \therefore \ 1-h = 1$

$$= \sqrt{\left(\frac{K_w}{K_a\cdot K_b}\right)}\times K_a = \sqrt{\left(\frac{K_wK_a}{K_b}\right)}$$

$$\therefore \quad pH = +\frac{1}{2}[\log K_b - \log K_w - \log K_a]$$

$$= \frac{1}{2}[pK_w + pK_a - pK_b]$$

$$= +\frac{1}{2}[\log 1.8\times10^{-5} - \log 10^{-14} - \log 1.8\times10^{-5}]$$

$$pH = 7$$

140. We have from Raoult's law

$$\frac{P^o - P_s}{P_s} = \frac{w\times M}{m\times W}$$

$$\therefore \quad \frac{w}{m\times W} = \frac{17.540 - 17.536}{17.536\times18} = 1.267\times10^{-5}$$

$$\therefore \text{ Molality} = \frac{w}{m\times W}\times1000 = 1.267\times10^{-5}\times10^3$$

$$= 1.267\times10^{-2} = \text{Molarity} = \text{Conc. of } [BOH]$$

For $BOH \rightleftharpoons B^+ + OH^-$

1	0	0
$(1-\alpha)$	α	α

Molarity is also given as 1×10^{-2}

$$\therefore \quad \frac{\text{Exp. value of molarity}}{\text{Normal value of molarity}} = 1+\alpha$$

$$\therefore \quad \frac{1.267\times10^{-2}}{1\times10^{-2}} = 1+\alpha \quad \therefore \quad \alpha = 0.267$$

Now, $K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.01\times0.267\times0.267}{(1-0.267)} = \mathbf{9.74\times10^{-4}}$

141.

$$HA \rightleftharpoons H^+ + A^-$$

1	0	0
$1-\alpha$	α	α

$$\therefore \quad \pi V = nST(1+\alpha) \quad \text{or} \quad 1+\alpha = \frac{\pi\times V}{n\times S\times T}$$

$$\therefore \quad 1+\alpha = \frac{0.293}{0.01\times0.0821\times298} \qquad \left(\frac{n}{V} = 0.01\right)$$

$$\therefore \quad \alpha = 1.197 - 1 = 0.197$$

$$\therefore \quad K_a \text{ for } HA = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.01\times(0.197)^2}{(1-0.197)} = \mathbf{4.83\times10^{-4}}$$

Similarly, K_a for $HB = \mathbf{2.85\times10^{-3}}$

142. (i) $Zn(OH)_2(s) \rightleftharpoons Zn^{2+} + 2OH^- \quad K_{sp} = [Zn^{2+}][OH^-]^2$

(ii) $Zn(OH)_2(s) + 2OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$

$$K_f = \frac{[Zn(OH)_4)]^{2-}}{[OH^-]^2}$$

Let the solubility be s in change (i) and thus solubility will also be s in change (ii) By coupling (i) and (ii),

$$2Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq.) + [Zn(OH)_4]^{2-}(aq.)$$

$$\therefore \quad K_{sp}\times K_f = s\times s$$

or $s = \sqrt{K_{sp}\times K_f} = \sqrt{1.2\times10^{-17}\times0.12} = 1.2\times10^{-9}\,M$

Thus total solubility, will be $2s = 2\times1.2\times10^{-9}$

$$= 2.4\times10^{-9}\,M$$

This solubility is minimum when $[Zn^{2+}][OH^-]^2$

$$= 1.2\times10^{-17}$$

$$1.2\times10^{-9}[OH^-]^2 = 1.2\times10^{-17}$$

$$\therefore \quad [OH^-] = \mathbf{10^{-4}}\,M$$

Note : If only I change than solubility of

$$Zn(OH)_2 = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2\times10^{-7}}{4}} = 1.44\times10^{-6}\,\text{m}$$

and at this conc. $[OH^-] = 2\times144\times10^{-6}\,M = \mathbf{2.88\times10^{-6}\,M}$

143. (a) $N_2O_4 \rightleftharpoons 2NO_2$

Let a mole of N_2O_4 and b mole of NO_2 were present in equilibrium mixture

$$\therefore\quad (a+b) = \frac{PV}{RT} = \frac{753\times0.5}{760\times0.0821\times298}$$

$$= 0.020 \qquad ...(1)$$

$$K_p = \frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left[\frac{P}{[n_{NO_2}+n_{N_2O_4}]}\right]^1$$

$$\therefore\quad 0.113 = \frac{b^2}{a}\times\left[\frac{753}{760\times(a+b)}\right]$$

$$\therefore\quad \frac{b^2}{a(a+b)} = 0.114 \qquad ...(ii)$$

By Eqs. (i) and (ii)

$$\therefore\quad \frac{b^2}{a} = 0.114\times0.020 = 2.3\times10^{-3} \qquad ...(iii)$$

$$b^2 = 2.3\times10^{-3}\,a = 2.3\times10^{-3}\times(0.02-b)$$

or $b^2 + 0.0023b - 4.6\times10^{-5} = 0$

$$\therefore\quad b = -\frac{0.0023\pm\sqrt{(0.0023)^2+4\times4.6\times10^{-5}\times1}}{2\times1}$$

$$= \frac{-0.0023\pm\sqrt{1.90\times10^{-4}}}{2}$$

$$b = 5.73\times10^{-3}$$

$\therefore$ By Eq. (i) $\quad a = 0.014$

(b) $2NO_2\,(aq.) + 2H_2O(l) \longrightarrow HNO_2\,(aq.) + H_3O^+\,(aq.) + NO_3^-\,(aq.)$

Total NO_2 mole $= 5.73\times10^{-3} + 2\times$ moles of N_2O_4 from NO_2

$$= 5.73\times10^{-3} + 2\times0.014$$

$$= 0.0337$$

$$2NO_2\,(aq.) + 2H_2O(l) \rightarrow HNO_2 + H_3O^+\,(aq.) + NO_3^-\,(aq.)$$

$$\begin{matrix}0.0337 & & 0 & 0 & 0\\ 0 & & \frac{0.0337}{2} & \frac{0.0337}{2} & \frac{0.0337}{2}\end{matrix}$$

$$\therefore\quad [HNO_2] = \frac{0.0337\times1000}{2\times250} = 0.0674\,M;$$

$$[H^+] = \frac{0.0337\times1000}{2\times250} = 0.0674\,M$$

Due to common ion effect (H_3O^+ furnished by HNO_3), the dissociation of HNO_2 is suppressed.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{0.0674\times[NO_2^-]}{0.0674} = 4.5\times10^{-4}$$

$$\therefore\quad [NO_2^-] = \mathbf{4.5\times10^{-4}}$$

Also $\quad pH = -\log[H^+] = -\log 0.0674 = \mathbf{1.17}$

(c) $\quad \pi = C.S.T.\times(\text{No. of particles present in solution})$

$$= 0.0674\times0.0821\times298\times3$$

($2NO_2$ furnishes three particles)

$$= \mathbf{4.95\ atm}$$

(d) Eq. of CaO required = Eq. of HNO_2 + Eq. of HNO_3

$$= \frac{0.0337}{2}\times1 + \frac{0.0337}{2}\times1 = 0.0337$$

$\therefore$ Mole of CaO required $= \frac{0.0337}{2}$ or $\frac{w}{56} = \frac{0.0337}{2}$

$$\therefore\quad w_{CaO} = \mathbf{0.924\ g}$$

144. $CH_3COOH + Na^+ + CN^- \rightleftharpoons CH_3COO^- + Na^+ + HCN$

$$K_{eq} = \frac{[CH_3COO^-][HCN]}{[CH_3COOH][CN^-]} \qquad ...(i)$$

For CH_3COOH and HCN in same solution

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ...(ii)$$

$$K_2 = \frac{[CN^-][H^+]}{[HCN]} \qquad ...(iii)$$

By Eqs. (ii) and (iii)

$$K_{eq} = \frac{K_1}{K_2} = \frac{1.8\times10^{-5}}{4.9\times10^{-10}} = \mathbf{3.674\times10^4}$$

145. $NaX + H_2O \longrightarrow$ No hydrolysis because $\quad pH = 7.0$

$NaY + H_2O \longrightarrow NaOH + HY \quad pH = 9.0$

$NaZ + H_2O \longrightarrow NaOH + HZ \quad pH = 11.0$

Thus acidic character order for acids is : $HX > HY > HZ$

Also for NaY: $\quad [OH^-] = 10^{-5} \quad \because pH = 9 \therefore pOH = 5$

$$Ch = 10^{-5}$$

$$C\cdot\sqrt{\frac{K_H}{C}} = 10^{-5} \quad \text{or} \quad \sqrt{\frac{K_w\times C}{K_a}} = 10^{-5}$$

$$\therefore\quad \frac{10^{-14}\times0.1}{K_a} = 10^{-10} \quad \therefore\quad K_a \text{ for } HY = 10^{-5}$$

Similarly, $\quad K_a$ for $HZ = \mathbf{10^{-9}}$

146. The conjugate base (here $HC_8H_4O_4^-$) of polybasic acid (here $H_2C_8H_4O_4$), is amphioprotic and can act as either an acid or a base because it can donate its remaining acidic hydrogen atom or accept an acidic hydrogen atom and revert to the original acid.

Acid :

$$HC_8H_4O_4^-\,(aq.) + H_2O(l) \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-};\quad pK_{a_2} = 5.44$$

$$K_{a_2} = \frac{[H_3O^+][C_8H_4O_4^{2-}]}{[HC_8H_4O_4^-]} \qquad ...(i)$$

Hydrolysis :

$$HC_8H_4O_4^-\,(aq.) + H_2O(l) \rightleftharpoons H_2C_8H_4O_4 + OH^-;\quad pK_H = 11.06$$

$$K_H = \frac{[H_2C_8H_4O_4][OH^-]}{[HC_8H_4O_4^-]} \qquad ...(ii)$$

Also for $H_2C_8H_4O_4$

$$H_2C_8H_4O_4 \rightleftharpoons H^+ + HC_8H_4O_4^-$$

$$K_{a_1} = \frac{[H^+][HC_8H_4O_4^-]}{[H_2C_8H_4O_4]} \qquad ...(iii)$$

By Eqs. (ii) and (iii)

$$K_H \times K_{a_1} = [H^+][OH^-] = K_w \quad ...(iv)$$

Assuming $HC_8H_4O_4^-$ having low degree of dissociation as well as low degree of hydrolysis, acidic nature of $HC_8H_4O_4^-$ and hydrolysis of $HC_8H_4O_4^-$ producing $C_8H_4O_4^{2-}$ and $H_2C_8H_6O_4$ of almost equal conc.

$$[H_2C_8H_4O_4] = [C_8H_4O_4^{2-}] \quad ...(v)$$

From Eqs. (i), (ii) and (v) $\frac{K_H}{K_{a_2}} = \frac{[OH^-]}{[H^+]}$ ...(vi)

Also $K_w = [H^+][OH^-]$ ...(vii)

By Eqs. (vi) and (vii)

$$\therefore \quad K_w = \frac{[H^+] \times K_H \times [H^+]}{K_{a_2}} \quad ...(viii)$$

By Eqs. (iv) and (viii) $K_H \times K_{a_1} = \frac{[H^+]^2 \times K_H}{K_{a_2}}$

or $[H^+]^2 = K_{a_1} \times K_{a_2}$ or $[H^+] = \sqrt{K_{a_1} \times K_{a_2}}$

$$pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$$

$$\frac{1}{2}[2.94 + 5.44] = 4.19$$

Note: 1. The pH is independent of salt concentration in case of acidic salt solution.

2. All polyprotic acids (except H_2SO_4) are weak acids and the relation $pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$ holds good.

3. The relation $pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$ is derived by using reasonable assumptions and doing some intricate algebra. The assumptions include that if pK_{a_2} is high HA^- is weak acid, the solution will have high pH. If pK_{a_1} is large HA^- is likely to act as 'strong' weak base. Thus, if both pK_{a_1} and pK_{a_2} are large, pH will be high.

147. $[H^+]$ formed due to electrolyte oxidation = 4 *m* moles

	Na_2HPO_4	+	Na_3PO_4
Initial mm	0.08×100		0.02×100
	$= 8$		2

$[H^+]$ will be used by PO_4^{3-} to give $H_2PO_4^-$

PO_4^{3-}	+	$2H^+$	$\longrightarrow$	$H_2PO_4^-$
2		4		0
0		0		2

Thus, a new buffer containing Na_2HPO_4 (8 mm) and $H_2PO_4^-$ (2 mm) will remain in solution

$$\therefore pH = pK_{a_{H_2PO_4^-}} + \log \frac{[Na_2HPO_4]}{[H_2PO_4^-]} = 7.2 + \log \frac{8}{2} = \mathbf{7.81}$$

148.

	CH_3COOH	+	$NaOH$	$\longrightarrow$	CH_3COONa	+	H_2O
at 1/3 neutralisation	$\frac{2}{3}$				$\frac{1}{3}$		

$$\therefore \quad [\text{Conjugate base}] = [CH_3COO^-] = \frac{1}{3}$$

$$[\text{Acid}] = [CH_3COOH] = \frac{2}{3}$$

$$\therefore \quad pH_1 = -\log K_a + \log \frac{1/3}{2/3} = -\log K_a - \log 2$$

at 2/3 neutralisation [conjugate base] $= \frac{2}{3}$

$$[\text{Acid}] = \frac{1}{3}$$

$$\therefore \quad pH_2 = -\log K_a + \log \frac{2/3}{1/3}$$

$$= -\log K_a + \log 2$$

$$\therefore \quad \Delta pH = pH_1 - pH_2 = \log \frac{1}{2} - \log 2$$

$$= \mathbf{-2\log 2}$$

149. (3)

$\Lambda_m(HX) = \frac{x}{10}$ $\quad \Lambda_m(HY) = x$. Also $\alpha = \frac{\Lambda_m}{\Lambda_0}$. Let α_1 and α_2 be degree of dissociation of 0.01 *M* *HX* and 0.1 *M* *HY*

$$\therefore \frac{\alpha_1}{\alpha_2} = \frac{\Lambda_m(HX)/\Lambda_m^0(HX)}{\Lambda_m(HY)/\Lambda_m^0(HY)} = \frac{(x/10)/\Lambda_m^0(HX)}{x/\Lambda_m^0(HY)} = \frac{1}{10}$$

$HX \rightleftharpoons$	H^+	+	X^-
0.01	–		–
$0.01(1-\alpha_1)$	$0.01\alpha_1$		$0.01\alpha_1$

$K_{a_1} = 0.01\alpha_1^2$ $\quad (\because \alpha_1 <<< 1)$

$HY \rightleftharpoons$	H^+	+	Y^-
0.1	–		–
$0.1(1-\alpha_2)$	$0.1\alpha_2$		$0.1\alpha_2$

$K_{a_2} = 0.1\alpha_2^2$ $\quad (\because \alpha_2 << 1)$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{0.01\alpha_1^2}{0.1\alpha_2^2} = \frac{1}{10} \cdot \frac{\alpha_1^2}{\alpha_2^2} = \frac{1}{10} \times \left(\frac{1}{10}\right)^2 = \frac{1}{1000}$$

$\log K_{a_1} - \log K_{a_2} = -3$

$pK_{a_1} - pK_{a_2} = 3$

SINGLE INTEGER ANSWER PROBLEMS

1. 500 mL of HCl of pH 4.3010 is allowed to react with 500 mL of pH 9.6990 NaOH solution at 300 K. If temperature remains constant, approximate pH of resulting solution is....
2. 300 mL of 5×10^{-2} M HCl is allowed to react with 200 mL of 5×10^{-2} M NaOH at 300 K. The pH of resulting solution at 300 K is.....
3. 500 mL of 0.01 M CH_3COOH + 500 mL of 0.02 M CH_3COONa gives a pH equal to 5.3010. The pK_b of CH_3COO^- is.....
4. K_b for MeOH an indicator is 10^{-9}. The pH at which it shows is a colour change is.....
5. K_{sp} of $M(OH)_2$ is 5×10^{-16} at 25°C. The pH of its saturated solution at 25°C is .....
6. The equilibrium constant of a strong acid (HA) with weak base BOH is 10^{11}. The pH of 0.10 M solution of BA is.....
7. 10 mL of 0.25 M H_2SO_4 is completely neutralised by 0.125 M solution of NH_3. The pH of the solution at the equivalence point is....., if K_b for NH_3 = 10^{-5}.
8. 100 mL of 0.20 M weak acid HA is completely neutralised by 0.20 M NaOH. K_b for A^- is 10^{-3}, the pOH at the equivalence point is.....
9. One litre of 1 M solution of an acid HA (K_a = 10^{-4} at 25°C) has pH = 2. It is diluted by water so that new pH becomes double. The solution was diluted to 5×10^{a} mL. The value of a is.....
10. K of pure water is 10^{-12} at 60°C. The pH of pure water at 60°C is.....
11. An aqueous solution of 0.24 M aniline ($K_b = 4.166\times10^{-10}$) is mixed with NaOH solution to maintain anilinium ion concentration to 1×10^{-8} M. The pOH of NaOH solution used was .....
12. A certain buffer solution equals concentration of X^- and HX. K_b for X^- is 10^{-10}. The pH of buffer is.....
13. Two weak acids HA and HB have same pH when their concentration ratio is 3 : 1. The ratio of the dissociation constants of HB and HA is.....
14. Conjugate base of a weak acid has K_b = 10^{-9}. The equilibrium constant for the reaction of acid with strong base is.....
15. K_{sp} of SrF_2 is 1×10^{-10}. The solubility of SrF_2 in 0.1 M NaF is 1×10^{-a} M. The value of a is.....
16. pH of 0.1 M NaCl solution is.....
17. The solubility of $RNH_{2(g)}$ in water at 1 atm and 27°C is 24.63 litre per litre water. If pK_b of RNH_2 = 4, the maximum pOH of the resulting solution will be ..... .
18. If K_{sp} of $HgSO_4$ is 6.4×10^{-5} mole^2 litre^2, then solubility of $HgSO_4$ in mole/m^3 is ..... .
19. The dissociation constant of a monoprotic acid, morphine a pain killer is 10^{-a}. Its 0.01 M solution with its 0.01M sodium salt shows a pH 6, the value of pK_a is.....
20. The molar concentration of SO_4^{2-} required to precipitate $RaSO_4$ for 2×10^{-4} mole of Ra^{2+} in 500 mL is 10^{-a} M. If K_{sp} of $RaSO_4$ is 4×10^{-11} then value of a is.....
21. The A^{2+} left in solution when 50.0 mL of 0.20 M $A(NO_3)_2$ is added to 50mL of 1.5M NaCl is 9.95×10^{-a} M. If K_{sp} of ACl_2 is 5.6×10^{-4} then the value of a is.....
22. The solubility of CoS in 0.10M H_2S and 0.15M H^+ solution is $a\times10^{-6}$ M. The value of a is..... Given K for $H_2S \rightleftharpoons 2H^+ + S^{2-}$ is 1×10^{-21} and K_{sp} CoS = 3.11×10^{-26}
23. If K_{a_1} and K_{a_2} for H_2S are 1×10^{-7} and 1×10^{-14} respectively. Then hydrolysis constant for $S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$ is.....
24. The pK_{eq} for $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is –6, then pK_{eq} for HA is.....
25. pH of 0.1M NaCl solution is.....
26. A buffer mixture containing equal mole of HB and its conjugate base B^- ($K_b = 10^{-10}$) has pH equal to.....
27. The pH at which an indicator pK_b = 5.00 changes its colour is.....
28. Ethylenediamine $NH_2C_2H_4NH_2$ a base (B) can add 1 or 2 protons. The successive pK_b values are 4 and 7 respectively. The $p^{[BH_2^{2+}]}$ in 0.001M solution of ethylenediamine is.....
29. The per cent error in $[H_3O^+]$ made by neglecting the ionisation of water in a 1.0×10^{-6} M NaOH solution.
30. The pH of solution resulting when 50 mL of 0.20M HCl is mixed with 50 mL of 0.20M CH_3COOH ($pK_a = 1.8\times10^{-5}$)
31. The pK_{eq} for the reaction of Na_2A and HCl at exactly half neutralisation of Na_2A is 6, then pK_{eq} for $A^{2-} + H^+ \rightleftharpoons HA^-$ will be.....
32. If $K_{eq.}$ for $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is 10^6, then pK_a for acid HA is.....
33. The solubility of $M(OH)_X$ is 10^{-4} M. If its pK_{sp} is 4×10^{-12}, then the value of X is.....
34. An acid indicator (K_a = 10^{-5}) will have 50% its basic form at pOH.
35. The solubility product of AgCl is 10^{-10} M^2 at 25°C. The minimum volume of water (in m^3) required to dissolve 1.435 g AgCl at 25°C.

36. The molar solubility of Ag_2CO_3 ($K_{sp} = 4 \times 10^{-13}$) in 0.1 M Na_2CO_3 is 10^{-a} M. The value of a is ..... .

37. The pH of an aqueous solution of 0.1 M NH_4Cl and 0.01M NH_4OH ($pK_b = 5$) is ..... .

38. The pOH of resulting 500 mL solution by mixing 25 mL of 0.1 M NaOH and 25 mL 0.08 M HCl, finally diluted with water is ..... .

39. If aM solution of weak acid HA has same pH as bM solution of weak acid HB. Also if $\frac{a}{b} = 4$, then the ratio of dissociation constant of two acids HB and HA will be ..... .

40. The minimum pH required to prevent the precipitation of ZnS in a solution having 0.1M $ZnCl_2$ and 0.1M H_2S if $Ka_1 \times Ka_2$ for H_2S is 10^{-20} and K_{sp} of ZnS $= 10^{-21}$.

41. The per cent error in $[H^+]$ made by neglecting ionisation of water in 1.0×10^{-6} M NaOH is ..... .

42. 0.01 mole of NaOH in 10 litre water are added. How much the pH water changes?

43. The approximate pH of a solution of benzoic acid ($K_a = 6.4 \times 10^{-5}$) having density 2.06 g/dm^3 is ..... .

44. A mixture of KOH and $Ca(OH)_2$ weighing 6.13 g is completely neutralized by an acid. If mass percent of KOH in mixture is 45.68 and normality of acid is 20 N, then find the approximate volume (in mL) of acid used in neutralisation.

45. 50 mL of 0.2 N NaCN is mixed with 50 mL of 0.2 M HCl. Calculate approximate concentration of $[H^+]$ in molarity $\times 10^{-6}$ if K_b for CN^- is 2×10^{-5}.

46. The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4}. The pH of a 0.01 M solution of its sodium salt is : **(IIT 2009)**

47. The total number of diprotic acids among the following is..... **(IIT 2010)**
H_3PO_4, H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$
H_3BO_3, H_3PO_2, H_2CrO_4, H_2SO_3

48. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper to blue is..... **(IIT 2010)**
KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$
$FeCl_3$, K_2CO_3, NH_4NO_3, LiCN

49. In one litre saturated solution of AgCl [K_{sp} of AgCl $= 1.6 \times 10^{-10}$], 0.1 mole of CuCl [K_{sp} of CuCl $= 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-X}. The value of X is ..... . **(IIT 2011)**

ANSWERS

1. Seven	2. Two	3. Nine	4. Five	5. Nine	6. Six	7. Five	8. Two	9. Six	10. Six	11. Two	12. Four
13. Three	14. Nine	15. Eight	16. Seven	17. Two	18. Eight	19. Six	20. Seven	21. Four	22. Seven	23. One	24. Six
25. Seven	26. Four	27. Nine	28. Seven	29. One	30. One	31. Six	32. Six	33. Two	34. Nine	35. One	36. Six
37. Eight	38. Three	39. Four	40. One	41. One	42. Four	43. Three	44. Seven	45. Seven	46. Eight	47. Six	48. Three
49. Seven											

OBJECTIVE PROBLEMS (One Answer Correct)

1. The equilibrium constant for :
$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ is :
(Given pK_b for $CN^- = 4.69$ and pH for $CH_3COO^- = 9.25$)
(a) 3.7×10^4 (b) 2.8×10^{-5}
(c) 1.97 (d) 0.5

2. The ionisation of codein in 0.01 M solution shows a pH = 10.1. The ionisation constant of codein is :
(a) 1.6×10^{-4} (b) 1.6×10^{-6}
(c) 1.6×10^{-8} (d) 1.6×10^{-3}

3. The solubility of a sparingly soluble salt $A(OH)_2$ (molar mass 192.3 g mol^{-1}) is 19.23 g/litre at 300 K. The pH of its saturated solution assuming 80% ionisation at 300 K is :
(a) 1.0970 (b) 12.9030
(c) 13.2041 (d) 12.0000

4. K_b for CH_2ClCOO^- is 7.41×10^{-12}. The pH of 0.1 M $CH_2ClCOONa$ in water is :
(a) 7.93 (b) 6.66
(c) 1.94 (d) 12.06

5. Equimolar solution of $CaCl_2$ and K_2SO_4 are mixed in equal volumes. If K_{sp} of $CaSO_4$ is 9.1×10^{-6}, the maximum molar concentrations of $CaCl_2$ and K_2SO_4 which will lead no precipitation of $CaSO_4$ is :
(a) 0.006 (b) 0.004
(c) 0.002 (d) 0.008

6. If K_{sp} of ZnS is 1.0×10^{-21}, the minimum volume of water is required for the dissolution of 0.097 g ZnS is :
(a) 3.16×10^5 litre (b) 3.16×10^7 litre
(c) 3.16×10^9 litre (d) 3.16×10^3 litre

7. K_{sp} of $M(OH)_x$ is 27×10^{-12} and its solubility in water is 10^{-3} mole $litre^{-1}$. The value of x is :
(a) 1 (b) 2
(c) 3 (d) 4

8. The dissociation constants for acetic acid are 1.8×10^{-5} and 1.805×10^{-5} at 300 and 310 K respectively. The enthalpy of deprotonation for acetic acid is :
(a) 50 cal (b) 52.8 cal
(c) 51.6 cal (d) 48.48 cal

9. Solubility product of $A_2X_3 \cdot 4H_2O$ is given by :
(a) $[A^{3+}]^2[X^{2-}]^3[H_2O]^4$
(b) $[2A^{3+}]^2[3X^{2-}]^3[H_2O]^4$
(c) $[2A^{2+}]^2[3X^{3-}]^3[H_2O]^4$
(d) $[A^{3+}]^2[X^{2-}]^3$

10. pH of some solutions is given by : $[H^+] = \frac{pK_{a_1} + pK_{a_2}}{2}$.
For which type of compounds this formula is not valid?
(a) NaHS (b) NaH_2PO_4
(c) NaH_2PO_3 (d) NaH_2BO_3

11. Which one is not correct statement about buffer mixture ?
(a) NH_4OH + its conjugate acid
(b) CH_3COONa + its conjugate base
(c) 1 millimole of NaCN + 0.5 millimole of HCl in 1 litre
(d) 0.5 millimole of NaCN + 1 millimole of HCl in 1 litre

12. A buffer solution is prepared by dissolving 1 mole of CH_3COOH and 'a' mole of Zn acetate. The pH of solution is 4.7447 and pK_a for CH_3COOH = 4.7447. The number of mole of zinc acetate are :
(a) 1 (b) 2
(c) 0.5 (d) 0.25

13. The percentage error in H^+ concentration provided by 10^{-8} M HCl if ionisation of water is not neglected is :
(a) 3% (b) 2%
(c) 5% (d) 4%

14. The degree of dissociation of water is 1.8×10^{-9} at 300 K. The self ionisation constant for water is :
(a) 1.0×10^{-14} (b) 1.8×10^{-16}
(c) 3.23×10^{-18} (d) none of these

15. The change in pH of water when 0.01 mole of NaOH are added in 10 litre water is :
(a) 11 units (b) 3 units
(c) 4 units (d) 2 units

16. Which of the following has concentration dependent pH?
(a) CH_3COONa (b) CH_2NH_2COOH
(c) CH_3COONH_4 (d) NaHS

17. An acid-base indicator (pK_a = 4.5271) has the acid form red and basic form blue. If we need 75% red to be converted into 75% blue form in solution, the change in pH of solution should be :
(a) 4.05 (b) 5.0
(c) 0.95 (d) 0.80

18. 0.1 mole of CH_3NH_2 (pK_b = 3.3010) is mixed with 0.08 mol of HCl and volume is made to 1 litre. The pH of solution is :
(a) 7.32 (b) 11.4642
(c) 10.097 (d) 11.5020

19. 0.08 mole of CH_3NH_2 (pK_b = 3.3010) is mixed with 1.0 mole of HCl and volume is made to 1 litre. The pH of solution is :
(a) 1.699 (b) 2.699
(c) 10.097 (d) 7.32

20. 0.04 M solution of CH_3NH_2 (pK_b = 3.3010) is diluted to reduce its molar concentration to half. The change in pH during dilution is :

(a) +0.1615 (b) −0.1615
(c) + 0.2615 (d) −0.2615

21. The enthalpy change for first proton neutralisation of H_2S is −33.7 kJ mol^{-1}. What is enthalpy change for first ionisation of H_2S ?
(a) 23.6 (b) 33.7
(c) 20.8 (d) 10.4

22. Which will have pH closer to 1.0 ?
(a) 100 mL of 0.1 *M* HCl + 100 mL 0.1 *M* NaOH
(b) 55 mL of 0.1 *M* HCl + 45 mL of 0.1 *M* NaOH
(c) 10 mL of 0.1 *M* HCl + 90 mL 0.1 *M* NaOH
(d) 75 mL of 0.2 *M* HCl + 25 mL 0.2 *M* NaOH

23. The pH of 0.1 *M* solution of the following salts increases in the order :
(a) NaCl < NH_4Cl < NaCN < HCl
(b) HCl < NH_4Cl < NaCl < NaCN
(c) NaCN < NH_4Cl < NaCl < HCl
(d) HCl < NaCl < NaCN < NH_4Cl

24. The conjugate acid of NH_2^- is :
(a) NH_3 (b) NH_2OH
(c) NH_4^+ (d) N_2H_4

25. The compound that is not Lewis acid is :
(a) BF_3 (b) $AlCl_3$
(c) $SnCl_4$ (d) CCl_4

26. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2 – 3 and the pH in the small intestine is about 8. Aspirin will be :
(a) unionised in small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

27. Which of the following is the strongest acid?
(a) $ClO_3(OH)$ (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

28. pK_b of NH_4OH is 5. The pH of a mixture containing 10mL of 0.3*M* NH_4OH and 200 mL of 0.1*M* $(NH_4)_3PO_4$ is :
(a) 5 (b) 5.3010
(c) 6.3010 (d) 7.6987

29. K_w for water is $9.5\times10^{-14}\ m^2$ at 60°C. An aqueous solution of a salt at 60°C has pH = 7, it is :
(a) acidic (b) basic
(c) neutral (d) none of these

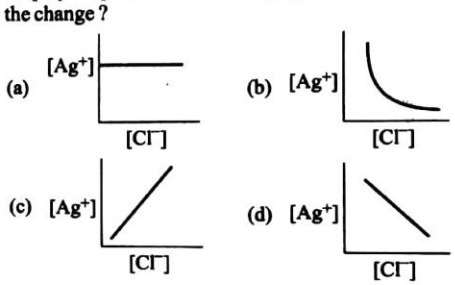
30. 100 mL of 0.005 *M* H_2SO_4 is diluted to one litre. The pH of resulting solution is :
(a) 3 (b) 4
(c) 5 (d) 2

31. How much water should be added to 300 mL of 0.2 *M* solution of acetic acid ($K_a = 1.8\times10^{-5}$) to increase its degree of dissociation two times ?
(a) 1.2 litre (b) 1.5 litre
(c) 0.9 litre (d) 0.7 litre

32. If pK_b for $C_6H_5O^-$ is 4, what is the pH of 0.1*M* $C_6H_5O^-$ in solution at 25°C?
(a) 13.0 (b) 12.5
(c) 11.5 (d) 10.5

33. 2, 4-dinitrophenol (pK_a = 4) acts as buffer and if pH of this buffer is adjusted to 5, the ratio of concentration of dissociated and undissociated molecules of 2, 4-di nitrophenol is :
(a) 1 (b) 10
(c) 0.1 (d) 0.01

34. In a saturated solution of AgCl, addition of NaCl is made drop by drop in excess. Which graph correctly represents the change ?



35. Solubility of Ag_2CrO_4 in 0.2 *M* K_2CrO_4 is '*a*' and solubility of Ag_2CrO_4 in 0.4 *M* $AgNO_3$ is '*b*', then :
(a) $a = b$
(b) $a > b$
(c) $a < b$
(d) cannot be predicted in absence of K_{sp} of Ag_2CrO_4

36. 0.1 *M* solution of H_3A being a weak tribasic acid having K_{a_1}, K_{a_2} and K_{a_3} as $10^{-5}, 10^{-9}$ and 10^{-13} respectively. If p*X* represents $-\log\dfrac{[A^{3-}]}{[HA^{2-}]}$, then the value of p*X* is :
(a) 7 (b) 8
(c) 10 (d) 9

37. pH of mixture having 0.1 *M* NH_4OH and 0.1 *M* NH_4Cl is equal to $pK_w - pK_b$. If 0.1 *M* NH_4OH and 0.1 *M* $(NH_4)_2SO_4$ are taken, the pH will be :
(a) $pK_w - pK_b$ (b) $pK_w + pK_b$
(c) $pK_w - pK_b + \log 2$ (d) $pK_w - pK_b - \log 2$

38. In the equilibrium : $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$ if $[Ba^{2+}]$ is increase two times, then $[F^-]$ in solution will :
(a) increase two times (b) increase four times
(c) decrease two times (d) decrease to $1/\sqrt{2}$ times

39. The pH of 100 mL solution containing 0.3 M NH_4^+, 0.2M NH_4OH ($K_b = 4.74$) and 0.01 M HCl in it is :
(a) 9.05 (b) 8.66
(c) 7.46 (d) 8.05

40. The pH of a 100 mL solution containing 0.3 mole of NH_4^+, 0.2 M NH_4OH and 0.01 M NaOH in it is :
(a) 10.12 (b) 9.12
(c) 8.12 (d) 8.5

41. A weak acid has pH = 4, then :
(a) $C = 10^{-3}, \alpha = 10\%$ (b) $C = 10^{-3}, \alpha = 10^{-6}$
(c) $[A^-] = 10^{-5}$ (d) $K_a = 10^{-2}, \alpha = 10$

42. An acidic buffer solution can be prepared by mixing the solution of :
(a) ammonium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide

43. The pH of a 10^{-8} molar solution of HCl in water is :
(a) 8 (b) -8
(c) between 7 and 8 (d) between 6 and 7

44. Of the given anions, the strongest Bronsted base is :
(a) ClO^- (b) ClO_2^-
(c) ClO_3^- (d) ClO_4^-

45. At 90°C, pure water has $[H_3O^+] = 10^{-6}$ mole litre^{-1}. What is the value of K_w at 90°C?
(a) 10^{-6} (b) 10^{-12}
(c) 10^{-14} (d) 10^{-8}

46. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed :
(a) 10^{-4} M Ca^{2+} + 10^{-4} M F^-
(b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
(c) 10^{-5} M Ca^{2+} + 10^{-3} M F^-
(d) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

47. A certain buffer solution contains equal concentration X^- and HX. Then K_b for X^- is 10^{-10}. The pH of the buffer is :
(a) 4 (b) 7
(c) 10 (d) 14

48. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is :
(a) 1.0×10^{-4} (b) 1.0×10^{-10}
(c) 1.0×10^{10} (d) 1.0×10^{14}

49. The best indicator for detection of end point in titration of a weak acid and a strong base is :
(a) methyl orange (3 to 4)
(b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5)
(d) phenolphthalein (8 to 9.6)

50. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid-base pairs is :
(a) (HCl, CH_3COOH) and ($CH_2COOH_2^+$, Cl^-)
(b) (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)
(c) ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

51. The compound insoluble in acetic acid is :
(a) calcium oxide (b) calcium carbonate
(c) calcium oxalate (d) calcium hydroxide

52. The compound whose 0.1 M solution is basic is :
(a) ammonium acetate (b) ammonium chloride
(c) ammonium sulphate (d) sodium acetate

53. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with :
(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

54. The degree of dissociation of water at 25°C is 1.9×10^{-7}% and density is 1.0 g cm^{-3}. The equilibrium constant for water is :
(a) 1.0×10^{-14} (b) 2.0×10^{-14}
(c) 2.0×10^{-16} (d) 1.0×10^{-8}

55. Which one is more acidic in aqueous solution ?
(a) $NiCl_2$ (b) $FeCl_3$
(c) $AlCl_3$ (d) $BeCl_2$

56. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order
ClOH (I), BrOH (II), IOH (III)
(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

57. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is :
(a) 1.74×10^{-5} (b) 3.52×10^{-3}
(c) 6.75×10^{-4} (d) 5.38×10^{-2}

58. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is :
(a) $6y^4$ (b) $64y^4$
(c) $36y^5$ (d) $108y^5$

59. Among the following the one having lowest K_{sp} is :
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

60. Which of the following is correct for 1.0 M solution of strong acid HA and 1.0 M solution of weak acid HB ?
(a) HA : pH = 0; HB : pH < 1
(b) HA : $[H^+] = [A^-]$; HB ; $[H^+] = [A^-]$
(c) HA ; $[HA] = 0$; HB : $[HB] = (1-\alpha)$
(d) All of these

61. Which order is not correct for basic nature ?
(a) $NH_3 > PH_3$ (b) $H_2O > H_2S$
(c) $NH_3 > NCl_3$ (d) $NF_3 > NH_3$

62. Which of the following acid-base neutralisation does not form water with salt ?
(a) $Al_2O_3(s) + NaOH(aq.)$ (b) $Al_2O_3 + HCl(aq.)$
(c) $SiO_2 + NaOH(aq.)$ (d) $ZnO + NaOH(aq.)$

63. How many mole of HCl must be added to 1 litre aqueous solution of HCl of pH = 3, in order to decrease its pH to 2?
(a) 0.009 (b) 0.001
(c) 1 (d) 0.1

64. Which one is correct decreasing order of solubility of AgCl ?
(i) in water (ii) in 0.1 M NaCl
(iii) in 0.1 M $BaCl_2$ (iv) in 0.1 M NH_3
(a) (iv > iii > ii > i) (b) (iv > i > ii > iii)
(c) (iv > ii > iii > i) (d) (i > ii > iii > iv)

65. 0.1 M aqueous solution of BOH (a weak base) has pH equal to 12 at 27°C. Assuming K_w at 27°C 1.0×10^{-14}, calculate the osmotic pressure of 0.1 M $BOH(aq.)$
(a) 2.71 atm (b) 2.46 atm
(c) 0.246 atm (d) 24.6 atm

66. 300 mL of saturated, clear solution of $CaC_2O_4(aq.)$ is completely oxidised by 6 mL of 0.001 M $KMnO_4$ in acid medium. The K_{sp} of CaC_2O_4 is :
(a) 25×10^{-8} (b) 25×10^{-9}
(c) 25×10^{-10} (d) 25×10^{-11}

67. Solubility of AgCl (in mole/litre) in a mixture of 1 litre solution containing 0.05M NaCl and 0.05 M $BaCl_2$ is : (Given K_{sp} of AgCl = 1.0×10^{-10})
(a) 6.6×10^{-8} (b) 6.6×10^{-10}
(c) 1.0×10^{-9} (d) 1.0×10^{-8}

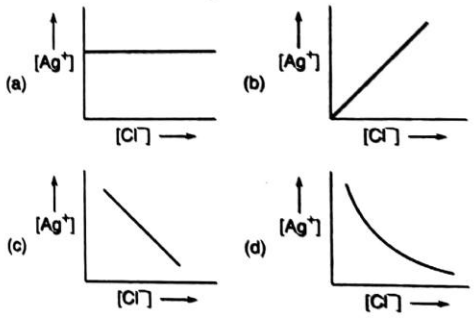
68. Select the correct choice when 100 mL of 0.5 M hydrazoic acid (N_3H having $K_a = 3.6 \times 10^{-4}$) and 400 mL of 0.1 M cyanic acid (HOCN having $K_a = 8 \times 10^{-4}$) are mixed :
(a) pH = 2 (b) $[N_3^-] = 3.6 \times 10^{-3}$
(c) $[OCN^-] = 6.4 \times 10^{-3}$ (d) all of these

69. Autoprotonation constant for liquid NH_3 is 3.46×10^{-27} at –50°C. The number of anions present in 1 mL of pure NH_3 at –50°C is :
(a) 2.08×10^9 (b) 1×10^{-15}
(c) 6.023×10^{-5} (d) 1×10^{15}

70. Solubility product of AgCl is 1.0×10^{-10}. What minimum volume of water in litre is required to dissolve 4.305 mg of AgCl?
(a) 1 (b) 2
(c) 3 (d) 4

71. How many mixed buffers can be obtained using KOH and H_3PO_4 ?
(a) 1 (b) 2
(c) 3 (d) 4

72. Which graph correctly represents addition of NaCl to a saturated solution of AgCl?



73. Which reagent can be used to separate one of ions as precipitate from a solution containing Cu^{2+} and Pb^{2+} ions ?
(a) $H_2S(g)$ (b) NH_4NO_3
(c) HNO_3 (d) H_2SO_4

74. Which can be used to separate F^- ion from a solution of F^- and Cl^- in solution ?
(a) $AgNO_3$ (b) $Pb(NO_3)_3$
(c) HNO_3 (d) H_2SO_4

75. Except one in rest all cases, K_2CO_3 solution on addition gives a precipitate :
(a) $BaCl_2(aq.)$ (b) $CaBr_2(aq.)$
(c) $(NH_4)_2SO_4$ (d) $Pb(NO_3)_2$

76. Arrange the following in increasing order of pH :
1. 0.1 M CH_3COONa + 0.1 M CH_3COOH
2. 0.1 M CH_3COOH + 0.1 M HCl
3. 0.1 M CH_3COOH
4. 0.1 M HCl
(a) 2 < 4 < 3 < 1 (b) 1 < 2 < 3 < 4
(c) 2 < 3 < 4 < 1 (d) 4 < 3 < 2 < 1

77. A solution has pH = 4. It is 1000 times less acidic than another solution of same species of pH :

(a) 1 (b) 2
(c) 3 (d) 4

78. pOH of 0.003 *M* HCl is :
(a) 11 + log 3 (b) 11 – log 3
(c) 7 + log 3 (d) 7 – log 3

79. 10 mL of 10^{-4} *N* H_2SO_4 is diluted with water to have 1 dm^3 solution : The pH of this solution is :
(a) 6 (b) slightly more than 6
(c) slightly less than 6 (d) 7

80. The pH of a solution obtained by mixing 10 mL of 0.1 *M* HCl and 10 mL of 0.01 *M* $Sr(OH)_2$.
(a) 1.40 (b) 1.50
(c) 11.70 (d) 7.00

81. If heat of ionisation $\Delta_i H°$ for HCN and $\Delta_i H°$ for CH_3COOH are 45.2 kJ mol^{-1} and 2.1 kJ mol^{-1}, then which one is not correct ?
(a) $pK_{a_{HCN}} > pK_{aCH_3COOH}$
(b) K_a of HCN < K_a of CH_3COOH
(c) acetic acid is stronger than HCN
(d) $pK_{a_{HCN}} < pK_{aCH_3COOH}$

82. The ratio of degree of dissociation of HCN ($K_a = 10^{-9}$) in its 0.1 *M* and 0.001 *M* solution :
(a) 0.1 (b) 0.2
(c) 0.3 (d) 0.4

83. Which of the following ions can exist in solution ?
(a) H_3O^+ (b) $H_3O_2^-$
(c) $H_5O_2^+$ (d) all of these

84. What will be degree of hydrolysis and pH respectively of an aqueous solution of ammonium formate : $pK_a = 4$, $pK_b = 5$; $pK_w = 14$:
(a) 3.16×10^{-3} , 7 (b) 4.16×10^{-3} , 6.5
(c) 3.16×10^{-3} , 6.5 (d) 4.16×10^{-3} , 7.0

85. The solubility product of AgCl is 10^{-10}. Applying Debye Huckel limiting law, the correct solubility order of AgCl is different solutions of 0.1 *M* concentration is :
(a) NaCl < H_2O < $NaNO_3$ < $Ca(NO_3)_2$
(b) H_2O < NaCl < $NaNO_3$ < $Ca(NO_3)_2$
(c) $NaNO_3$ < $Ca(NO_3)_2$ < H_2O < NaCl
(d) $Ca(NO_3)_2$ < $NaNO_3$ < H_2O < NaCl

86. For, $Ag(CN^-)_2 \rightleftharpoons Ag^+ + 2CN^-$
$K_C = 4 \times 10^{-19}$ at 25°C
Calculate Ag^+ concentration in a solution which is originally 0.1 *M* in KCN and 0.03 *M* in $AgNO_3$.
(a) 7.5×10^{-18} *M* (b) 7.5×10^{-15} *M*
(c) 6.2×10^{-15} *M* (d) 3.4×10^{-15} *M*

87. The solubility product of PbI_2 is 7.47×10^{-9} and 1.39×10^{-8} at 15°C and 25°C respectively. The molar heat of solution of PbI_2 is :
(a) 9.969 k cal (b) 10.66 k cal
(c) 8.88 k cal (d) 11.11 k cal

88. A solution of a weak monobasic acid has $\wedge_M$ for 0.1 *N* solution and $\wedge_\infty$ equal to 60 S $cm^2 mol^{-1}$ and 400 *S* $cm^2 mol^{-1}$ respectively. The pH of this solution and K_a of acid is :
(a) 1.82, 2.65×10^{-3} (b) 2.82, 2.65×10^{-3}
(c) 1.82, 2.25×10^{-3} (d) 2.82, 2.25×10^{-3}

89. The dissociation constant of *HA* and A^- are equal. The pH of 0.001 *HA* solution is :
(a) 3 (b) 4
(c) 5 (d) 6

90. pK_a of acetic acid is 4.74. What mass of KOH is required to be added in 500 mL of 1 M acid in order to prepare a buffer solution of maximum capacity.
(a) 28 g (b) 14 g
(c) 7 g (d) 10 g

91. K_a of HCOOH is 10^{-5} and solubility of HCOOAg is 10^{-2} M. The solubility of HCOOAg in a buffer solution of pH = 3 is .....
(a) 0.01 M (b) 0.1 M
(c) 0.2 M (d) 0.02 M

92. From the following informations, select the strongest base :

Acid	$H_2PO_4^-$	HPO_4^{2-}	HCO_3^-	HSO_3^-
K_a	6.0×10^{-8}	4.8×10^{-13}	4.7×10^{-11}	6.3×10^{-8}

(a) PO_4^{3-} (b) HPO_4^{2-}
(c) CO_3^{2-} (d) SO_3^{2-}

93. 0.125 mole of Ca A_2 are present in 0.5 litre solution. If K_a of *HA* is 8.0×10^{-4} and salt CaA_2 is completely ionised, the pH of solution is :
(a) 5.60 (b) 5.75
(c) 8.40 (d) 8.25

94. At what $\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$, the following cell shows equilibrium :
$Ag(s) | Ag_2CO_3(s), Na_2CO_3(aq.) || AgBr(aq.) | Ag(s)$
K_{SP} of $Ag_2CO_3 = 8 \times 10^{-12}$ and
K_{SP} of AgBr = 4×10^{-13}
(a) 2×10^{-7} (b) $\sqrt{2} \times 10^{-7}$
(c) $\sqrt{3} \times 10^{-7}$ (d) 2

95. Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol L^{-1}. Solubility product of $Ag_2C_2O_4$ is :
(a) 2.42×10^{-8} (b) 2.66×10^{-12}
(c) 4.5×10^{-11} (d) 5.3×10^{-12}

SOLUTIONS (One Answer Correct)

1. (a) $K_{eq.} = \dfrac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$;

$K_{CH_3COOH} = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$;

$K_{HCN} = \dfrac{[H^+][CN^-]}{[HCN]}$

$pK_{bCN^-} = 4.69 \;\therefore\; pK_{HCN} = 9.31$;

$pK_{CH_3COOH} = 4.75$

$\therefore \quad K_{eq.} = \dfrac{K_{CH_3COOH}}{K_{HCN}} = \dfrac{1.77\times10^{-5}}{4.9\times10^{-10}} = 3.7\times10^{4}$

2. (b) pH of Codein = 10.1 $\therefore$ it is a base.

Now $\text{Codein} + H_2O \rightleftharpoons \text{Codein}^+ + OH^-$

$$K_b = \frac{[\text{Codein}^+][OH^-]}{[\text{Codein}]};$$

Also, $[OH^-] = c\alpha = 0.01\times\alpha$

$-\log 3.9 = 0.01\alpha$

$\therefore \quad \alpha = \dfrac{1.259\times10^{-4}}{0.01} = 0.0125$

$K_a = \dfrac{c\alpha^2}{(1-\alpha)}$

$K_a = \dfrac{0.01\times(0.0125)^2}{(1-0.0125)} = 1.6\times10^{-6}$

3. (c) $S = \dfrac{19.23}{192.3}$ mol/litre $= 0.1\ M$

$A(OH)_2 \rightleftharpoons A + \underset{2S}{2OH^-}$

$\therefore \quad [OH^-] = \dfrac{0.1\times2\times80}{100} = 0.16$

$\therefore \quad pOH = 0.7958$

$\therefore \quad pH = 13.2041$

4. (a) $CH_2ClCOO^- + H_2O \rightleftharpoons CH_2ClCOOH + OH^-$

$$[OH^-] = ch = \sqrt{\frac{K_H}{c}}\cdot c = \sqrt{K_H\cdot c} = \sqrt{\frac{K_w\times c}{K_a}}$$

$$= \sqrt{K_b\times c} = \sqrt{7.41\times10^{-12}\times0.1}$$

$$= 8.606\times10^{-7}$$

$\therefore \quad pOH = 6.065$

$pH = 7.93$

5. (a) Let molar concentration of salts be $a\ M$

$[Ca^{2+}][SO_4^{2-}] = K_{sp}$

$\left[\dfrac{a\times V}{2V}\right]\left[\dfrac{a\times V}{2V}\right] = 9.1\times10^{-6}$

$\therefore \quad a^2 = 4\times9.1\times10^{-6} \quad \therefore \quad a = 6.033\times10^{-3}$

6. (b) Solubility of ZnS $= S = \sqrt{K_{sp}} = \sqrt{1\times10^{-21}}$

$= 3.16\times10^{-11}$ mol/litre

$= 3.16\times10^{-11}\times97$ g / L

$= 3.065\times10^{-9}$ g / L

$\therefore$ Volume of water in litre required $= \dfrac{0.097}{3.065\times10^{-9}}$

$= 3.16\times10^{7}$ litre

7. (c) K_{sp} of $M(OH)_X = X^X\cdot(S)^{X+1} = 27\times10^{-12}$

$\therefore \quad X^X\cdot(10^{-3})^{X+1} = 27\times10^{-12}$

By putting $X = 1, 2, 3$.....

$\therefore \quad X = 3$

8. (c) $2.303\log\dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\dfrac{[T_2 - T_1]}{T_1T_2}$

$2.303\log\dfrac{1.805\times10^{-5}}{1.8\times10^{-5}} = \dfrac{\Delta H}{R}\times\dfrac{10}{300\times310}$

$\therefore \quad \Delta H = 51.6$ cal

9. (d) Hydrated water molecules do not interfere in K_{sp}.

10. (d) The formula is valid for acidic salts as well as for zwitter ionic molecules. NaH_2BO_3 is neither an acid salt nor it exists.

11. (d) $NaCN + HCl \rightarrow NaCl + HCN$

1	0.5	0	0
0.5	0	0.5	0.5

i.e., 0.5 NaCN+0.5 HCN, buffer

$NaCN + HCl \longrightarrow NaCl + HCN$ Not a buffer

0.5	1	0	0
0	0.5	0.5	0.5

12. (c) $pH = pK_a + \log\dfrac{2a}{1}$

$(CH_3COO)_2Zn$ gives 2 mol CH_3COO^-

$4.7447 = 4.7447 + \log\dfrac{2a}{1} \quad \therefore \quad a = 1/2$

13. (c) $10^{-8}\ M$ HCl $\therefore$ $[H^+] = 10^{-8} = 10\times10^{-9}$ if dissociation of water is neglected

if not neglected then : $H_2O \rightleftharpoons \underset{a+10^{-8}}{H^+} + \underset{a}{OH^-}$

$\therefore \quad a\times(a+10^{-8}) = 10^{-14}$

$a = 0.95\times10^{-7}$

$\therefore$ % error $= \dfrac{(10\times10^{-9} - 9.5\times10^{-9})}{10\times10^{-9}}\times100 = 5\%$

14. (c) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$[H_3^+O] = C\alpha = 10^{-7} = [OH^-]$

$\therefore \quad C = \dfrac{10^{-7}}{1.8\times10^{-9}} = 55.6$

$K_{s.l.} = \dfrac{[H_3O^+][OH^-]}{[H_2O]^2} = \dfrac{10^{-14}}{(55.6)^2} = 3.23\times10^{-18}$

15. (c) $[OH^-]=\frac{0.01}{10}=10^{-3}$ $\therefore$ pOH = 3 or pH = 11

Thus, pH changes from 7 to 11 by 4 units.

16. (a) pH of acidic salts, salts of weak-acid + weak-base and zwitter ionic species is independent of concentration.

17. (c) For 75% red from $HI_n \rightleftharpoons H^+ + I_n^-$

(Red) 75 — 25 — (Blue) 25

$$K_a=\frac{[H^+][I_n^-]}{[HI_n]}$$

$$pH=pK_a+\log\frac{25}{75}=4.5271-0.4771=4.05$$

For 75% blue form $pH=4.5271+\log\frac{75}{25}$

$$=4.5271+0.4771=5.0$$

$\therefore$ $\Delta pH=5.0-4.05=0.95$

18. (c) $CH_3NH_2+HCl\longrightarrow CH_3NH_3^+ + Cl^-$

0.1	0.08	0	0
0.02	0	0.08	0.08

$[CH_3NH_2]=\frac{0.02}{1}$, $[CH_3NH_3^+]=0.08$

This acts as basic buffer.

$$pOH=pK_b+\log\frac{0.08}{0.02}=3.3010+0.6020$$

$$pOH=3.903$$

$\therefore$ pH = 10.097

19. (a) $CH_3NH_2+HCl\longrightarrow CH_3NH_3^+ + Cl^-$

0.08	1	0	0
0	0.02	0.08	0.08

$\therefore$ $[H^+]=0.02=2\times10^{-2}$; $\therefore$ pH = 1.699

20. (a) **I** : $[CH_3NH_2]=0.04$

$$K_b=\frac{c\alpha^2}{(1-\alpha)}=5\times10^{-4}=\frac{0.04\times\alpha^2}{(1-\alpha)} \quad (1-\alpha\neq1)$$

$\therefore$ $\alpha=0.1056$

$$[OH^-]=c\alpha=0.04\times0.1056=4.224\times10^{-3}$$

$$pOH=2.3743$$

II : $[CH_3NH_2]=0.02$

$$K_b=\frac{c\alpha^2}{(1-\alpha)}=5\times10^{-4}=\frac{0.02\times\alpha^2}{(1-\alpha)} \quad (1-\alpha\neq1)$$

$\therefore$ $\alpha=0.1456$

$\therefore$ $[OH^-]=c\alpha=0.02\times0.1456=2.912\times10^{-3}$

$$pOH=2.5358$$

$\therefore$ $-\Delta pOH=\Delta pH=+0.1615$, *i.e.*, pOH increases on dilution or pH decreases.

21. (a) $H_2S+OH^-\longrightarrow H_2O+HS^-$; $\Delta H=-33.7$ kJ

$H^+ + OH^-\longrightarrow H_2O$; $\Delta H=-57.3$ kJ

$\therefore$ $H_2S\rightleftharpoons H^+ + HS^-$; $\Delta H=+57.3-33.7=+23.6$ kJ

22. (d)

HCl	+ NaOH	⟶ NaCl	+ H_2O
75×0.2	25×0.2		
= 15	5	0	0
10	0	5	5

$$[H^+]=\frac{10}{100}=0.1$$

$\therefore$ pH = 1

23. (b) HCl is an acid having lowest pH, $NaCN_{aq.}$ is alkaline and NH_4Cl is acidic due to hydrolysis.

24. (a) $NH_2^- + H^+ \longrightarrow NH_3$

base conjugate acid

25. (d) CCl_4 has complete octet and can not expand its octet.

26. (d) Aspirin an acid will be completely ionised in alkaline medium.

27. (a) $HClO_4$ is strongest acid among these because of higher oxidation number of Cl (*i.e.*, +7).

28. (d) mM of $NH_4OH=10\times0.3=3$

mM of $[NH_4^+]$ from $(NH_4)_3PO_4=200\times0.1\times3=60$

$\therefore$ $pOH=5+\log\frac{60}{3}=5+\log20=6.3010$

$\therefore$ $pH=14-6.3010=7.6987$

29. (b) $K_w=[H^+]^2=9.65\times10^{-14}$ for pure water

$\therefore$ $[H^+]=3.1\times10^{-7}$

If $[H^+]>3.1\times10^{-7}$ acidic

$<3.1\times10^{-7}$ basic

Thus, if $[H^+]=10^{-7}$ *i.e.*, $<3.1\times10^{-7}$, solution is basic.

30. (a) Meq. of H_2SO_4 present initially = Meq. of H_2SO_4 after dilution.

$$0.005\times2\times100=1000\times N$$

$\therefore$ $[H^+]=1\times10^{-3}$

$\therefore$ pH = 3

31. (c) Initially, $\alpha_1=\sqrt{\frac{K_a}{c_1}}=\sqrt{\frac{1.8\times10^{-5}}{0.2}}=9.49\times10^{-3}$

If α is doubled, then new $\alpha_2=1.898\times10^{-2}$

Since α remains negligible in both cases, therefore

$$c_1\alpha_1^2=c_2\alpha_2^2$$

$\therefore$ $c_2=0.2\times\left(\frac{1}{2}\right)^2=0.05$

On dilution $c_1V_1=c_2V_2$ (or $M_1V_1=M_2V_2$)

$$300\times0.2=0.05\times V_2$$

$\therefore$ $V_2=1200$ mL

$\therefore$ Volume of water added = 900 mL

32. (c) $C_6H_5O^- + H_2O\longrightarrow C_6H_5OH+OH^-$

$$[OH^-]=c\cdot h=c\cdot\sqrt{\frac{K_H}{c}}=\sqrt{\frac{K_w}{K_a}\cdot c}$$

$$=\sqrt{K_b\cdot c}=\sqrt{10^{-4}\times0.1}=3.16\times10^{-3}$$

$\therefore$ pOH = −2.5

$\therefore$ pH = 11.5

33. (b) $pH=pK_a+\log\frac{[\text{conjugate base}]}{[\text{acid}]}$

$$5=4+\log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\log\frac{[\text{conjugate base}]}{[\text{acid}]}=1$$

$$\therefore\quad \frac{[\text{conjugate base}]}{[\text{acid}]}=\frac{[\text{dissociated ions}]}{[\text{undissociated acid}]}=10$$

34. (b) $[Ag^+][Cl^-]=K_{sp}$ or $[Ag^+]=\dfrac{K_{sp}}{[Cl^-]}$

if $[Cl^-]$ increases, then to have K_{sp} constant and thus $[Ag^+]$ decreases. Also after sufficient addition of $[Cl^-]$, $[Ag^+]$ will become almost constant.

35. (d) $K_{sp}Ag_2CrO_4=[Ag^+]^2[CrO_4^{2-}]$

$=(2s)^2\times s=4s^3$

Now in 0.2 M K_2CrO_4	In 0.4 M $AgNO_3$
$K_{sp}=[Ag^+]^2\times 0.2$	$K_{sp}=[0.4+S]^2\times S$
$\therefore\quad [Ag^+]=\sqrt{\dfrac{K_{sp}}{0.2}}$	$\therefore\quad s=\dfrac{K_{sp}}{0.16}$
or $\quad a=\sqrt{\dfrac{K_{sp}}{0.2}}$	$b=\dfrac{K_{sp}}{0.16}$
$=2.23\times\sqrt{K_{sp}}$	$=6.25\times K_{sp}$

36. (c) $[H^+]$ are obtained in dissociation of H_3A in all the three steps, but the $[H^+]$ obtained in II & III steps are too low. Thus $[H^+]$ can be obtained from 1 step

$$[H^+]=\sqrt{Ka_1\times c}\qquad(1-\alpha\simeq 1)$$

$$=\sqrt{10^{-5}\times 0.1}=10^{-3}$$

Now, $K_3=\dfrac{[H^+][A^{3-}]}{[HA^{2-}]}$

$(HA^{2-}\rightleftharpoons H^+ + A^{3-}$ II Step)

$$10^{-13}=\frac{10^{-3}\times[A^{3-}]}{[HA^{2-}]}$$

$$\therefore\quad \frac{[A^{3-}]}{[HA^{2-}]}=10^{-10}\quad\therefore\quad pX=10$$

37. (d) **In I Case :**

$$pOH=pK_b+\log\frac{[NH_4^+]}{[NH_4OH]}=pK_b$$

$$\therefore\quad pH=pK_w-pK_b\quad[\because[NH_4^+]=[NH_4OH]=0.1]$$

In II Case :

$$pOH=pK_b+\log\frac{[NH_4^+]}{[NH_4OH]}=pK_b+\log 2$$

$$\therefore\quad pH=pK_w-pK_b-\log 2\quad[\because[NH_4^+]=0.1\times 2]$$

38. (d) $\underset{(s)}{BaF_2}\rightleftharpoons Ba^{2+}+2F^-$

$K_{sp}=[Ba^{2+}][F^-]^2$

$$\therefore\quad [F^-]=\sqrt{\frac{K_{sp}}{Ba^{2+}}}$$

Again $K_{sp}=2\times[Ba^{2+}][F^-]^2$

$[Ba^{2+}$ is increased two times]

$$[F^-]^2=\frac{K_{sp}}{2\times[Ba^{2+}]}$$

or $$[F^-]=\sqrt{\frac{K_{sp}}{2[Ba^{2+}]}}$$

39. (a) $NH_4OH+HCl\rightleftharpoons NH_4Cl+H_2O$

0.2 0.01 0s

0.19 0 0.01

$$\therefore\quad [NH_4^+]=0.30+0.01=0.31$$

$$[NH_4OH]=0.19$$

$$\therefore\quad pOH=4.74+\log\frac{0.31}{0.19}$$

$$=4.95$$

$$\therefore\quad pH=14-4.95=9.05$$

40. (b) $NH_4^+ + NaOH\longrightarrow NH_4OH+Na^+$

0.3 0.01 0 0

0.29 0 0.01

$$\therefore\quad [NH_4^+]=0.29$$

$$[NH_4OH]=0.2+0.01=0.21$$

$$\therefore\quad pOH=4.74+\log\frac{0.29}{0.21}$$

$$=4.880$$

$$\therefore\quad pH=14-4.880=9.12$$

41. (a) $HA\rightleftharpoons H^+ + A^-$

$$[H^+]=[A^-]=\alpha\cdot c=\frac{10}{100}\times 10^{-3}=10^{-4}$$

$$\therefore\quad pH=4$$

42. (a) Weak acid (CH_3COOH) and its conjugate base CH_3COO^- and this buffer is an acidic buffer.

43. (d) HCl is an acid.

44. (a) Stronger is the acid, weaker is its conjugate base.

45. (b) $K_w=[H_3O^-][OH^-]$. Also $[H_3O^+]=[OH^-]$

$$10^{-6}\times 10^{-6}=10^{-12}$$

46. (b) Q for $CaF_2=[Ca^{2+}][F^-]^2$

$$=\left[\frac{10^{-2}\times V}{2V}\right]\left[\frac{10^{-3}\times V}{2V}\right]^2=\frac{1}{8}\times 10^{-8}=1.2\times 10^{-9}$$

$Q>K_{sp}$

47. (a) $pH=-\log K_a+\log\dfrac{[\text{conjugate base}]}{[\text{acid}]}=10^{-4}+\log\dfrac{1}{1}=4$

$[\because\ pK_a+pK_a=14]$

48. (c) $HX\rightleftharpoons H^+ + X^-$

$$K_a=10^{-4}=\frac{[H^+][X^-]}{[HX]}\qquad\text{...(i)}$$

$HX+NaOH\rightleftharpoons NaX+H_2O$

$$K_{eq} = \frac{[Na^+][X^-][H_2O]}{[HX][Na^+][OH^-]} = \frac{[X^-][H_2O]}{[HX][OH^-]} \quad ...(ii)$$

By Eqns. (i) and (ii)

$$\frac{K_{eq}}{K_a} = \frac{1}{K_w} \quad \therefore \quad K_{eq} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

49. (d) Phenolphthalein is good indicator for strong alkali titrations.

50. (d) $\underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{C-base}}{Cl^-}$

51. (c) Calcium oxalate is weaker base.

52. (d) $CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

53. (a) Q for $AgCl = [Ag^+][Cl^-] = \left[\frac{10^{-4}\times V}{2V}\right]\left[\frac{10^{-4}\times V}{2V}\right]$

$$= 2.5\times10^{-9}$$

$\because$ $Q > K_{sp}$, precipitation will occur.

54. (c) $K_{eq.} = \frac{[H^+][OH^-]}{[H_2O]}$

for $\underset{1-\alpha}{H_2O} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{OH^-}$

$\therefore$ $[H^+] = c\alpha$ and $c_{H_2O} = \frac{1000}{18} = 55.6$

$$K_{eq.} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} \quad (1-\alpha = 1)$$

$\therefore$ $$K_{eq.} = \frac{(55.6\times1.9\times10^{-9})^2}{55.6} = 2\times10^{-16}$$

55. (b) Both $FeCl_3$ and $AlCl_3$ will furnish $3OH^-$ ions and $Fe(OH)_3$ is relatively stronger base than others.

56. (a) HOCl > HOBr > HOI due to more electronegative nature of halogen.

57. (c) $HF \rightleftharpoons H^+ + F^-$

$pK_a + pK_b = 14$

$pK_a + 10.83 = 14$

$\therefore$ $pK_a = 3.17$

$K_a = 6.76\times10^{-4}$

58. (d) K_{sp} of $A_2X_3 = 2^2\cdot(S)^2\times3^3\times S^3$

$$= 108(S)^5 = 108y^5$$

59. (d) The solubility of alkaline earth metal hydroxides increases down the gp. more is solubility, more is K_{sp}.

60. (d) $HA \longrightarrow H^+ + A^-$

$HB \rightleftharpoons H^+ + B^-$

61. (d) F is more electronegative than H and thus it reduces electron pair donation nature in NF_3.

62. (a) $Al_2O_3 + 2NaOH(aq.) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4$

63. (a) $[H^+] = [HCl]$ or mole of HCl of pH = 3 in 1 litre is 10^{-3} = 0.001

$[H^+] = [HCl]$ or mole of HCl of pH = 2 in 1 litre is 10^{-2} = 0.01

$\therefore$ Mole of HCl to be added in HCl of pH = 3 are 0.01 − 0.001 = 0.009

64. (b) AgCl forms complex with NH_3 and thus more soluble. Also solubility of a salt decreases in presence of common ion.

65. (a) $\underset{C}{BOH} \rightleftharpoons \underset{0}{B^+} + \underset{0}{OH^-}$

$\underset{C(1-\alpha)}{} \quad \underset{C\alpha}{} \quad \underset{C\alpha}{}$

$[OH^-] = C\alpha = 10^{-2}$

[For BOH, pH = 12 $\therefore$ $[OH^-] = 10^{-2}$]

$\therefore$ $$\alpha = \frac{10^{-2}}{0.1} = 10^{-1} = 0.1$$

$\therefore$ Total number of particles present are $(1-\alpha+\alpha+\alpha) = 1+\alpha = 1.1$

Now $\pi = CST(1+\alpha)$

$= 0.1\times0.0821\times300\times1.1$

$= 2.71$ atm

66. (c) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

meq. of $C_2O_4^{2-}$ = meq. of $KMnO_4$

$M\times2\times300 = 0.001\times5\times6$

$\therefore$ $M_{C_2O_4^{2-}} = 5\times10^{-5}$

For $CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 5\times10^{-5}\times5\times10^{-5}$

$= 25\times10^{-10}$

67. (b) $[Cl^-]$ in mixture = $\underset{\text{from NaCl}}{0.05} + \underset{\text{from } BaCl_2}{2\times0.05} = 0.15\,M$

For $AgCl \rightleftharpoons Ag^+ + Cl^-$

$K_{sp} = [Ag^+][Cl^-] = S\times0.15 = 1.0\times10^{-10}$

$S = 6.6\times10^{-10}$

68. (d) After mixing the two $[N_3H] = \frac{100\times0.5}{500} = 10^{-1}$

$$[HOCN] = \frac{400\times0.1}{500} = 8\times10^{-2}$$

$N_3H \rightleftharpoons N_3^- + H^+$

at eq. $\underset{(0.1-x)}{} \quad \underset{x}{} \quad \underset{x+y}{}$

$$K_{N_3H} = \frac{x(x+y)}{(0.1-x)}$$

$HOCN \rightleftharpoons OCN^- + H^+$

$\underset{(0.08-y)}{} \quad \underset{y}{} \quad \underset{x+y}{}$

$$K_{HOCN} = \frac{y(x+y)}{0.08-y}$$

[Both are weak, thus $0.1-x \approx 0.1$ $0.08-y \approx 0.08$]

$\therefore$ $$\frac{K_{N_3H}}{K_{HOCN}} = \frac{x(x+y)/0.1}{y(x+y)/0.08}$$

or $$\frac{3.6\times10^{-4}}{8\times10^{-4}} = \frac{0.08x}{0.1y}$$

or $\frac{x}{y} = \frac{3.6\times10^{-5}}{6.4\times10^{-5}} = 0.5625$

Also, $8\times10^{-4} = \frac{y(x+y)}{0.08} = \frac{y(0.5625y+y)}{0.08}$

or $1.5625\ y^2 = 8\times10^{-4}\times0.08$

or $y = \sqrt{\frac{8\times10^{-4}\times0.08}{1.5625}} = 6.4\times10^{-3} = [OCN^-]$

$\therefore$ $x = 0.5625\times6.4\times10^{-3} = 3.6\times10^{-3} = [N_3^-]$

$H^+ = 6.4\times10^{-3} + 3.6\times10^{-3} = 10\times10^{-3} = 10^{-2}$

$\therefore$ pH = 2

69. (a) Given $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

$$K = \frac{[NH_4^+][NH_2^-]}{[NH_3]^2\,(l)}$$

or $3.46\times10^{-27} = \frac{[NH_4^+][NH_2^-]}{(58.82)^2}$

$$[NH_3] = \frac{1000}{17} = 58.82\ M$$

$\therefore$ $[NH_4^+] = [NH_2^-] = 3.46\times10^{-12}\ M$

$= 6.023\times10^{23}\times3.46\times10^{-12}$

$= 2.08\times10^{12}$ anions / litre

$= 2.08\times10^{9}$ anions / mL

70. (c) K_{sp} of AgCl $= 1\times10^{-10} = S^2$

$\therefore$ $S = 10^{-5}$ mole/l $= 10^{-5}\times143.5$ g/l

$= 1.435\times10^{-3}$ g/l $= 1.435$ mg/l

$\because$ 1.435 g of AgCl requires 1 litre

$\therefore$ 4.305 g of AgCl requires $\frac{1\times4.305}{1.435} = 3$ litre

71. (c) $KH_2PO_4 + H_3PO_4$, $KH_2PO_4 + K_2HPO_4$ and $K_2HPO_4 + K_3PO_4$

72. (d) $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$,

Addition of Cl^- shows a decrease in $[Ag^+]$.

or $[Ag^+] \propto \frac{1}{[Cl^-]}$ (K_{sp} is constant)

73. (d) $PbSO_4$ is insoluble. H_2S precipitates both CuS and PbS.

74. (a) AgF is soluble in water.

75. (c) K_2SO_4 and $(NH_4)_2CO_3$ both are water soluble

$K_2CO_3 + (NH_4)_2SO_4 \longrightarrow K_2SO_4 + (NH_4)_2CO_3$

76. (a) pH of 0.1 M HCl + 0.1 M CH_3COOH is lowest as it has strong acid and CH_3COOH

77. (a) $[H^+] = 10^{-4}$

$[H^+] = 10^{-1}$

10^3 times more acidic than $[H^+] = 10^{-4}$

78. (a) $[H^+] = 3\times10^{-3}$

$\therefore$ pH $= 3 - \log 3$

pOH $= 14 - 3 + \log 3 = 11 + \log 3$

79. (b) meq. of dil solution = meq. of conc. solution

$N\times1000 = 10\times10^{-4}$

$\therefore$ $N = \frac{10^{-3}}{1000} = 10^{-6}$

$H^+ \approx 10^{-6} + 10^{-7} = 1.01\times10^{-7}$

$\therefore$ pH > 6

80. (a) meq. of HCl $= 10\times0.1 = 1$

meq. of $Sr(OH)_2 = 10\times0.01\times2 = 0.2$

meq. of HCl left $= 1 - 0.2 = 0.8$

$\therefore$ $N_{HCl} = \frac{0.8}{10+10} = \frac{0.8}{20} = 0.04$

$\therefore$ $pH = -\log\frac{4}{100} = -\log 4 + \log 100$

$= 2 - 0.6020 = 1.3979$

81. (d) Lesser amount of energy is required for dissociation of acetic acid or acetic acid is stronger than HCN.

82. (a) $\alpha = \sqrt{\frac{K_a}{C}}$

$\therefore$ $\alpha_1 = \sqrt{\frac{K_a}{0.1}}$

$\alpha_2 = \sqrt{\frac{K_a}{0.001}}$

or $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{0.001}{0.1}} = 10^{-1} = 0.1$

83. (d) $H_2O + H^+ \longrightarrow H_3O^+$

$H_3O^+ + H_2O \longrightarrow H_5O_2^+$

$H_2O + OH^- \longrightarrow H_3O_2^-$

84. (c) $h = \sqrt{\frac{k_w}{k_a\cdot k_b}} = \sqrt{\frac{10^{-14}}{10^{-5}\times10^{-4}}} = \sqrt{10^{-5}}$

$= 3.16\times10^{-3}$

$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

$= \frac{14}{2} + \frac{4}{2} - \frac{5}{2}$

$= 9 - 2.5 = 6.5$

85. (a) Solubility of AgCl in NaCl is lower than H_2O. Also other orders are derived by Debye-Huckel limiting law.

86. (a) $AgNO_3 + KCN \longrightarrow AgCN\downarrow + KNO_3$

$AgCN + KCN \longrightarrow KAg(CN)_2$

or $\underset{0.03}{\underset{0.0}{AgNO_3}} + \underset{0.1}{\underset{0.04}{2KCN}} \longrightarrow \underset{0}{\underset{0.03}{K[Ag(CN)_2]}} + \underset{0}{\underset{0.03}{KNO_3}}$

For $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$

$\therefore$ $K_C = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} = \frac{[Ag^+][0.04]^2}{[0.03]}$

$= 4\times10^{-19}$

$[Ag^+] = 7.5\times10^{-18}$ M

87. (b) $$2.303 \log \frac{K_{sp_2}}{K_{sp1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$2.303 \log \frac{1.39\times10^{-8}}{7.47\times10^{-9}} = \frac{\Delta H}{2}\times\left[\frac{298-288}{288\times298}\right]$$

$$\Delta H = 10.66 \text{ k cal mol}^{-1}$$

88. (a) $$\alpha = \frac{\wedge_m}{\wedge_\infty} = \frac{60}{400} = \frac{3}{20} = 0.15$$

Now $$[H^+] = C\alpha = 0.1\times\frac{3}{20}$$

$\therefore$ $$pH = -\log H^+$$

$$= -\log\frac{3}{200} = -0.4771 + 2.3010$$

$$= 1.8239$$

Also $$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.1\times(0.15)^2}{(1-0.15)}$$

$$= 2.65\times10^{-3}$$

89. (c) $$HA \rightleftharpoons H^+ + A^-$$

Acid Conjugate base

$$pKa_{HA} + pKb_{A^-} = 14$$

$\therefore$ $$pKa_{HA} = \frac{14}{2} = 7 \quad (\because\ pKa_{HA} + pKb_{A^-})$$

$\therefore$ $$K_a = 10^{-7}$$

$$[H^+] = \sqrt{Ka\times C} = \sqrt{10^{-7}\times0.001} = 10^{-5}$$

$\therefore$ $$pH = 5$$

90. (b) Maximum buffer capacity = $pKa \pm 1$

This is possible when $\frac{[\text{conjugate base}]}{[\text{acid}]} = 1$

Thus milli mole of acetic acid taken = 500 × 1 = 500

milli mole of acetic acid to be neutralised = 250

$\because$ milli mole of KOH required = 250

$$\frac{w}{56}\times1000 = 250$$

$$w_{KOH} = 14\text{g}$$

91. (b) Let solubility of HCOOAg be a mol/litre

$$H^+ + HCOO^- \rightleftharpoons HCOOH$$

10^{3-} a a

10^{3-} — —

(buffer)

Since HCOOH is a weak acid and has low degree of dissociation. Also its dissociation is suppressed in presence of H^+. Thus,

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

or $$Ka = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$[HCOO^-] = \frac{K_a\times[HCOOH]}{[H^+]} = \frac{10^{-5}\times a}{10^{-3}}$$

$$= a\times10^{-2}$$

Also for HCOOAg :

$$HCOOAg(s) \rightleftharpoons HCOO^-(aq.) + Ag^+(aq.)$$

$$K_{SP} = S^2 = (10^{-2})^2 = 10^{-4}$$

Also $$K_{SP} = [HCOO^-][Ag^+]$$

$$10^{-4} = a\times10^{-2}\times a$$

$\therefore$ $$a = 10^{-1} = 0.1M$$

92. (a) Lesser is Ka, weaker is acid (HPO_4^{2-}), stronger is its conjugate base (PO_4^{3-})

93. (c) $$[CaA_2] = \frac{0.125}{0.5} = 0.25\text{ M}$$

$$[A^-] = 2\times0.25 = 0.50M$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$[OH^-] = C\cdot h = C\sqrt{\frac{K_H}{C}}$$

$$= \sqrt{\frac{K_w\cdot C}{K_a}} = \sqrt{\frac{10^{-14}\times0.5}{8\times10^{-4}}}$$

$$= \sqrt{6.25\times10^{-12}} = 2.5\times10^{-6}$$

$$pOH = 5.60$$

or $$pH = 14 - 5.60 = 8.40$$

94. (b) $$E_{Cell} = E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{2}\log[Ag^+]_{LHS} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{1}\log[Ag^+]_{RHS}$$

$\because$ at equilibrium $E_{Cell} = 0$ and $E^\circ_{OP_{Ag/Ag^+}} = -E^\circ_{RP_{Ag^+/Ag}}$

$$0 = \frac{0.059}{2}\log\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}$$

or $$\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}} = 1 \quad \text{or} \quad [Ag^+]_{RHS} = [Ag^+]_{LHS}$$

At LHS :

$$[Ag^+]^2[CO_3^{2-}] = K_{SP}\ Ag_2CO_3 = 8\times10^{-12}$$

$\therefore$ $$[Ag^+] = \sqrt{\frac{8\times10^{-12}}{[CO_3^{2-}]}} = \frac{2\sqrt{2}\times10^{-6}}{\sqrt{[CO_3^{2-}]}}$$

At RHS : $[Ag^+][Br^-] = K_{SP\ AgBr} = 4\times10^{-13}$

$\therefore$ $$[Ag^+] = \frac{4\times10^{-13}}{[Br^-]}$$

$\therefore$ $$\frac{4\times10^{-13}}{[Br^-]} = \frac{2\sqrt{2}\times10^{-6}}{\sqrt{[CO_3^{2-}]}}$$

or $$\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}} = \sqrt{2}\times10^{-7}$$

95. (d) $$Ag_2C_2O_4(s) \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{C_2O_4^{2-}}$$

Given $[Ag^+] = 2s = 2.2\times10^{-4}$

$$s = 1.1\times10^{-4}$$

$$K_{sp} = (2s)^2\times s = 4s^3$$

$$= 4(1.1\times10^{-4})^3 = 5.3\times10^{-12}$$

PREVIOUS YEARS PROBLEMS

1. The correct acidic strength order is : **(IIT 2001)**
   (a) $HClO < HClO_2 < HClO_3 < HClO_4$
   (b) $HClO_4 < HClO_3 < HClO_2 < HClO$
   (c) $HClO < HClO_4 < HClO_3 < HClO_2$
   (d) $HClO_4 < HClO_2 < HClO_3 < HClO$
2. For a sparingly soluble salt A_pB_q, the relationship of its solubility product L_s with its solubility (S) is : **(IIT 2001)**
   (a) $L_S = S^{p+q} \cdot p^p \cdot q^q$ (b) $L_S = S^{p+q} \cdot p^q \cdot q^p$
   (c) $L_S = S^{pq} \cdot p^p \cdot q^q$ (d) $L_S = S^{pq} \cdot (pq)^{p+q}$
3. The correct order of acidic strength is : **(IIT 2002)**
   (a) $CaO < CuO < H_2O < CO_2$
   (b) $H_2O < CuO < CaO < CO_2$
   (c) $CaO < H_2O < CuO < CO_2$
   (d) $H_2O < CO_2 < CaO < CuO$
4. H_3BO_3 is : **(IIT 2003)**
   (a) monobasic and weak Lewis acid
   (b) monobasic and weak Bronsted acid
   (c) monobasic and strong Lewis acid
   (d) tribasic and weak Bronsted acid
5. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-45} respectively which one will precipitate first ? **(IIT 2003)**
   (a) FeS (b) MgS
   (c) HgS (d) ZnS
6. A weak-acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is : **(IIT 2004)**
   (a) 0.0001% (b) 0.01%
   (c) 0.1% (d) 0.15%
7. 0.1 mole of CH_3NH_2 ($K_b = 5\times10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. The $[H^+]$ in solution is : **(IIT 2005)**
   (a) 8×10^{-2} M (b) 8×10^{-11} M
   (c) 1.6×10^{-11} M (d) 8×10^{-5} M
8. The species present in solution when CO_2 is dissolved in water : **(IIT 2006)**
   (a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
   (b) H_2CO_3, CO_3^{2-}
   (c) CO_3^{2-}, HCO_3^-
   (d) CO_2, H_2CO_3
9. 2.5 mL of $\frac{2M}{5}$ weak monoacidic base ($K_b = 1\times10^{-12}$ at 25°C) is titrated with $\frac{2M}{15}$ HCl in water at 25°C. The concentration of H^+ at equivalence point is : **(IIT 2008)**
   (a) 3.7×10^{-13} M (b) 3.2×10^{7} M
   (c) 3.2×10^{-2} M (d) 2.7×10^{-2} M
10. Solubility product K_{sp} of salt of type MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubilities of these salts in mol dm^{-3} at temperature T are in the order : **(IIT 2008)**
    (a) $MX > MX_2 > M_3X$ (b) $M_3X < MX_2 > MX$
    (c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$
11. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01M solution of its sodium salt is : **(IIT 2009)**
    (a) 10 (b) 8
    (c) 12 (d) 6
12. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[JEE (Main) 2013]**
    (a) 2.0 L (b) 9.0 L
    (c) 0.1 L (d) 0.9 L
13. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is : **[JEE (Advanced) I 2013]**
    (a) 1.1×10^{-11} (b) 1.1×10^{-10}
    (c) 1.1×10^{-12} (d) 1.1×10^{-9}
14. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is $1/100^{th}$ of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is : **[JEE (Advanced) II 2013]**
    (a) 1×10^{-4} (b) 1×10^{-5}
    (c) 1×10^{-6} (d) 1×10^{-3}
15. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is : **[JEE (Main) 2017]**
    (a) 7.2 (b) 6.9
    (c) 7.0 (d) 1.0
16. In the following reactions, ZnO is respectively acting as a/an : **[JEE (Main) 2017]**
    (1) $ZnO + Na_2O \longrightarrow Na_2ZnO_2$
    (2) $ZnO + CO_2 \longrightarrow ZnCO_3$
    (a) base and acid (b) base and base
    (c) acid and acid (d) acid and base

SOLUTIONS (Previous Years Problems)

1. (a) Higher is the oxidation number of central non-metal, more is acidic nature.

2. (a) $A_pB_q \rightleftharpoons pA^{q+} + qB^{p-}$

$pS \quad qS$

$\therefore \quad K_{sp} = (pS)^p (qS)^q$

$= p^p \cdot q^q \cdot (S)^{p+q}$

3. (a) CaO is strongest base, CO_2 is acidic. Also, CuO is strong base than H_2O.

4. (a) $H_3BO_3 + OH^- \longrightarrow B(OH)_4^- + H^+$

Accepts lone pair of electron thus Lewis acid but weak.

5. (c) K_{sp} of HgS is minimum and thus possesses less solubility. Note all salts are AB type.

6. (b) $h = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}}$

$= \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = \sqrt{10^{-8}}$

$= 10^{-4}$

or $h = 10^{-4} \times 100 = 10^{-2} = 0.01\%$

7. (b) $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+Cl$

0.1	0.08	0
0.02	0	0.08

This is basic buffer solution.

$[OH^-] = K_b \times \frac{[\text{base}]}{[\text{conjugate acid}]}$

$= 5 \times 10^{-4} \times \frac{0.02}{0.08} = 1.25 \times 10^{-4}$

$\therefore \quad [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{1.25 \times 10^{-4}} = 8 \times 10^{-11} M$

8. (a) All the following equilibrium exist together

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

9. (d) $BOH + HCl \longrightarrow BCl + H_2O$

Meq. of BOH = Meq. of HCl = Meq. of BCl

$2.5 \times \frac{2}{5} \times 1 = V \times \frac{2}{15} \times 1 = 1$

$\therefore \quad V = 7.5\,mL$

$\therefore$ Total volume = 2.5 + 7.5 = 10 mL

Thus, $[BCl] = \frac{1}{10} = 0.1$

Now for hydrolysis of BCl; $K_H = \frac{Ch^2}{1-h} = \frac{K_w}{K_b}$

$\therefore \quad h = 0.27$

or $[H^+] = c \cdot h = 0.27 \times 0.1 = 2.7 \times 10^{-2}\ M$

10. (d) Solubility of MX, MX_2 and M_3X are respectively

$S = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}\ M$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.2 \times 10^{-14}}{4}} = 2 \times 10^{-5}\ M$

$S = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{2.7 \times 10^{-15}}{27}} = 1 \times 10^{-4}\ M$

11. (b) $C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$

$\therefore \quad [OH^-] = ch = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \cdot c}{K_a}}$

$= \sqrt{\frac{10^{-14} \times 0.01}{1 \times 10^{-4}}} = 10^{-6}$

$\therefore \quad [H^+] = 10^{-8}$ or pH = 8

12. (b) meq. of I HCl = meq of II HCl

$1 \times 10^{-1} = V \times 10^{-2}$

$\therefore \quad V = 10$ litre

$\therefore$ volume of water added = (10 – 1) = 9L

13. (b) Ionic product of $Ag_2CrO_4 = [Ag^+]^2[CrO_4^{-2}]$

$= (2S + 0.1)^2 \times S = 1.1 \times 10^{-12}$

neglecting S as compared to 0.1

$S = 1.1 \times 10^{-10}$

14. (a) Rate = K[Ester] $[H^+]$

For strong acid $[H^+] = 1\ M$

For weak acid $[H^+] = \sqrt{K_a.C}$

$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[H^+]_1 \text{ for strong acid}}{[H^+]_2 \text{ for weak acid}}$

$\frac{1}{1/100} = \frac{1}{\sqrt{K_a \times 1}}$ ($C = 1M$ for weak acid)

$K_a = 10^{-4}\ M$

15. (b) $pH = 7 + \frac{1}{2}(pK_a - pK_b)$

$= 7 + \frac{1}{2}(3.2 - 3.4)$

$= 6.9$

16. (d) In (a), Na_2O is basic oxide and thus ZnO acts as acidic oxide.

In (b), CO_2 is acidic oxide and thus ZnO acts as basic oxide.

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which one is not acidic salts ?
   (a) Na_2HPO_4 (b) NaH_2PO_2
   (c) Na_2HPO_3 (d) NaH_2PO_4
2. The resulting mixtures which act buffer are :
   (a) 10 mL 0.1 M HCl + 20 mL 0.1 M NaCN
   (b) 10 mL 0.1 M NaOH + 20 mL 0.1 M NH_4CN
   (c) 10 mL 0.1 M NH_4OH + 20 mL 0.1 M CH_3COONH_4
   (d) 10 mL 0.1 M CH_3COOH + 20 mL 0.1 M CH_3COONH_4
3. Which one is correct for the saturated solution of $Ca_3(PO_4)_2$ salt if its K_{sp} is 2.05×10^{-33} ?
   (a) Solubility of Ca_3PO_4 is $1.63\times10^{-6}M$
   (b) $[Ca^{2+}]_{eq.} = 4.9\times10^{-6}\ M$
   (c) $[PO_4^{3-}]_{eq.} = 3.26\times10^{-6}\ M$
   (d) $[Ca_3PO_4]_{eq.}$ = Zero
4. Which of the following are correct ?
   (a) Aniline is a weak-acid in acetic acid
   (b) Ammonium salts act as acid in liquid NH_3
   (c) The reaction CsF + LiI $\longrightarrow$ CsI + LiF is acid-base reaction
   (d) HCl acts as base in HF.
5. Which of the following acid-base reactions are possible?
   (a) $PH_3 + NH_4^+ \longrightarrow PH_4^+ + NH_3$
   (b) $NH_3 + PH_4^+ \longrightarrow NH_4^+ + PH_3$
   (c) $(CH_3)_3P + NH_4^+ \longrightarrow (CH_3)_3P^+H + NH_3$
   (d) $(CH_3)_3N + PH_4^+ \longrightarrow (CH_3)_3NH^+ + PH_3$
6. Select the correct statements :
   (a) All Bronsted bases are Lewis bases
   (b) All Bronsted acids are Lewis acids
   (c) All Arrhenius acids are Bronsted acids
   (d) All Arrhenius bases are Bronsted bases
7. The correct acidic orders are :
   (a) $Li^+ > Na^+ > K^+$ (b) $Li^+ < Be^{2+} < B^{3+}$
   (c) $Fe^{3+} > Fe^{2+} > Fe^+$ (d) $NF_3 < NCl_3 < NBr_3$
8. Select the correct statements :
   (a) HCN is weak acid
   (b) Reaction of $HCl_{(g)}$ and $NH_{3(l)}$ is Arrhenius acid-base reaction
   (c) Pure H_2SO_4 and $HClO_4$ do not conduct current but in presence of each other they are good conductor
   (d) Mn_2O_7 is acidic oxide.
9. The oxo acids of P_2O_5 are :
   (a) H_3PO_4 (b) $H_4P_2O_7$
   (c) HPO_3 (d) H_3PO_3
10. Which of the following statement(s) is (are) correct?
    (a) pH of $1.0\times10^{-18}\ M$ solution of HCl is 8
    (b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
    (c) Autoprotolysis constant of water increases with temperature
    (d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = (1 / 2) pK_a
11. A buffer solution can be prepared from a mixture of :
    (a) sodium acetate and acetic acid in water
    (b) sodium acetate and hydrochloric acid in water
    (c) ammonia and ammonium chloride in water
    (d) ammonia and sodium hydroxide in water
12. In a buffer solution of NaH_2PO_4 and Na_2HPO_4 :
    (a) NaH_2PO_4 is acid and Na_2HPO_4 is salt
    (b) pH = pK_2 of $H_3PO_4 + \log\dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]}$
    (c) Na_2HPO_4 is acid and NaH_2PO_4 is salt
    (d) pH = pK_3 of $H_3PO_4 + \log\dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]}$
13. Select the correct statments :
    (a) The K_{a_1} values for H_2SO_3 is 1.3×10^{-2}
    (b) H_2SO_3 exist in only minute concentration in aqueous solution of SO_2
    (c) The K_{a_1}, values of H_2SO_3 refers for the process $H_2SO_3 \rightleftharpoons H^+ + SO_3^{2-}$
    (d) The K_a, value of H_2SO_3 refers for the process $\underset{(g)}{SO_2} + \underset{(l)}{H_2O} \rightleftharpoons \underset{(aq.)}{H^+} + \underset{(aq.)}{HSO_3^-}$
14. Select the correct statements :
    (a) HF is a weak acid
    (b) The strength of weak acids increases with dilution ($HA \rightleftharpoons H^+ + A^-$)
    (c) The strength of HF increases with concentration ($HF \rightleftharpoons H^+ + F^-$)
    (d) The F^- furnished by HF reacts with HF to give HF_2^- and thereby shifting the reaction to right
15. An aqueous solution of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pairs of solution which form a buffer upon mixing is/are : **(IIT 2010)**
    (a) HNO_3 and CH_3COOH
    (b) KOH and CH_3COONa
    (c) HNO_3 and CH_3COONa
    (d) CH_3COOH and CH_3COONa

16. The correct statement(s) for orthoboric acid is/are : **[JEE (Advanced) 2014]**

(a) It behaves as a weak acid in water due to self ionization.

(b) Acidity of its aqueous solution increases upon addition of ethylene glycol.

(c) It has a three dimensional structure due to hydrogen bonding.

(d) It is a weak electrolyte in water.

SOLUTIONS (More Than One Answer Correct)

1. (b,c) H_3PO_2 is monobasic and H_3PO_3 is dibasic.

2. (a,b,c,d)

	HCl	+ NaCN	⟶ NaCl	+ HCN
	10×0.1	20×0.1		
	$=1$	$=2$	0	0
	0	1	1	1

$$[HCN]=\frac{1}{30} \text{ and } [NaCN]=\frac{1}{30}$$

3. (a,b,c,d) $Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

$3s \quad 2s$

$$\therefore \quad K_{sp} = 2.05\times10^{-33} = 108s^5$$

$$\therefore \quad s = 1.63\times10^{-6}\,M$$

$$\therefore \quad [Ca^{2+}] = 3\times1.63\times10^{-6} = 4.9\times10^{-6}\,M$$

$$[PO_4^{3-}] = 2\times1.63\times10^{-6} = 3.26\times10^{-6}\,M$$

$[Ca_3PO_4]_{eq.} = 0$, because all the salt is in ionic state.

4. (b,c,d) Aniline is strong base in acetic acid. $NH_{3(l)}$ ionises as :

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-;$$

$$\underset{\text{Soft-hard}}{CsF} + \underset{\text{Hard-soft}}{LiI} \longrightarrow \underset{\text{Soft-soft}}{CsI} + \underset{\text{Hard-hard}}{LiF}$$

This reaction is an interesting example of soft acid-hard base and hard acid-soft base combination

$$HF + HCl \longrightarrow F^- + H_2Cl^+$$

5. (b,c) Proton affinity of NH_3 is greater than PH_3. Proton affinity of $(CH_3)_3P$ is greater than NH_3.

6. (a,c) NaOH is Arrhenius base but not Bronsted base. HCl is Bronsted acid but not Lewis acid.

7. (a,b,c,d) Higher is effective nuclear charge more is acidic nature of Lewis acid cations. The increasing electronegativity from I to F in NX_3 give rise to lesser tendency for N to donate electron pair as it acquires more +ve charge on N-atom.

8. (a,b,c,d) Arrhenius concept is in aqueous medium

$$HClO_4 + H_2SO_4 \longrightarrow H_3SO_4^+ + ClO_4^-$$

$$Mn_2O_7 + H_2O \longrightarrow \underset{\text{Acid}}{2HMnO_4}$$

9. (a,b,c) Each has P^{5+} state.

10. (b,c) HCl is acid; for (d) $pH = pK_a$

11. (a,b,c) For (b) $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ (more, less)

12. (a,b) HPO_4^{2-} is conjugate base of $H_2PO_4^-$ and thus.

13. (a,b,d) Choice (b) is correct explanation for H_2SO_3.

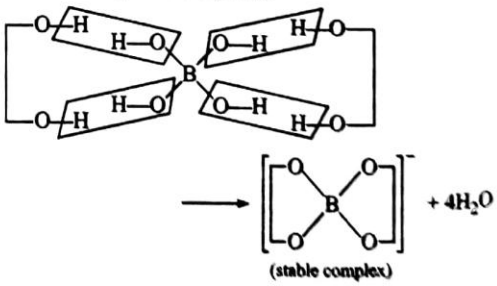
14. (a,b,c,d) All are facts. Choice (d) is correct explanation for HF in aqueous medium.

15. (c,d) CH_3COONa (in more amount) than HNO_3 forms a buffer mixture of $(CH_3COONa + CH_3COOH)$ in solution.

16. (b,d) Orthoboric acid H_3BO_3 is a weak monobasic Lewis acid as it accepts OH^- ions

$$H_3BO_3 + H{-}OH \rightleftharpoons B(OH)_4^- + H^+$$

The equilibrium is shifted in forward direction by the addition of ethylene glycol (a syndiol) which forms a stable complex with $B(OH)_4^-$.



$\longrightarrow$ $+ 4H_2O$

(stable complex)

It has a planar sheet like structure due to sp^2 hybridization of B atom as well as hydrogen bonding.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Solubility of a substance in its saturated solution can be derived from its K_{sp} values. Higher is the K_{sp} for same type of compound more is the solubility. If S is the solubility in mol/litre then K_{sp} of a compound A_xB_y is expressed as

$$K_{sp} = x^x \cdot y^y [S]^{x+y}$$

Consider a compound $M(OH)_x$ having $= K_{sp} = 27 \times 10^{-12}$ and solubility in pure water is 10^{-3} mol litre^{-1}.

[1] The value of x is :
(a) 1 (b) 2
(c) 3 (d) 4

[2] The solubility (in M) of $M(OH)_x$ in 0.1 M NaOH solution is :
(a) 2.7×10^{-10} (b) 2.7×10^{-3}
(c) 2.7×10^{-8} (d) 2.7×10^{-4}

[3] The solubility (in M) of $M(OH)_x$ in 0.1 $Ca(OH)_2$ solution is :
(a) 6.46×10^{-4} (b) 2.7×10^{-8}
(c) 2.7×10^{-4} (d) 3.375×10^{-9}

[4] The solubility (in mole/litre) of $M(OH)_x$ in $0.1\,M(NO_3)_x$ solution is :
(a) 2.15×10^{-4} (b) 2.15×10^{-5}
(c) 2.15×10^{-6} (d) 2.15×10^{-7}

Comprehension 2: K_b of CH_3COO^- is 5.26×10^{-10}. Calculate for 0.01 N solution of sodium acetate.

[1] Hydrolysis constant of CH_3COO^- is :
(a) 5.26×10^{-10} (b) 5.26×10^{-11}
(c) 5.26×10^{-12} (d) 5.26×10^{-9}

[2] Degree of hydrolysis of CH_3COO^- is :
(a) 2.29×10^{-6} (b) 2.29×10^{-4}
(c) 2.29×10^{-3} (d) 2.29×10^{-5}

[3] pH of solution is :
(a) 8.56 (b) 5.44
(c) 8.36 (d) 9.56

Comprehension 3: Oxides of metals are usually basic and oxides of non metals are usually acidic. However some acidic oxides of metals and neutral oxides of non metals such as N_2O, NO, CO, H_2O are known.

[1] Which of the following oxide is acidic ?
(a) Cr_2O_3 (b) CrO_3
(c) MnO_2 (d) MnO

[2] In the reaction of CO with NaOH at high P and T to give sodium formate, CO acts as :
(a) acid (b) base
(c) neutral (d) amphoteric

[3] Number of OH gp present in H_3PO_2 are :
(a) 1 (b) 2
(c) 3 (d) none of these

Comprehension 4 : The dissolution of ammonia gas in water does not obey Henry's law. On dissolving, a major portion of ammonia, molecules unite with H_2O to form NH_4OH molecules. NH_4OH again dissociates into NH_4^+ and OH^- ions. In solution therefore, we have NH_3 molecules, NH_4OH molecules and NH_4^+ ions and the following equilibrium exist :

$NH_3(g)$ (pressure P and concentration C) initially $\rightleftharpoons$ $NH_3(l) + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Let C_1 mol/L of NH_3 pass in solution state a part of which on dissolution in water forms C_2 mol/L of NH_4OH. The solution contains C_3 mol/L of NH_4^+ ions.

[1] Total concentration of ammonia, which can be determined by volumetric analysis is equal to :
(a) $C_1 + C_2$ (b) $C_1 + C_2 + C_3$
(c) $C_1 + C_3$ (d) $C_2 + C_3$

[2] Concentration of undissociated ammonium hydroxide is :
(a) $C_1 + C_2$ (b) $C_2 - C_3$
(c) $C_1 + C_3$ (d) $C_1 - C_2$

[3] Degree of dissociation of ammonium hydroxide is :
(a) C_1 (b) C_3 / C_1
(c) C_3 / C (d) C_3 / C_2

[4] If p is the partial pressure of ammonia at equilibrium, then which of the following is constant? α is degree of dissociation of NH_3.
(a) $\frac{p}{C_1}$ (b) $\frac{p}{C}$
(c) $\frac{p}{C_2}$ (d) $\frac{p}{C_3}$

[5] The dissociation constant of NH_4OH can be given as :
(a) $K_b = \frac{(C_3)^2}{(C_2 - C_3)}$ (b) $K_b = \frac{(C_3)^2}{C_2}$
(c) $K_b = \frac{C_3}{(C_2 - C_1)}$ (d) $K_b = \frac{C_3}{C_1 - C_2}$

[6] The pH of solution can be given by :
(a) $pK_w + \log C_3$
(b) $pK_w - \frac{1}{2} pK_b + \frac{1}{2} \log C_2$
(c) $pK_a + \frac{1}{2} \log C_2 + \frac{1}{2} pK_b$
(d) either of these

Comprehension 5 : The pH of pure water at 25°C and 60°C are 7 and 6.5 respectively. HCl gas is passed through water at 25°C till the resulting 1 litre solution acquires a pH of 3. Now 4×10^{-3} mole of NaCN are added into this solution. Also a fresh 0.1 *M*HCN solution has pH 5.1936. Now in the one part of solution obtained after addition of NaCN, one millimole of NaOH are added and in the second part of this solution 0.5 millimole of HCl are added.

[1] The heat of formation of water from H^+ and OH^- is :
(a) 13.06 kcal (b) – 13.06 kcal
(c) 16.32 kcal (d) – 16.32 kcal

[2] The volume of HCl passed through the solution at 25°C and 1 atm is :
(a) 24.46 mL (b) 2.446 mL
(c) 244.6 mL (d) 0.2446 mL

[3] The dissociation constant of HCN is :
(a) 4.1×10^{-10} (b) 4.1×10^{-6}
(c) 4.1×10^{-3} (d) 4.1×10^{-8}

[4] The degree of dissociation of 0.1 *M* HCN solution is :
(a) 6.4×10^{-5} (b) 6.4×10^{-3}
(c) 6.4×10^{-2} (d) 6.4×10^{-6}

[5] The pH of resulting solution after addition of NaCN is :
(a) 9.86 (b) 8.86
(c) 6.86 (d) 5.86

[6] The pH of resulting solution after addition of 0.1 millimole of HCl is :
(a) 9.68 (b) 9.39
(c) 9.21 (d) 9.98

[7] The pH of resulting solution after addition of 0.05 millimole of NaOH is :
(a) 10.23 (b) 11.23
(c) 9.23 (d) 8.23

SOLUTIONS

Comprehension 1

[1] (c) $M(OH)_x \rightleftharpoons \underset{S}{M^{+x}} + \underset{x_s}{xOH^-}$

$K_{sp} = x^x \cdot (S)^{1+x} = 27\times10^{-12}$

$\therefore \quad x = 3$

[2] (c) $K_{sp} = [M^{+x}][OH^-]^x = [M^{+3}][OH^-]^3$

$27\times10^{-12} = S\times[3S+0.1]^3 \; [3S <<< 0.1]$

$\therefore \quad S = \dfrac{27\times10^{-12}}{(0.1)^3} = \mathbf{2.7\times10^{-8}}$

[3] (d) $K_{sp} = [M^{+3}][OH^-]^3$

$27\times10^{-12} = S\times[3S+0.2]^3 \; [3S <<< 0.2]$

$S = \dfrac{27\times10^{-12}}{(0.2)^3} = \mathbf{3.375\times10^{-9}}$

[4] (a) $K_{sp} = [M^{+3}][OH^-]^3$

$= [S+0.1][3S]^3 \; [S <<< 0.1]$

$27S^3 = \dfrac{27\times10^{-12}}{0.1}$

$S = 2.15\times10^{-4}$

Comprehension 2

For $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

K_b for $CH_3COO^- = 5.26\times10^{-10}$

$\therefore \quad K_a$ for $CH_3COOH = 1.9\times10^{-5}$

[1] (a) $K_H = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{1.9\times10^{-5}} = \mathbf{5.26\times10^{-10}}$

[2] (b) $h = \sqrt{\left(\dfrac{K_H}{C}\right)} = \sqrt{\left(\dfrac{5.26\times10^{-10}}{0.01}\right)} = \mathbf{2.29\times10^{-4}}$

[3] (c) $[OH^-]$ from NaOH, a strong alkali $= Ch$

$= 0.01\times2.29\times10^{-4}$

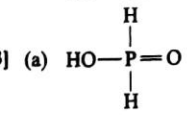
$= 2.29\times10^{-6}\ M$

$\therefore \quad pOH = 5.64 \quad \therefore \; pH = \mathbf{8.36}$

Comprehension 3

[1] (b) Some metal oxides in their highest oxidation state are acidic.

[2] (a) $\underset{\text{acid}}{CO} + \underset{\text{base}}{NaOH} \xrightarrow{P.T.} \underset{\text{(salt)}}{HCOONa}$

[3] (a) 

Comprehension 4

[1] (b) The intermediate solution of acid will react with all the NH_3 present in solution.

[2] (b) NH_4OH left undissociated $= C_2 - C_3$.

[3] (d) $\alpha = \dfrac{\text{Mole of } NH_4OH \text{ dissociated}}{\text{Total mole}} = \dfrac{C_3}{C_2}$.

[4] (a) Acc. to Henry's law $a \propto P_{NH_3}$

Where a is the amount of gas dissolved per unit volume of solvent.

or $C_{NH_3} \propto P_{NH_3}$

$\therefore \quad K = \dfrac{P_{NH_3}}{C_{NH_3}} = \dfrac{P}{C_1}$

[5] (a) $\underset{\substack{C_2\\(C_2-C_3)}}{NH_4OH} \rightleftharpoons \underset{C_3}{NH_4^+} + \underset{C_3}{\overset{0}{OH^-}}$

$\therefore \quad K_b = \dfrac{C_3^2}{C_2 - C_3}$

[6] (d) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$t = 0 \quad C_2 \quad 0 \quad 0$

At eq. $C_2(1-\alpha) \quad C_2\alpha \quad C_2\alpha$

Also $C_2\alpha = C_3$

$\therefore [OH^-] = C_3$

or $pOH = -\log C_3$

$\therefore pH = pK_w - pOH = pK_w + \log C_3$

Also $[OH^-] = C_2\alpha = C_2\sqrt{\dfrac{K_b}{C_2}} = \sqrt{K_b \cdot C_2}$

$\therefore pOH = -\dfrac{1}{2}\log K_b - \log C_2$

$= \dfrac{1}{2}pK_b - \dfrac{1}{2}\log C_2$

$\therefore \quad pH = pK_w - pOH = pK_w - \dfrac{1}{2}pK_b + \dfrac{1}{2}\log C_2$

$= pK_a + \dfrac{1}{2}pK_b + \dfrac{1}{2}\log C_2$

Comprehension 5

[1] (b) At 25°C pH = 7 $\quad \therefore \; K_w = 10^{-14}$;

At 60°C, pH = 6.5 $\quad K_w = 10^{-13}$

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = ?$

$2.303\log\dfrac{10^{-13}}{10^{-14}} = \dfrac{\Delta H}{R}\left[\dfrac{35}{333\times298}\right]$

$\therefore \quad \Delta H = 13.06$ kcal

$\therefore \quad H^+ + OH^- \rightarrow H_2O; \qquad \Delta H = -13.06$ kcal

[2] (a) pH of solution after passage of HCl = 3

$\therefore \quad [H^+] = 10^{-3}\ M$ or $[HCl] = 10^{-3}\ M$

From $PV = nRT$

$1\times V = 10^{-3}\times0.0821\times298$

$V = 24.46$ mL

[3] (a) $\underset{1}{HCN} \rightleftharpoons \underset{0}{H^+} + \underset{0}{CN^-}$
$\quad\quad\quad

In each sub question given below a statement **S** and explanation **E** is given. Choose the correct answers from the codes a, b, c and d given for each question :

(a) **S** is correct but **E** is wrong

(b) **S** is wrong but **E** is correct

(c) Both **S** and **E** are correct and **E** is correct explanation for **S**

(d) Both **S** and **E** are correct but **E** is not correct explanation for **S**

1. **S :** The pH of a basic buffer mixture is given by : $pH = pK_a + \log \frac{[base]}{[conjugate\ acid]}$

   E : The pH of an acidic buffer mixture is given by : $pH = pK_a + \log \frac{[conjugate\ base]}{[acid]}$

2. **S :** On passing $HCl(g)$ through a saturated solution of $BaCl_2$, a white turbidity appears.

   E : The common ion effect is responsible for white turbidity.

3. **S :** Degree of hydrolysis and pH of a salt say NH_4CN is independent of concentration of NH_4CN.

   E : The solution of NH_4CN in water has pH slightly greater than 7.

4. **S :** In a pair of two electrolytes one having higher value of K_{sp} is more soluble in water than the other having lower value of K_{sp}.

   E : Solubility of electrolyte depends upon K_{sp} as well as on the nature of electrolyte.

5. **S :** $HgCl_2$ and $SnCl_2$ cannot coexist in a solution.

   E : Increase in concentration of Cl^- in solution brings in precipitation of either of them.

6. **S :** The solubility of HgI_2 in water decreases in presence of KI.

   E : HgI_2 is insoluble in water but it becomes soluble in $KI(aq)$.

7. **S :** The pH of $NH_4OH(aq)$ decreases on addition of little NH_4Cl in it.

   E : The pH of NH_4Cl brings in decrease in degree of dissociation of NH_4OH due to common ion effect.

8. **S :** The $[H^+]$ in 10^{-8} N HCl is 1.05×10^{-7} M.

   E : The H^+ is obtained from HCl and H_2O ; the later furnishes less H^+ than 10^{-7} due to common ion effect.

9. **S :** HCl acts as weak base in liquid HF but weak acid in acetic acid.

   E : The tendency to act as acid or base also depends upon the nature of other substance to accept or donate a proton.

10. **S :** Cu^+, Ag^+ are soft acids whereas CN^-, H^- are soft bases.

    E : Soft acids do not possess noble gas configuration whereas soft bases have donor atom of easily polarised nature.

11. **S :** Metal oxides are usually either acidic or amphoteric but Mn_2O_7 is acidic.

    E : On dissolution in water, Mn_2O_7 forms per manganic acid.

12. **S :** The dissociation constants of polyprotic acid are in the order $K_1 > K_2 > K_3$.

    E : The $[H^+]$ furnished in first step of dissociation exerts common ion effect to reduce the second dissociation so on.

13. **S :** All strong acid in water show almost same acidic nature.

    E : This is due to levelling effect of water on account of its high dielectric constant and strong proton accepting tendency.

14. **S :** CCl_4, C_6H_6 and liquid SO_2 are aprotic solvents.

    E : Aprotic solvents do not influence the acidic or basic nature of solute.

15. **S :** The acidic nature of some cations is :

    $$Al^{3+} > Be^{2+} > Na^+ > K^+$$

    E : More is the effective nuclear charge on cation more is its acidic nature.

16. **S :** Acidic nature of boron trihalides is in the order :

    $$BF_3 < BCl_3 < BBr_3 < BI_3$$

    E : Basic nature of nitrogen trihalides is in the order :

    $$NF_3 > NCl_3 > NBr_3 > NI_3$$

17. **S :** $CO + NaOH \xrightarrow[\text{High } T]{\text{High } P} HCOONa$.

    E : CO although being neutral can acts as acid in the given reaction.

18. **S :** The dissociation constant of water at 60°C is 10^{-13}.

    E : The pH of water is 6.5 and that it behaves as acid at 60°C.

19. **S :** Salting out action of sodium soap in presence of NaCl is based on common ion effect.

    E : Salting out action of soap is based on the fact that as the concentration of Na^+ increases, the $RCOONa$ shows precipitation because $[RCOO^-][Na^+] > K_{sp}$.

20. **S :** Hydrolysis of salt is an exothermic phenomenon.

    E : It involves breaking up of water molecule of produce acid and base respectively.

21. **S :** 0.1 *M* NaCN + 0.05 *M* HCl solution on mixing in equal volume form a buffer solution.
E : The solution after mixing contains a weak acid and its conjugate base and thus act as buffer.

22. **S :** The pH of NH_4OH remains unchanged on addition of NH_4Cl.
E : Addition of NH_4Cl suppresses the dissociation of NH_4OH due to common ion effect.

23. **S :** Heat given out during neutralisation of NaOH and HF is –13.7 kcal/eq.
E : F^- ion is more easily hydrated and thus heat of neutralisation of HF and NaOH is more.

24. **S :** The pH of pure water is less than 7 at 60°C.
E : As the temperature increases, pure water becomes slightly acidic.

25. **S :** The pH of human blood at body temperature is found to be 6.9.
E : Blood is alkaline in nature.

26. **S :** Solubility of AgCl is more in conc. HCl than in water.
E : AgCl form a complex with conc. HCl and thus solubility of AgCl increases in conc. HCl.

27. **S :** All Arrhenius acids are also Bronsted acids.
E : All Bronsted bases are also Lewis bases.

28. **S :** Cl^- is weak base than $C_2H_5O^-$.
E : Stronger is acid, weaker is its conjugate base.

29. **S :** H_3BO_3 in water behaves as monobasic acid.
E : The ionisation reaction is :

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

30. **S :** Solubility of AgCl is less in 0.1 *M* NaCl than in water.
E : In presence of NaCl, the solubility of AgCl is lowered on account of common ion effect.

31. **S :** In water orthoboric acid behaves as a weak monobasic acid.
E : In water orthoboric acid behaves as a proton donor.

32. **S :** HNO_3 is a stronger acid than HNO_2.
E : In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one.

ANSWERS (Statement Explanation Problems)

1. (d) For basic buffer $pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]}$

$\therefore pH = pK_w - pOH$

2. (a) This is not common ion effect (At least one should be weak electrolyte). Here product of ionic concentration exceeds K_{sp} of $BaCl_2$.

3. (d) NH_4OH is relatively stronger than HCN.

4. (b) $K_{sp} = p^p \cdot q^q \cdot s^{(p+q)}$ for A_pB_q.

5. (a) $SnCl_2 + 2HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2\downarrow$

$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + 2Hg\downarrow$

This is redox change.

6. (b) HgI_2 forms soluble complex with KI

$$2KI + HgI_2 \longrightarrow K_2HgI_4$$

7. (c) Explanation is correct reason for statement.

8. (c) —do—

9. (c) —do—

10. (c) —do—

11. (c) —do—

12. (c) Explanation is correct reason for statement.

13. (c) Explanation is correct reason for statement.

14. (c) Explanation is correct reason for statement.

15. (c) Explanation is correct reason for statement.

16. (a) Statement is correct due to back bonding in boron. In nitrogen halides the order is $NF_3 < NCl_3 < NBr_3 < NI_3$. On account of decreasing electronegativity of halogens, in NF_3, the lone pair is not released easily, due to more +ve charge on N.

17. (c) CO is acid, NaOH is base and salt formed is HCOONa.

18. (a) $K_w = 10^{-13}$ at 60°C $\therefore$ pH = 6.5; but water is neutral because pH scale contracts to 0 to 13.

19. (b) $RCOONa \rightarrow RCOO^- + Na^+$; In presence of NaCl, $[Na^+]$ increases and $[RCOO^-][Na^+]$ exceeds than K_{sp} of RCOONa.

20. (b) Breaking up of bonds is endothermic.

21. (c) $\underset{0.1}{NaCN} + \underset{0.05}{HCl} \longrightarrow \underset{0.05}{NaCl} + \underset{0.05}{HCN}$

The solution contains a weak acid HCN and its conjugate base CN^- and thus acts as buffer.

22. (b) The dissociation of NH_4OH is suppressed in presence of NH_4Cl and thus pH of NH_4OH decreases.

23. (b) Heat given out during complete neutralisation of HF and NaOH is – 16.4 kcal/eq. due to extensive hydration of F^- on NaF account of its smaller size.

24. (a) The scale of pH (0 to 14 at 25°C) changes to (0 to less than 14) as the temperature rises because K_w of water increases with temperature. Note that $[H^+] = [OH^-]$ and thus water remains neutral.

25. (d) Blood is alkaline and at body temperature (98°F) scale of pH lies between 0 to 13.6.

26. (c) Explanation is correct reason for statement.

27. (a) All Bronsted bases are not Lewis bases.

28. (c) Explanation is correct reason for statement.

29. (c) Explanation is correct reason for statement.

30. (a) The equilibrium $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

$$K_{sp} = [Ag^+][Cl^-]$$

if $[Cl^-]$ increases, the equilibrium is shifted in the backward direction, *i.e.*, solubility of AgCl decreases in presence of NaCl. Note this is Le Chatelier's principle application to solubility product. In common ion effect, there must be a weak electrolyte.

31. (a) $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$

32. (a) $HO-\overset{+5}{N}(=O)-O$ $\qquad$ $HO-\overset{+3}{N}=O$

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List A	List B
(a) Adsorption indicator	(i) $K_3Fe(CN)_6$
(b) External indicator	(ii) Starch
(c) Self indicator	(iii) Methyl red
(d) Acid-base indicator	(iv) $KMnO_4$

2.

List A	List B
(a) pH of amphioprotic salt	1. $-\frac{1}{2}[\log(K_{a_1}c_1 + K_{a_2}c_2)$
(b) pH of mixtures of two weak acids	2. $\frac{1}{2}[pK_{a_1} + pK_{a_2}]$
(c) pH of a basic buffer mixture	3. $pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$
(d) pH of an acidic buffer mixture	4. $pK_a + \log\frac{[\text{base}]}{[\text{conjugate acid}]}$
(e) pH of a salt solution of weak acid + strong base	5. $\frac{1}{2}[pK_w + pK_a + \log c]$
(f) pH of a salt solution of strong acid + weak base	6. $\frac{1}{2}[pK_w - pK_b - \log c]$

3.

List A	List B
(a) K_{sp} of $BaCl_2 \cdot 2H_2O$	1. $[Ba^{2+}][Cl^-]^2[H_2O]^2$
(b) K_{a_2} of dibasic acid	2. $[Ba^{2+}][Cl^-]^2$
(c) Conjugate acid of RNH_2	3. $[A^{-2}]$
(d) Conjugate base of RNH_2	4. RNH^-
(e) Solubility of AgCl in NaCl	5. RNH_3^+
	6. $S = \frac{K_{sp}}{[Cl^-]}$

Type II : More Than One Match Possible

4.

List A	List B
(a) Solubility of PbS	1. Increases in dil. HCl. *aq.*
(b) Solubility of Ag_2S	2. Increases in dil. NaCN *aq.*
(c) Solubility of CuS	3. Increases in dil. NH_3 *aq.*
(d) Solubility of $BaSO_4$	4. Increases in conc. HCl

Type III : Only One Match From Each List

5.

List A	List B	List C
A. Melting of ice	1. Favoured with decrease in P	a. $pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$
B. Freezing of water	2. Favoured with increase in P	b. $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$
C. 0.1 M NaHS (*aq.*)	3. Hydrolysis and protonation	c. Favoured by addition of ice
D. 0.1 M CH_3COONH_4 (*aq.*)	4. Hydrolysis	d. Not favoured by addition of ice
E. 0.1 M NH_4Cl (*aq.*)	5. Acidic	e. $pH = \frac{1}{2}[pK_a - \log C]$

ANSWERS

1. a–ii; b–i; c–iv; d-iii
2. a–2; b–1; c–4; d-3; e–5; f–6
3. a–2; b–3; c–5; d-4; e–6;
4. a–1,3,4; b–1,2,3,4; c–1,2,3,4; d-4
5. A–2–d; B–1–c; C–3–a; D–4–b; E–5–e

14 Conductance of a Solution

Resistance of solution : The hinderance provided by solution in the passage of current (R). (R expressed in ohm)

Conductance of solution : The ease provided by solution in the passage of current (C).

$$\therefore \quad C = \frac{1}{R};$$

(C expressed in ohm^{-1} or mho)

Conductivity : The conducting power of 1 cm^3 of a solution (κ).

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = C \times \frac{l}{a}$$

(κ expressed in ohm^{-1}cm^{-1} or mho cm^{-1} or S cm^{-1})

where l = length of electrolyte solution in between electrodes,

a = area of cross-section.

The factor $\frac{l}{a}$ is known as **cell constant** expressed in cm^{-1} or m^{-1}.

Equivalent conductivity : The conducting power of all the ions present in a solution having 1g equivalent of electrolyte (λ).

$$\Lambda_{eq.} = \kappa \times V_{\text{in mL}} = \kappa \times \frac{1000}{N}$$

where V is volume having 1 g equivalent of electrolyte; N is conc. in eq./litre, *i.e.*, normality; λ is expressed in ohm^{-1}cm^{2}eq.$^{-1}$. In MKS system κ in S m^{-1} and C_N in eq./m^3 and $\Lambda_{eq.}$ in S m^{2}eq^{-1} and the expression becomes $\Lambda_{eq.} = \frac{\kappa}{C_N}$.

Molecular conductivity : The conducting power of all the ions present in a solution having 1 mole of electrolyte (Λ). where V is volume containing 1 mole of electrolyte.

$$\Lambda_M = \kappa \times V_{\text{in mL}} = \kappa \times \frac{1000}{M}$$

where V is volume having 1 mole of electrolyte; M is concentration in mol/litre, *i.e.*, molarity; Λ is expressed in ohm^{-1}cm^{2}mol^{-1}. In MKS system κ in S m^{-1} and C_M in mol/m^3 and Λ_M in S m^{2}mol^{-1} and the expression is $\Lambda_M = \frac{\kappa}{C_M}$.

Infinite dilution : It means that the electrolyte is 100% ionised. The λ, Λ values increase with dilution and become constant at infinite dilution.

For weak electrolytes,

$$\text{Degree of dissociation } '\alpha' = \frac{\Lambda_v}{\Lambda^\circ}$$

where Λ_v, Λ° are equivalent conductances of electrolyte at dilution v and ∞ or zero concentration respectively.

Important Conversions :

$$1 \text{ S m}^2\text{mol}^{-1} = 10^4 \text{S cm}^2\text{mol}^{-1}$$

$$1 \text{ S cm}^2 \text{ mol}^{-1} = 10^{-4} \text{S m}^2 \text{ mol}^{-1}$$

$$1 \text{ S cm}^{-1} = 10^2 \text{ S m}^{-1}$$

$$1 \text{ S m}^{-1} = 10^{-2} \text{ S cm}^{-1}$$

Kohlrausch law : This law states that at infinite dilution where dissociation of all electrolytes is complete and where all interionic effects disappear, each ion migrates independently of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature and not at all on the ions with which it is associated. Thus, equivalent conductance at infinite dilution is equal to the sum of ionic conductances of its component ions at infinite dilution.

i.e., $\quad \Lambda^\circ_{\text{electrolyte}} = \lambda^\circ_{\text{cation}} + \lambda^\circ_{\text{anion}}$

where $\lambda^\circ_{\text{cation}}$ and $\lambda^\circ_{\text{anion}}$ are ionic equivalent conductances of cation and anion respectively at infinite dilution expressed in ohm^{-1}cm^{2}eq.$^{-1}$.

Thus, $\quad \Lambda^\circ_{eq.\,NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$ ...(1)

$$\Lambda^\circ_{eq.\,BaCl_2} = \frac{1}{2}\lambda^\circ_{Ba^{2+}} + \frac{1}{1}\lambda^\circ_{Cl^-} \quad \text{...(2)}$$

$$\Lambda^\circ_{eq.\,AlCl_3} = \frac{1}{3}\lambda^\circ_{Al^{3+}} + \frac{1}{1}\lambda^\circ_{Cl^-} \quad \text{...(3)}$$

$$\Lambda^{\circ}_{eq.\,Al_2(SO_4)_3} = \frac{1}{3}\lambda^{\circ}_{Al^{3+}} + \frac{1}{2}\lambda^{\circ}_{SO_4^{2-}} \quad \ldots(4)$$

Thus, in general $\Lambda^{\circ}_{eq.} = \frac{1}{n^+}\cdot\lambda^{\circ}_{+} + \frac{1}{n^-}\cdot\lambda^{\circ}_{-}$

where n^+ and n^- are charge on each ion furnished by electrolyte

For molar conductance (Λ_M) at infinite dilution

$$\Lambda^{\circ}_{M\,BaCl_2} = \lambda^{\circ}_{Ba^{2+}} + 2\lambda^{\circ}_{Cl^-}$$

$$\Lambda^{\circ}_{M\,AlCl_3} = \lambda^{\circ}_{Al^{3+}} + 3\lambda^{\circ}_{Cl^-}$$

$$\Lambda^{\circ}_{M\,Al_2(SO_4)_3} = 2\lambda^{\circ}_{Al^{3+}} + 3\lambda^{\circ}_{SO_4^{2-}}$$

Thus, in general $\Lambda^{\circ}_{M} = \gamma_+\lambda^{\circ}_{+} + \gamma_-\lambda^{\circ}_{-}$

where γ_+ and γ_- are the number of +ve and –ve ions furnished by each formula unit of electrolyte.

Also, $\lambda^{\circ}_{cation} = u^{\circ}_{cation} \times \text{Faraday}$

$\lambda^{\circ}_{anion} = u^{\circ}_{anion} \times \text{Faraday}$

where u°_{cation} and u°_{anion} are ionic mobilities of cation and anion at infinite dilution respectively.

Transport no. of cations and anions in an electrolyte:

Transport no. of an ion of an electrolyte in a solution is the fraction of total current carried by that ion in solution.

$$t_{ion} = \frac{\text{Current carried by an ion}}{\text{Total current carried by both the ions}}$$

or $$t_{cation} = \frac{\text{Current carried by cation}}{\text{Current carried by anion and cation both}}$$

$$t_{anion} = \frac{\text{Current carried by anion}}{\text{Current carried by anion and cation both}}$$

$\therefore\ t_{cation} + t_{anion} = 1$

$\therefore$ Current carried by an ion $\propto$ speed or ionic mobility of that ion $\propto u$

$$\therefore \quad t_{cation} = \frac{u_{cation}}{u_{cation} + u_{anion}}$$

and $$t_{anion} = \frac{u_{anion}}{u_{cation} + u_{anion}}$$

At infinite dilution

Also, $$t^{\infty}_{cation} = \frac{u^{\infty}_{cation}}{u^{\infty}_{cation} + u^{\infty}_{anion}}$$

$$t^{\infty}_{anion} = \frac{u^{\infty}_{anion}}{u^{\infty}_{cation} + u^{\infty}_{anion}}$$

Also, $t^{\infty}_{cation} \times \lambda^{\infty}_{electrolyte} = \lambda^{\circ}_{cation}$

and $t^{\infty}_{anion} \times \lambda^{\circ}_{electrolyte} = \lambda^{\circ}_{anion}$

• NUMERICAL PROBLEMS •

1. The resistance of a 0.01 N solution of an electrolyte was found to be 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm^{-1}. Calculate conductivity and equivalent conductivity of solution.
2. The conductivity of $N/50$ solution of a cell of KCl at 25°C is 0.002765 S cm^{-1}. If the resistance of a cell containing this solution is 400 ohm, find out cell constant.
3. The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 32ohm. Calculate the conductivity and equivalent conductivity of solution.
4. When a certain conductance cell was filled with 0.02 M KCl solution (conductivity 0.002768 S cm^{-1}), it had a resistance of 82.4 ohm at 298 K. When filled with 0.005 N K_2SO_4, it had a resistance of 324 ohm. Calculate :
   (a) cell constant.
   (b) conductance of 0.005 N K_2SO_4 solution.
   (c) conductivity of 0.005 N K_2SO_4 solution.
   (d) equivalent conductivity of 0.005 N K_2SO_4 solution.
   (e) molecular conductivity of 0.005 N K_2SO_4.
5. At 18°C, the velocity of migration of Ag^+ ion is 0.00057cm sec^{-1} and that of NO_3^- is 0.00063 cm sec^{-1} at infinite dilution. What is the equivalent conductivity of $AgNO_3$ at infinite dilution?
6. The molar conductivity of acetic acid at infinite dilution is 390.7 and for 0.1 M acetic acid solution is 5.2 S $cm^2 mol^{-1}$. Calculate the :
   (1) degree of dissociation of acetic acid.
   (2) $[H^+]$ in solution.
7. 0.04 N solution of a weak acid has a conductivity 4.23×10^{-4} S cm^{-1}. The degree of dissociation of acid at this dilution is 0.0612. Calculate the equivalent conductivity of weak acid at infinite solution.
8. The equivalent conductivity of 0.05 N solution of a monobasic acid is 15.8 S $cm^2 eq.^{-1}$. If equivalent conductivity of the acid at infinite dilution is 350 S cm^2 $eq.^{-1}$, calculate the
   (1) degree of dissociation of acid.
   (2) dissociation constant of acid.
9. The resistance of a solution 'A' is 50 ohm and that of solution 'B' is 100 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solutions A and B are mixed, what will be the resistance of the mixture using the same cell? (Assume that there is no increase in the degree of dissociation of A and B on mixing)
10. A big irregular shaped vessel contained water, the conductivity of which was 2.56×10^{-5} S cm^{-1}. 500 g of NaCl was then added to the water and the conductivity after the addition of NaCl, was found to be 3.10×10^{-5} S cm^{-1}. Find the capacity of the vessel if it is fulfilled with water (Λ°_M of NaCl = 149.9).
11. The equivalent conductivity of 0.10 N solution of $MgCl_2$ is 97.1 S $cm^2 eq.^{-1}$ at 25°C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when the potential difference between the electrodes is 5 volts?
12. At 18°C the conductance of H^+ and CH_3COO^- at infinite dilution are 315 and 35 S $cm^2 eq.^{-1}$ respectively. The conductivity of 0.001 N solution of acetic acid is 4.1×10^{-5} S cm^{-1} at the same temperature. What is the degree of dissociation of acetic acid?
13. The equivalent conductivity of acetic acid at infinite dilution is 387 S cm^2 $eq.^{-1}$. At the same temperature, 0.001 M solution of acetic acid, it is 55 S $cm^2 eq.^{-1}$. What is the degree of dissociation of 0.1 N acetic acid? Assume $1-\alpha \approx 1$.
14. Ionic conductivity at infinite dilution of Al^{3+} and SO_4^{2-} ions are 189 S cm^2 $eq.^{-1}$ and 160 S cm^2 $eq.^{-1}$ respectively. Calculate the equivalent and molar conductivity of $Al_2(SO_4)_3$ at infinite dilution.
15. The equivalent conductivity of CH_3COONa, HCl and NaCl at infinite dilution are 91.6, 425.0 and 128.1 S cm^2 $eq.^{-1}$ respectively. Calculate equivalent conductivity of acetic acid at infinite dilution. Also if degree of dissociation of 0.1 N acetic acid is 0.001, find the equivalent conductivity at this concentration of acetic acid.
16. Calculate molar conductivity for NH_4OH, given that molar conductivity for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 S cm^2 mol^{-1} respectively.
17. Calculate the dissociation constant of water at 25°C from the following data :
    Conductivity of $H_2O = 5.8 \times 10^{-8}$ S cm^{-1}, $\lambda^\circ_{H^+} = 350.0$ and $\lambda^\circ_{OH^-} = 198.0$ S cm^2 $eq.^{-1}$.
18. The equivalent conductivity of KCl at infinite dilution is 130 S cm^2 $eq.^{-1}$. The transport no. of Cl^- ion in KCl at the same temperature is 0.505. What is the limiting ionic mobility and ionic conductance of K^+ ion?
19. At a certain temperature, the saturated solution of silver chloride has conductivity 1.12×10^{-6} S cm^{-1}. The ionic conductances of Ag^+ and Cl^- ions at infinite dilution are

54.3 and 65.5 S cm^2 $eq.^{-1}$ at same temperature. Find the solubility of AgCl in g $litre^{-1}$ at this temperature.

20. Conductivity of a saturated aqueous solution of $Co_2[Fe(CN)_6]$ is 2.06×10^{-6} S cm^{-1}. The conductivity of water used to prepare the solution has conductivity 4.1×10^{-7} S cm^{-1}. If ionic molar conductivities of Co^{2+} and $[Fe(CN)_6]^{4-}$ are 86 S cm^2 mol^{-1} and 444.0 S cm^2 mol^{-2} respectively. Calculate the solubility product of $Co_2[Fe(CN)_6]$.

21. Explain the conducting power order of the following ions:

$Li^+(aq.) < Na^+(aq.) < K^+(aq.) < Rb^+(aq.) < Cs^+(aq.)$

22. A dilute solution of KCl was placed between two Pt electrodes 10.0 cm apart, across which a potential difference of 6.0 volt was applied. How far would K^+ ions move in 2 hours at 25°C? Ionic conductivity of K^+ at infinite dilution is 73.52 S cm^2 $eq.^{-1}$ at 25°C.

23. The molar conductivities at infinite dilution of $AgNO_3$, NaCl and $NaNO_3$ are 116.5, 110.3 and 105.2 S cm^2 mol^{-1} respectively. The conductivity of AgCl in water is 2.40×10^{-6} S cm^{-1} and of water used is 1.16×10^{-6} S cm^{-1}. Find the solubility of AgCl in g $litre^{-1}$.

24. A water sample of swimming pool shows the resistance of 9.2×10^3 ohm at 25°C using a conductivity cell. The same cell dipped in 0.02 *M* KCl has the resistance of 85 ohm. Now 0.5 kg sodium chloride is dissolved in pool and throughly stirred. The solution sample now shows the resistance of 7.6×10^3 ohm. If Λ°_M for NaCl and Λ_v for 0.02 *M* KCl are 126.5 S $cm^2 mol^{-1}$ and 138.0S $cm^2 mol^{-1}$, calculate the volume of water in pool.

25. At 298 K, the conductivity of pure water is 5.51×10^{-8} S cm^{-1}. The ionic conductances of H^+ and OH^- at this temperature are 349.8 and 198.5 S $cm^2 eq.^{-1}$ respectively. Calculate the ionic product of water.

26. A decinormal solution of $AgNO_3$ was electrolysed between Pt electrodes. After passing a small current for two hour, a fall of concentration of 0.0005124 equivalent occurred in anodic solution. The mass of copper deposited in copper coulometer placed in series was found to be 0.03879 g. Find the transport no. of Ag^+ and NO_3^- in $AgNO_3$.

27. A solution of $AgNO_3$ was electrolysed between silver electrodes. Before electrolysis, 10 g of solution contained 0.01788 g of $AgNO_3$. After the experiment, 20.09 g of the anodic solution contained 0.06227 g of $AgNO_3$. At the same time, 0.009479 g of Cu was deposited in the copper coulometer placed in series. Calculate transport no. of Ag^+ and NO_3^-.

28. Calculate the transport no. of H^+ and Cl^- ions from the following data obtained by moving boundary method using $CdCl_2$ as the indicator electrolyte:

Concentration of HCl solution = 0.1 *N*
Wt. of Ag deposited in coulometer = 0.1209 g
Movement of boundary = 7.50 cm
Cross-section of tube = 1.24 cm^2

29. Calculate the conductivity (in 1×10^{-7} S m^{-1} unit) of a solution prepared by dissolving 10^{-7} mole of $AgNO_3$ in 1 litre of saturated aqueous solution of AgBr.
K_{sp} of AgBr = 12×10^{-14} and $\lambda^\circ_{Ag^+}$, $\lambda^\circ_{Br^-}$ and $\lambda^\circ_{NO_3^-}$ are 6×10^{-3}, 8×10^{-3} and 7×10^{-3} S m^2 mol^{-1} respectively. Neglect the contribution of solvent. **(IIT 2006)**

SOLUTIONS (Numerical Problems)

1. Given for 0.01 N solution;

$R = 210$ ohm, $\frac{l}{a} = 0.88\ \text{cm}^{-1}$

$\therefore \quad \kappa = \frac{1}{R} \times \frac{l}{a}$

$\kappa = \frac{1}{210} \times 0.88 = \mathbf{4.19 \times 10^{-3}\ mho\ cm^{-1}\ or\ S\ cm^{-1}}$

Also, $\Lambda_{eq.} = \kappa \times \frac{1000}{N} = 4.19 \times 10^{-3} \times \frac{1000}{0.01}$

$= \mathbf{419.05\ S\ cm^2\ eq.^{-1}}$

2. Given for $\frac{N}{50}$ solution; $\kappa = 0.002765\ \text{S cm}^{-1}$, $R = 400$ ohm

$\because \quad \kappa = \frac{1}{R} \times \frac{l}{a}$

$0.002765 = \frac{1}{400} \times$ cell constant

$\therefore$ Cell constant $= \mathbf{1.106\ cm^{-1}}$

3. Given, $R = 32$ ohm, $l = 1.80$ cm, $a = 5.4\ \text{cm}^2$

$\because \quad \kappa = \frac{1}{R} \times \frac{l}{a}$

$\kappa = \frac{1}{32} \times \frac{1.8}{5.4} = \mathbf{0.01041\ S\ cm^{-1}}$

Also,

$\Lambda_{eq.} = \kappa \times \frac{1000}{N} = 0.01041 \times \frac{1000}{0.1} = \mathbf{104.1\ S\ cm^2\ eq.^{-1}}$

4. **From KCl data :** $\kappa = \frac{1}{R} \times \frac{l}{a}$

$\therefore \quad \frac{l}{a} = \kappa \times R = 0.002768 \times 82.4 = \mathbf{0.2281\ cm^{-1}}$

From K_2SO_4 data : $R = 324$ ohm

$\therefore \quad C = \frac{1}{R} = \frac{1}{324} = \mathbf{3.086 \times 10^{-3}\ S}$

Also, $\kappa = C \times \frac{l}{a} = 3.086 \times 10^{-3} \times 0.2281$

$= \mathbf{7.04 \times 10^{-4}\ S\ cm^{-1}}$

Now, $\Lambda_{eq.} = \kappa \times \frac{1000}{N} = 7.04 \times 10^{-4} \times \frac{1000}{0.005}$

$= \mathbf{140.80\ S\ cm^2\ eq.^{-1}}$

Also, $\Lambda_M = \kappa \times \frac{1000}{M} = 7.04 \times 10^{-4} \times \frac{1000 \times 2}{0.005}$

$= \mathbf{281.6\ S\ cm^2\ mol^{-1}}$

($N = 2M$, because K_2SO_4 is bivalent)

5. We have, $\lambda^\circ_{cation} = u^\circ_{cation} \times$ Faraday $= 0.00057 \times 96500$

$\lambda^\circ_{Ag^+} = 55.005\ \text{S cm}^2\ \text{eq.}^{-1}$

Also, $\lambda^\circ_{anion} = u^\circ_{anion} \times$ Faraday $= 0.00063 \times 96500$

or $\lambda^\circ_{NO_3^-} = 60.795\ \text{S cm}^2\text{eq.}^{-1}$

Now from Kohlrausch law,

$\lambda^\circ_{AgNO_3} = \lambda^\circ_{Ag^+} + \lambda^\circ_{NO_3^-} = 55.005 + 60.795$

$= \mathbf{115.8\ S\ cm^2\ eq.^{-1}}$

6. (1) The degree of dissociation 'α' is given by

$\because \quad \alpha = \frac{\Lambda_v}{\Lambda^\circ} = \frac{5.2}{390.7}$

$\alpha = \mathbf{0.0133\ or\ 1.33\%}$

(2) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Before dissociation	1	0	0
After dissociation	$(1-\alpha)$	α	α

$\therefore \quad [H^+] = C\alpha = 0.1 \times 0.0133 = \mathbf{0.00133\ M}$

7. Given, $\alpha = 0.0612$

$\kappa_v = 4.23 \times 10^{-4}\ \text{S cm}^{-1}$

Now, $\Lambda_{eq.} = \kappa_v \times \frac{1000}{N} = 4.23 \times 10^{-4} \times \frac{1000}{0.04}$

$= 10.575\ \text{S cm}^2\ \text{eq.}^{-1}$

Also, $\alpha = \frac{\Lambda_{eq.}}{\Lambda^\circ_{eq.}}$

$0.0612 = \frac{10.575}{\Lambda^\circ_{eq.}}$

$\therefore \quad \Lambda^\circ_{eq.} = \mathbf{172.79\ S\ cm^2\ eq.^{-1}}$

8. (1) Degree of dissociation, $\alpha = \frac{\Lambda_{eq.}}{\Lambda^\circ_{eq.}} = \frac{15.8}{350} = \mathbf{0.04514}$

(2) For acid of monobasic nature

$HA \rightleftharpoons H^+ + A^-$

$K = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 = 0.05 \times (0.04514)^2 = 1.019 \times 10^{-4}$

$= \mathbf{1.019 \times 10^{-4}}$

Note : Since, $\alpha = 0.04514$ and thus, $1 - \alpha = 1$

Concentration C in mol litre^{-1}

Since, HA is monobasic acid and thus normality = molarity.

9. Let κ_1 and κ_2 be the conductivity of the solutions A and B respectively and the constant of the cell be x.

$\therefore$ **For solution A :**

Conductivity = Conductance × Cell constant

$\kappa_1 = \frac{1}{50} \times x \qquad \ldots(1)$

For solution B : Conductivity, $\kappa_2 = \frac{1}{100} \times x \qquad \ldots(2)$

When equal volumes of A and B are mixed, both the solutions get doubly diluted, hence their individual contribution towards the conductivity of the mixture will be $\frac{\kappa_1}{2}$ and $\frac{\kappa_2}{2}$ respectively and the conductivity of the mixture will be $\frac{1}{2}(\kappa_1 + \kappa_2)$.

$\therefore$ For the mixture : $\frac{1}{2}(\kappa_1 + \kappa_2) = \frac{1}{R} \times x \qquad \ldots(3)$

(R is the resistance of mixture)

From Eqs. (1), (2) and (3),

$R = \mathbf{66.67\ ohm}$

10. Let the volume of the vessel be V litre

Equivalent of NaCl $= \dfrac{\text{Mass in grams}}{\text{Eq. mass}} = \dfrac{500}{58.5} = 8.547$

Let 8.547 eq. of NaCl be present in V litre

$\therefore \quad N = \dfrac{8.547}{V}$

The conductivity of the NaCl solution (only due to presence of Na^+ and Cl^- ions)

$$\kappa_v = 3.10\times10^{-5} - 2.56\times10^{-5}$$

$$\kappa_v = 0.54\times10^{-5}\ \text{S cm}^{-1}$$

$$\Lambda_{M\,\text{NaCl}} = 0.54\times10^{-5}\times\frac{1000\times V}{8.547}$$

Since, the vessel is big, the resulting solution may be supposed to be dilute.

$\therefore \quad \Lambda_{M\,\text{NaCl}} = \Lambda^\circ_{M\,\text{NaCl}}$

$$0.54\times10^{-5}\times\frac{1000\times V}{8.547} = 149.9$$

$$V = 2372.5\times10^2 \text{ litre}$$

$$= \mathbf{2372.5\times10^2\ litre}$$

11. Cell constant $= \dfrac{0.50}{1.50} = \dfrac{1}{3}$

$\because$ Conductivity $= \dfrac{\text{Equivalent conductivity}}{\text{Volume (cc) containing 1 eq.}}$

$$= \frac{97.1\times0.1}{1000} = 0.00971\ \text{S cm}^{-1}$$

$\because$ Conductance = Conductivity/Cell constant

$$= \frac{0.00971}{1/3}\ \text{S} = 0.02913\ \text{S}$$

$\therefore \quad$ Resistance $= \dfrac{1}{0.02913}$ ohm

$\therefore$ Current in ampere $= \dfrac{\text{Potential difference (by Ohm's law)}}{\text{Resistance (ohm)}}$

$$= \frac{5}{1/0.02913} = \mathbf{0.1456\ ampere}$$

12. $\Lambda^\circ_{eq.\,CH_3COOH} = \lambda^\circ_{H^+} + \lambda^\circ_{CH_3COO^-}$

$$= 315 + 35 = 350\ \text{S cm}^2\ \text{eq.}^{-1}$$

Now given $\kappa = 4.1\times10^{-5}$ S cm^{-1} for 0.001 N CH_3COOH

Therefore, $\Lambda_{eq.} = \kappa\times\dfrac{1000}{N} = 4.1\times10^{-5}\times\dfrac{1000}{0.001}$

$$= 41\ \text{S cm}^2\ \text{eq.}^{-1}$$

Now, degree of dissociation 'α' $= \dfrac{\Lambda_{eq.}}{\Lambda^\circ_{eq.}} = \dfrac{41}{350}$

$$\alpha = \mathbf{0.117\ or\ 11.7\%}$$

13. For 0.001 M CH_3COOH

$\because \quad \alpha = \dfrac{\Lambda_{eq.}}{\Lambda^\circ_{eq.}} \qquad \left(\Lambda_{eq.} = 55\ \text{S cm}^2\text{eq.}^{-1},\ \Lambda^\circ_{eq.} = 387\ \text{S cm}^2\text{eq.}^{-1}\right)$

$\therefore \quad \alpha = \dfrac{55}{387} = 0.142$ or 14.2%

Since, $K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{0.001\times(0.142)^2}{1-0.142}$

$$K_a = 2.35\times10^{-5}$$

$\therefore$ Now again $K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{0.1\times\alpha^2}{1-\alpha} = 2.35\times10^{-5}$

and assume $1-\alpha = 1$

$\therefore \quad \alpha_{\text{at } 0.1} = \mathbf{0.015\ or\ 1.5\%}$

14. $\Lambda^\circ_{eq.\,Al_2(SO_4)_3} = \dfrac{1}{n^+}\lambda^\circ_{Al^{3+}} + \dfrac{1}{n^-}\lambda^\circ_{SO_4^{2-}}$

$$= \frac{1}{3}\times189 + \frac{1}{2}\times160 = \mathbf{143\ S\ cm^2 eq.^{-1}}$$

Also, $\Lambda^\circ_{M\,Al_2(SO_4)_3} = 6\times\Lambda^\circ_{eq.\,Al_2(SO_4)_3} = 6\times143$

$$= \mathbf{858\ S\ cm^2\ mol^{-1}}$$

or $\Lambda^\circ_{M\,Al_2(SO_4)_3} = \gamma_+\lambda^\circ_{Al^{3+}} + \gamma_-\lambda^\circ_{SO_4^{2-}}$

$$= 2\times189 + 3\times160 = \mathbf{858\ S\ cm^2 mol^{-1}}$$

15. According to Kohlrausch law

$\Lambda^\circ_{eq.CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$

Given, from Kohlrausch law

$\Lambda^\circ_{eq.\,CH_3COONa} = 91.6 = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}$ ...(1)

$\Lambda^\circ_{eq.\,HCl} = 425.0 = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$ ...(2)

$\Lambda^\circ_{eq.\,NaCl} = 128.1 = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$ ...(3)

Adding Eqs. (1) and (2) and then subtracting Eq. (3),

$\Lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} = \lambda^\circ_{CH_3COONa} + \lambda^\circ_{HCl} - \lambda^\circ_{NaCl}$

$$= 91.6 + 425.0 - 128.1$$

or $\Lambda^\circ_{eq.\,CH_3COOH} = \mathbf{388.5\ S\ cm^2 eq^{-1}}$

Also, $\alpha = \dfrac{\Lambda_{eq.}}{\Lambda^\circ_{eq.}}$

$$0.001 = \frac{\Lambda_{eq.}}{388.5}$$

$\therefore \quad \Lambda_{eq.} = \mathbf{0.3885\ S\ cm^2 eq.^{-1}}$

16. $\Lambda^\circ_{M\,Ba(OH)_2} = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{OH^-} = 523.28$ ...(1)

$\Lambda^\circ_{M\,BaCl_2} = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{Cl^-} = 280.00$ ...(2)

$\Lambda^\circ_{M\,NH_4Cl} = \lambda^\circ_{NH_4^+} + \lambda^\circ_{Cl^-} = 129.80$ ...(3)

Multiply Eq. (3) by two and subtract from Eq. (2)

$\lambda^\circ_{Ba^{2+}} - 2\lambda^\circ_{NH_4^+} = 280 - 2\times129.8$ ...(4)

$\therefore \quad \lambda^\circ_{Ba^{2+}} - 2\lambda^\circ_{NH_4^+} = 20.40$ ...(5)

Now subtract Eq. (5) from Eq. (1)

$$2\lambda^\circ_{NH_4^+} + 2\lambda^\circ_{OH^-} = 502.88$$

$\therefore \quad \lambda^\circ_{NH_4^+} + \lambda^\circ_{OH^-} = \Lambda^\circ_{M\,NH_4OH} = \dfrac{502.88}{2}$

$$= \mathbf{251.44\ S\ cm^2 mol^{-1}}$$

17. Suppose water contains N mol/litre or N eq./litre of H^+ ions or OH^- ions.

$\because \quad$ Eq. of H^+ = Eq. of H_2O

$\therefore$ Eq. conductivity of water = Conductivity $\times\dfrac{1000}{N}$

$$= 5.8\times10^{-8}\times\frac{1000}{N}$$

Since, water dissociates feebly, *i.e.*, water may be considered to be a dilute solution of H^+ and OH^- iors.

$\therefore \quad \Lambda_{eq.\,H_2O} = \Lambda^\circ_{eq.\,H_2O} = \lambda^\circ_{H^+} + \lambda^\circ_{OH^-}$

$\therefore \quad 5.8\times10^{-8}\times\frac{1000}{N} = 350+198 = 548$

$\therefore \quad N = 1.058\times10^{-7}$

$\therefore \quad [H^+] = [OH^-] = 1.058\times10^{-7}$

For the equilibrium, $H_2O \rightleftharpoons H^+ + OH^-$

Equilibrium constant $(K) = \frac{[H^+][OH^-]}{[H_2O]}$

or $K_w = K\times[H_2O] = [H^+][OH^-]$

$= 1.058\times10^{-7}\times1.058\times10^{-7}$

$= 1.119\times10^{-14}$

$\therefore \quad K = \frac{K_w}{[H_2O]} = \frac{1.119\times10^{-14}}{55.5} = \mathbf{2\times10^{-16}\ mol/litre}$

$\left[[H_2O] = \frac{1000}{18} = 55.5\ \text{mol/litre}\right]$

Alternate solution

Molarity of water is 55.6 mol litre^{-1}. Also for the dissociation

$H_2O \rightleftharpoons H^+ + OH^-; \quad M_{H_2O} = N_{H_2O}$

$\therefore$ Equivalent conductivity of water $= 5.8\times10^{-8}\times\frac{1000}{55.6}$

Also, $\Lambda^\circ_{eq.\,H_2O} = \lambda^\circ_{H^+} + \lambda^\circ_{OH^-}$

$= 350.0+198.0 = 548$

Now, $\alpha_{H_2O} = \frac{\Lambda_{eq.\,H_2O}}{\Lambda^\circ_{eq.\,H_2O}} = \frac{5.8\times10^{-8}\times1000}{55.6\times548} = 1.9\times10^{-9}$

Also for $H_2O \rightleftharpoons H^+ + OH^-$

$$K_{eq.} = \frac{C\alpha\cdot C\cdot\alpha}{C(1-\alpha)} = C\alpha^2 = 55.6\times(1.9\times10^{-9})^2$$

$$= \mathbf{2.0\times10^{-16}\ mol\ litre^{-1}}$$

18. Transport no. $t_{Cl^-} = 0.505$

$\because \quad t_{K^+} + t_{Cl^-} = 1 \quad \therefore t_{K^+} = 1-0.505 = 0.495$

Also we have,

Ionic conductance $\lambda^\circ_{K^+} = \lambda^\circ_{KCl}\times t^\circ_{K^+}$

$= 130\times0.495 = 64.35$

Also, $\lambda^\circ_{K^+} = u^\circ_{K^+}\times F$

$\therefore$ Limiting ionic mobility $(u^\circ_{K^+}) = \frac{64.35}{96500}$

$$= \mathbf{6.67\times10^{-4}\ cm^2\,sec^{-1}\,volt^{-1}}$$

19. Given, $\lambda^\circ_{Ag^+} = 54.3$

$\lambda^\circ_{Cl^-} = 65.5$

$\therefore \quad \Lambda^\circ_{eq.\,AgCl} = \lambda^\circ_{Ag^+} + \lambda^\circ_{Cl^-}$

$= 54.3+65.5 = 119.8\ S\ cm^2eq.^{-1}$

We also have, $\Lambda_{eq.} = \kappa\times V = \kappa\times\frac{1000}{N}$

$(\because \Lambda_{eq.} = \Lambda^\circ_{eq.}$ for sparingly soluble salts)

$\therefore \quad 119.8 = 1.12\times10^{-6}\times\frac{1000}{N}$

$\therefore \quad N = \frac{1.12\times10^{-3}}{119.8}$ eq./litre

$S = \frac{1.12\times10^{-3}}{119.8}\times143.5$ g/litre

$$S = \mathbf{1.34\times10^{-3}\ g/litre}$$

Note : In case of sparingly soluble salts $\Lambda_v = \Lambda°$, since solubility is very low and electrolyte is assumed to be 100% ionised at normal conditions.

20. The complex forming saturated solution is assumed to be 100% ionised, *i.e.*, the condition at infinite dilution. Thus,

For, $Co_2[Fe(CN)_6]\Lambda^\circ_M = 2\times\Lambda^\circ_{Co^{2+}} + \Lambda^\circ_{Fe(CN)_6}$

$= 2\times86+444 = 616\ S\ cm^2mol^{-1}$

Also, $\kappa_{complex} = \kappa_{sol} - \kappa_{H_2O} = 2.06\times10^{-6} - 0.41\times10^{-6}$

$= 1.65\times10^{-6}\ S\ cm^{-1}$

If C_M is molarity then

$\therefore \quad \Lambda^\circ_M = \kappa\times\frac{1000}{C_M}$

$616 = \frac{1.65\times10^{-6}\times1000}{C_M}$

$\therefore \quad C_M = 2.68\times10^{-6}$ mol/litre

$Co_2[Fe(CN)_6] \rightleftharpoons \underset{2s}{2Co^{2+}} + \underset{s}{[Fe(CN)_6]^{4-}}$

$K_{sp} = 4s^3 = 4\times(2.68\times10^{-6})^3$

$= \mathbf{7.699\times10^{-17}}$

21. The size of ions is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, thus smallest ion should move more rapidly, however ionic mobility shows the reverse trend because smaller ions are more easily hydrated and thus hydrated ion size for these ions is $Li^+(aq.) > Na^+(aq.) > K^+(aq.) > Rb^+(aq.) > Cs^+(aq.)$. Thus, ionic mobility of $Li^+(aq.)$ is minimum.

22. $\lambda^\circ_{K^+} = 73.52$

Ionic mobility, $u^\circ_{K^+} = \frac{\lambda^\circ_{K^+}}{F} = \frac{73.52}{96500}$

$= 7.619\times10^{-4}\ cm^2sec^{-1}volt^{-1}$

Potential gradient applied $= \frac{6.0}{10} = 0.6$ volt cm^{-1}

$\therefore$ Speed of K^+ = ionic mobility × potential gradient

$= 7.619\times10^{-4}\times0.6\ cm\ sec^{-1}$

$= 45.714\times10^{-5}\ cm\ sec^{-1}$

$\therefore$ Distance travelled by K^+ in 2 hours

$= 45.714\times2\times60\times60\times10^{-5} = \mathbf{3.292\ cm}$

23. For monovalent electrolytes

Equivalent conductance = Molar conductance

Given, $\Lambda^\circ_{M\,AgNO_3} = 116.5 = \lambda^\circ_{Ag^+} + \lambda^\circ_{NO_3^-}$ ...(1)

$$\Lambda^{\circ}_{M\,NaCl} = 110.3 = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-} \quad \ldots(2)$$

$$\Lambda^{\circ}_{M\,NaNO_3} = 105.2 = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{NO_3^-} \quad \ldots(3)$$

$\therefore$ $\Lambda^{\circ}_{M\,AgCl} = (1)+(2)-(3) = 116.5+110.3-105.2$

$= 121.6\ S\ cm^2\ mol^{-1}$

For sparingly soluble salt $\Lambda_M = \Lambda^{\circ}_M$

$\therefore$ $\Lambda_{M\,AgCl} = 121.6\ S\ cm^2 mole^{-1}$

Now, $\kappa_{AgCl+water} = 2.40\times10^{-6}\ S\ cm^{-1}$

$\kappa_{water} = 1.16\times10^{-6}\ S\ cm^{-1}$

$\therefore$ $\kappa_{AgCl} = (2.40-1.16)\times10^{-6}\ S\ cm^{-1}$

$= 1.24\times10^{-6}\ S\ cm^{-1}$

Therefore, $\Lambda_M = \kappa\times\dfrac{1000}{N}$

$$121.6 = 1.24\times10^{-6}\times\frac{1000}{M}$$

$\therefore$ $$M = N = \frac{1.24\times10^{-3}}{121.6}\ \text{mol/litre}$$

$$= \frac{1.24\times10^{-3}}{121.6}\times143.5\ \text{g/litre}$$

Solubility of AgCl = $\mathbf{1.463\times10^{-3}\ g\ litre^{-1}}$

24. $$\Lambda_M\,KCl = \kappa\times\frac{1000}{M}$$

$$138 = \kappa\times\frac{1000}{0.02}$$

$\therefore$ $\kappa = 2.76\times10^{-3}$

Also, $\kappa_{KCl} = C\times\dfrac{l}{a}$

$$2.76\times10^{-3} = \frac{1}{85}\times\frac{l}{a} \qquad \left(C=\frac{1}{R}=\frac{1}{85}\right)$$

$\therefore$ Cell constant $\dfrac{l}{a} = 0.2346\ cm^{-1}$

$$C_{pool\ water} = \frac{1}{9.2\times10^3} = 1.087\times10^{-4}\ S$$

(Note : Conductivity is an additive property but not resistance.)

$$C_{NaCl\,(aq.)} = \frac{1}{7.6\times10^3} = 1.316\times10^{-4}\ S$$

$\therefore$ $$C_{NaCl} = C_{NaCl\,(aq.)} - C_{pool\ water}$$

$$= [1.316-1.087]\times10^{-4} = 2.29\times10^{-5}$$

$\therefore$ $$\kappa_{NaCl} = C\times\frac{l}{a} = 2.29\times10^{-5}\times0.2346$$

$$= 5.37\times10^{-6}\ S\ cm^{-1}$$

$\therefore$ $$\Lambda^{\circ}_{NaCl} = \kappa\times\frac{1000}{M}$$

$$\left(M = \frac{500}{58.5\times V_{(l)}} = \frac{8.55}{V_l}\right)$$

V is volume of water $\simeq$ volume of solution

$$126.5 = 5.37\times10^{-6}\times\frac{1000\times V_{(l)}}{8.55}$$

$\therefore$ $\mathbf{V_{(l)} = 2.01\times10^5\ litre}$

25. $$\Lambda^{\circ}_{eq.\,H_2O} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{OH^-}$$

$$= 349.8+198.5 = 548.3\ S\ cm^2 eq.^{-1}$$

Now, $\Lambda^{\circ}_{eq.} = \Lambda_{eq.}$ for water

$\therefore$ $\Lambda_{eq.} = 548.3\ S\ cm^2 eq.^{-1}$

Also, $\Lambda_{eq.} = \kappa_v\times\dfrac{1000}{N}$

$$548.3 = \frac{5.51\times10^{-8}\times1000}{N}$$

$\therefore$ $N = 1.005\times10^{-7}$ eq. litre^{-1}

or $[H^+] = [OH^-] = 1.005\times10^{-7}$

For water $K_w = [H^+][OH^-] = [1.005\times10^{-7}]^2$

$\mathbf{K_w = 1.01\times10^{-14}}$

26. Fall of concentration around anode = 0.0005124 eq.

Mass of copper deposited in coulometer = 0.03879 g

$\therefore$ Equivalent of copper deposited in coulometer

$$= \frac{0.03879}{31.8} = 0.001219\ \text{eq.}$$

Now transport no. t_{Ag^+}

$$= \frac{\text{No. of equivalent of } Ag^+ \text{ ion lost in anode}}{\text{No. of equivalent of } Cu^{2+} \text{ deposited in coulometer}}$$

or total fall in concentration of solution

$$= \frac{0.0005124}{0.001219}$$

$t_{Ag^+} = \mathbf{0.4303}$

Also, $t_{Ag^+} + t_{NO_3^-} = 1$

$\therefore$ $t_{NO_3^-} = 1-0.4303 = \mathbf{0.5697}$

27. After electrolysis :

$\because$ 20.09 g of anodic solution contained 0.06227 g of $AgNO_3$

$\therefore$ Mass of water in solution = 20.09 – 0.06227 = 20.02773 g

Thus, 20.02773 g H_2O has 0.06227 g $AgNO_3$

$$= \frac{0.06227}{170}\ \text{eq. } AgNO_3$$

$= 0.0003664$ equivalent $AgNO_3$ or Ag^+

Before electrolysis :

$\because$ 10.0 g of solution contained 0.01788 g of $AgNO_3$

$\therefore$ Mass of water in solution = 10 – 0.01788 = 9.98212 g

Thus, 9.98212 g water has = 0.01788 g $AgNO_3$

$$= \frac{0.01788}{170}\ \text{eq. } AgNO_3$$

$\therefore$ 20.02773 g water has $= \dfrac{0.01788\times20.02773}{170\times9.98212}$ eq. $AgNO_3$

$= 0.0002111$ equivalent of $AgNO_3$ or Ag^+

Thus, increase in concentration of Ag^+ during electrolysis

$= 0.0003664 - 0.0002111 = 0.0001553$ eq.

Also, mass of Cu deposited in coulometer

$= 0.009479$ g

$\therefore$ Eq. of Cu deposited in coulometer $= \frac{0.009479}{31.8}$

$\therefore$ Eq. of Cu deposited or actual increase around anodic solution $= 0.0002982$ eq.

(Since, equal equivalents are discharged at either electrode)

Since, Ag^+ has migrated from anode, which brings a fall in concentration around anode but due to attacked electrodes, (*i.e.*, Ag in $AgNO_3$), apparent increase is noticed.

Thus, fall in concentration of Ag^+ around anode

= Actual increase which would have occur around anode − Apparent increase in Ag^+ around anode

$= 0.0002982 - 0.0001553$

$= 0.0001429$ equivalent of Ag^+

$\therefore$ Transport no. of t_{Ag^+}

$$= \frac{\text{Eq. of } Ag^+ \text{ lost in anodic cell}}{\text{Eq. of } Cu^{2+} \text{ deposited in coulometer}}$$

$$= \frac{0.0001429}{0.0002982}$$

$$t_{Ag^+} = \mathbf{0.4792}$$

Now, $t_{Ag^+} + t_{NO_3^-} = 1$

$\therefore$ $t_{NO_3^-} = 1 - 0.4792 = \mathbf{0.5208}$

28. Transport no. of H^+ ions $= \frac{l \cdot A \cdot C}{1000Q}$

l is length of migration = 7.50 cm

A is area of cross-section = 1.24 cm^2

C is concentration of solution = $0.1N$

Q is charge passed = Equivalent of Ag deposited

$$= \frac{0.1209}{108} \text{ Faraday} \qquad \left(Q = \frac{W}{E}\right)$$

$\therefore$ $t_{H^+} = \frac{7.5 \times 1.24 \times 0.1 \times 108}{0.1209 \times 1000} = \mathbf{0.8308}$

Now, $t_{H^+} + t_{Cl^-} = 1$

$\therefore$ $t_{Cl^-} = 1 - 0.8308 = \mathbf{0.1692}$

29. Solubility of AgBr in presence of 10^{-7} mole of $AgNO_3$ solution

$$K_{sp\,AgBr} = [Ag^+][Br^-]$$

$$12 \times 10^{-14} = [S + 10^{-7}] \times S$$

$\therefore$ $S = 3 \times 10^{-7} M$

$\therefore$ $[Ag^+] = [3 \times 10^{-7} + 10^{-7}] = 4 \times 10^{-7} M$

$[Br^-] = 3 \times 10^{-7} M$

$[NO_3^-] = 1 \times 10^{-7} M$

$\because$ $\kappa = \frac{\Lambda^\circ \times M}{1000}$

(λ in S $m^2 mol^{-1} = \lambda \times 10^4$ S $cm^2 mol^{-1}$)

$\therefore$ $\kappa_{Ag^+} = \frac{6 \times 10^{-3} \times 10^4 \times 4 \times 10^{-7}}{1000}$

$= 24 \times 10^{-9}$ S cm^{-1}

$\kappa_{Br} = \frac{8 \times 10^{-3} \times 10^4 \times 3 \times 10^{-7}}{1000} = 24 \times 10^{-9}$ S cm^{-1}

$\kappa_{NO_3^-} = \frac{7 \times 10^{-3} \times 10^4 \times 10^{-7}}{1000} = 7 \times 10^{-9}$ S cm^{-1}

$\therefore$ $\kappa_{Total} = \kappa_{Ag^+} + \kappa_{Br^-} + \kappa_{NO_3^-}$

$= 24 \times 10^{-9} + 24 \times 10^{-9} + 7 \times 10^{-9}$

$= \mathbf{55 \times 10^{-9}}$ **S cm^{-1}** $= \mathbf{55 \times 10^{-7}}$ **S m^{-1}**

In the unit of 1×10^{-7} S m^{-1}, **the conductivity is 55.**

● SINGLE INTEGER ANSWER PROBLEMS ●

1. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross-section of 1 cm^2. The conductance of this solution was found to be 5×10^{-7} S. The pH of the solution is 4. The value of limiting molar conductivity (Λ^0_M) of this weak monobasic acid in aqueous solution is $Z \times 10^2$ S $cm^{-1} mol^{-1}$. The value of Z is :

[JEE (Main) 2017]

ANSWERS

1. Six

OBJECTIVE PROBLEMS (One Answer Correct)

1. The resistance of 0.05 N solution of an electrolyte A_aB_b was found to be 210 ohm at 300 K. If cell constant is 0.88 cm^{-1}, the molar conductivity is in S m^2mol^{-1} is :
(a) $83.81\times(a+b)$ (b) $83.81\times(a+b)\times10^{-4}$
(c) $83.81\times(a\cdot b)$ (d) $83.81\times(a\cdot b)\times10^{-4}$

2. If Λ_M of a solution is 419×10^{-4} S m^2mol^{-1} for an electrolyte K_2SO_4 at 300 K. The resistance offered by the solution with cell constant 0.88 m^{-1} is 210 ohm, the molarity of K_2SO_4 solution is :
(a) 1×10^{-4} M (b) 0.02 M
(c) 0.05 M (d) 0.03 M

3. The molar conductivity of $LiNO_3$ at infinite dilution is 10^5 S cm^2mol^{-1}. If 0.02 M solution shows conductance 0.158 ohm^{-1} using cell of cell constant 1 cm^{-1}. The concentration of Li^+ ion in g $litre^{-1}$ is :
(a) 0.01106 (b) 0.1106
(c) 11.06 (d) 0.2212

4. One needs some experimental data to determine $\Lambda^\circ_{H_2C_2O_4}$. Which value is also needed in addition of $\Lambda^\circ_{HNO_3}$ and $\Lambda^\circ_{K_2C_2O_4}$?
(a) Λ°_{NaCl} (b) $\Lambda^\circ_{KNO_3}$
(c) Λ°_{KCl} (d) $\Lambda^\circ_{Na_2C_2O_4}$

5. The transport number of Ag^+ in $AgNO_3$ is 0.4 and of NO_3^- in KNO_3 is 0.4. The ratio of transport number of NO_3^- in $AgNO_3$ and KNO_3 is:
(a) 1 (b) 1.5
(c) 2.0 (d) 2.5

6. The absolute velocity of Ag^+ and NO_3^- are 5.7×10^{-4} and 6.9×10^{-4} cm sec^{-1} respectively. Assuming complete dissociation of $AgNO_3$, calculate the molar conductivity of $AgNO_3$ at infinite dilution:
(a) 121.59 S cm^2mol^{-1} (b) 141.59 S cm^2mol^{-1}
(c) 131.59 S cm^2mol^{-1} (d) none of these

7. The conductivity of 20 mL of 0.2 N NaOH solution is a S cm^{-1}. If 10 mL of 0.4 N HCl solution is added to this solution, the conductivity decreases by b S cm^{-1}. The resultant solution has equivalent conductivity in S cm^2 $eq.^{-1}$ is :
(a) $a-b$ (b) $\dfrac{(a-b)\times30}{4}$
(c) $\dfrac{(a-b)\times3\times10^4}{4}$ (d) $\dfrac{(a-b)\times4}{3}$

8. Molar conductivity of $AgNO_3$, HCl and HNO_3 at infinite dilution are a, b, c S cm^2 mol^{-1} respectively. If the conductivity of saturated AgCl solution is Z S cm^{-1}, then K_{sp} of AgCl will be :
(a) $\dfrac{1000Z}{a+b-c}$ (b) $\left[\dfrac{1000\,Z}{a+b-c}\right]^2$
(c) $\left[\dfrac{a+b-c}{Z}\right]$ (d) $\left[\dfrac{a+b-c}{Z\times1000}\right]^2$

9. Which of the following correctly represents the equivalent conductance of $Al_2(SO_4)_3$ at infinite dilution :
(a) $2\lambda^\infty_{Al^{3+}}+3\lambda^\infty_{SO_4^{2-}}$ (b) $2\lambda^\infty_{Al^{3+}}+\lambda^\infty_{SO_4^{2-}}$
(c) $[\lambda^\infty_{Al^{3+}}+\lambda^\infty_{SO_4^{2-}}]\times6$ (d) $\frac{1}{3}\lambda^\infty_{Al^{3+}}+\frac{1}{2}\lambda^\infty_{SO_4^{2-}}$

10. The best conductor of electricity in 0.1M aqueous solution :
(a) Boric acid (b) Sulphuric acid
(c) Acetic acid (d) Propionic acid

11. An increase in equivalent conductivity of strong electrolytes with dilution is mainly due to :
(a) increase in ionic molility of ions
(b) 100% ionisation of electrolyte at normal dilution
(c) increase in both *i.e.*, molility and ionisation
(d) increase in number of ions

12. The molar conductivity of 1M HCl is greater than 1 M NaCl at a particular temperature. This is due to :
(a) molar mass of HCl < molar mass of NaCl
(b) ionic mobility of H^+ > ionic mobility of Na^+
(c) HCl being an acid has lower pH
(d) degree of ionisation of HCl > degree of ionisation of NaCl

13. SI Unit of ionic mobility is :
(a) $m^2volt^{-1}sec^{-1}$ (b) $cm^2volt^{-1}sec^{-1}$
(c) $cm\ volt^{-1}sec^{-1}$ (d) $cm^2volt^{-1}sec^{-1}$

14. Molten sodium chloride conducts electricity due to the presence of :
(a) Free electrons
(b) Free ions
(c) Free molecules
(d) Atoms of sodium and chlorine

15. Which of the following is always an additive property :
(a) Conductance (b) Resistance
(c) Surface tension (d) Viscosity

16. Which of the following ion has exceptionally higher values of $\wedge_\infty$:
(a) H^+ (b) K^+
(c) NH_2^- (d) NH_2^+

17. At infinite dilution the solution of CH_3COOH does not contain :
(a) H^+ (b) CH_3COO^-
(c) CH_3COOH (d) None of these

18. Select the correct statement :
(a) Λ^{∞} of strong electrolytes can be obtained only by Kohlrausch's law
(b) Mobility of ions depends only on nature of ions
(c) Speed of ions depends only on nature of ion
(d) Conductance of solution decreases with increase in temperature

19. The molar conductivity of NaCl, KCl and K_2SO_4 at 25°C and infinite dilution are 126.45, 149.84, 306.60 Scm^2mol^{-1} respectively. If $\lambda^{\circ}_{Na^+}$ at 25°C is 50.11 Scm^2mol^{-1}, what is $\lambda^{\circ}_{SO_4^{2-}}$ (in S cm^2mol^{-1}) at 25°C.
(a) 159.6 (b) 209.77
(c) 259.82 (d) 359.82

20. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field?
(a) Na (b) K
(c) Rb (d) Li

SOLUTIONS (One Answer Correct)

1. (d) $\Lambda_M = \kappa \times \frac{1000}{C_M}$ (C_M in mol/litre) $\left(\kappa = C \times \frac{l}{a}\right)$

$$= \frac{0.88\times10^2}{210} \times \frac{1000}{\frac{0.05}{a\cdot b}} \times 10^{-6}$$

$$= 83.81 \times a \times b \times 10^{-4}\ S\ m^2mol^{-1}$$

2. (a) $\Lambda_M = \kappa \times \frac{1}{c}$

(where, c in mol m^{-3} and κ in $ohm^{-1}m^{-1}$)

$$419\times10^{-4} = \frac{0.88}{210} \times \frac{1}{c}$$

$$C = 0.1\ mol\ m^{-3}$$

$$\therefore \quad C = 1\times10^{-4}\ M$$

3. (a) $\Lambda_v = \frac{\kappa \times 1000}{M}$

$$= \frac{0.158\times1000}{0.02}$$

$$= 7900\ S\ cm^2mol^{-1}$$

Also, $\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{7900}{10^5} = 0.079$

$$\therefore \quad [Li^+] = c\alpha = 0.02\times0.079 = 1.58\times10^{-3}$$

$$\therefore \quad w_{Li^+} = 1.58\times10^{-3}\times7 = 0.01106\ g/litre$$

4. (b) $\Lambda^{\circ}_{H_2C_2O_4} = 2\Lambda^{\circ}_{H^+} + \Lambda^{\circ}_{C_2O_4^{2-}}$

$$= 2\Lambda^{\circ}_{HNO_3} - \Lambda^{\circ}_{K_2C_2O_4} - 2\Lambda^{\circ}_{KNO_3}$$

5. (b) $t_{NO_3^-}$ in $Ag^+ = 1 - 0.4 = 0.6$

$t_{NO_3^-}$ in $K^+ = 0.4$

$$\therefore \quad \frac{t_{NO_3^-} \text{ in } Ag^+}{t_{NO_3^-} \text{ in } K^+} = \frac{0.6}{0.4} = 1.5$$

6. (a) $\lambda^{\circ}_{Ag^+} = 5.7\times10^{-4}\times96500 \quad (\lambda^{\circ} = u^{\circ}\times F)$

$$\lambda^{\circ}_{NO_3^-} = 6.9\times10^{-4}\times96500$$

$$\therefore \quad \Lambda^{\circ}_{M\,AgNO_3} = \lambda^{\circ}_{Ag^+} + \lambda^{\circ}_{NO_3^-}$$

$$= (5.7\times10^{-4} + 6.9\times10^{-4})\times96500$$

$$= 121.59\ S\ cm^2\ mol^{-1}$$

7. (c)

	NaOH	+ HCl	⟶ NaCl	+ H_2O
	20×0.2	10×0.4		
	$=4$	$=4$	0	0
	0	0	4	4

$$[NaCl] = \frac{4}{30}$$

$$\therefore \quad \Lambda_{eq.} = \kappa \times \frac{1000}{N} = \frac{(a-b)\times1000\times30}{4}$$

$$= \frac{(a-b)}{4} \times 3\times10^4\ S\ cm^2eq^{-1}$$

8. (b) $\Lambda^{\circ}_{AgNO_3} = \Lambda^{\circ}_{Ag^+} + \Lambda^{\circ}_{NO_3^-} = a$

$$\Lambda^{\circ}_{HCl} = \Lambda^{\circ}_{H^+} + \Lambda^{\circ}_{Cl^-} = b$$

$$\Lambda^{\circ}_{HNO_3} = \Lambda^{\circ}_{H^+} + \Lambda^{\circ}_{NO_3^-} = c$$

Also, $\Lambda^{\circ}_{AgCl} = \Lambda^{\circ}_{Ag^+} + \Lambda^{\circ}_{Cl^-} = (a+b-c)$

Also, $\Lambda^{\circ}_{AgCl} = \kappa \times \frac{1000}{M}$

$$(a+b-c) = Z \times \frac{1000}{M}$$

$$\therefore \quad M = \frac{1000Z}{(a+b-c)}$$

Now, $K_{sp} = [Ag^+][Cl^-] = M^2 = \left[\frac{1000Z}{a+b-c}\right]^2$

9. (d) Follow Kohlrausch law

10. (b) H_2SO_4 is strong electrolyte and furnishes maximum no. of ions.

11. (a) Ionic mobility increases with dilution

12. (b) Ionic mobility of H^+ is maximum because of lightest ion

13. (a) Ionic mobility $= \frac{\text{Speed of ion}}{\text{Potential gradient}} = \frac{m\times m}{\text{sec}\times\text{volt}}$

14. (b) $NaCl_{fused} \longrightarrow Na^+ + Cl^-$

15. (a) $C_{solution} = C_{electrolyte} + C_{water}$

16. (a) Due to smallest size

17. (c) At infinite dilution $\alpha = 1$

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

18. (b) Mobility is speed of ion under unit potential gradient.

19. (a) $\Lambda^{\circ}_{Na_2SO_4} = 2\Lambda^{\circ}_{NaCl} + \Lambda^{\circ}_{K_2SO_4} - 2\Lambda^{\circ}_{KCl}$

$$= 2\times126.45 + 306.60 - 2\times149.84$$

$$= 259.82$$

$$\lambda^{\circ}_{SO_4^{2-}} = \Lambda^{\circ}_{Na_2SO_4} - 2\times\lambda_{Na^+}$$

$$= 259.82 - 2\times50.11$$

$$= 159.6\ S\ cm^2mol^{-1}$$

20. (d) Enthalpy of hydration of Li^+ is maximum among given species.

Size of ion : $r_{Li^+} < r_{Na^+} < r_{K^+} < r_{Rb^+}$

Size of hydrated ion :

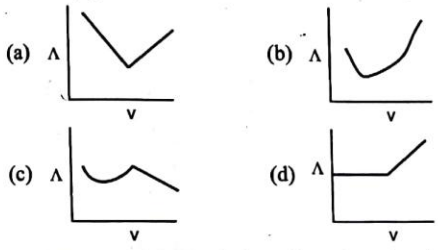
$r_{Li^+(aq.)} > r_{Na^+(aq.)} > r_{K^+(aq.)} > r_{Rb^+(aq.)}$

Thus, ionic mobility will be minimum for $Li^+_{aq.}$

PREVIOUS YEARS PROBLEMS

1. The correct order of equivalent conductivity at infinite dilution of LiCl, NaCl and KCl is : **(IIT 2001)**
   (a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
   (c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

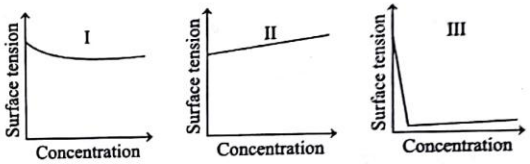
2. $AgNO_{3(aq)}$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measused. The plots of conductance Λ *vs* volume of $AgNO_{3(aq)}$ is : **(IIT 2011)**



3. Resistance of 0.2 *M* solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 *M* solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 *M* solution of the electrolyte in S m^2 mol^{-1} is : **[JEE (Main) 2014]**
   (a) 5×10^{-4} (b) 5×10^{-3}
   (c) 5×10^{3} (d) 5×10^{2}

4. The equivalent conductance of NaCl at concentration *C* and at infinite dilution are λ_C and λ_∞ respectively. The correct relationship between λ_C and λ_∞ is given as : (where the constant *B* is positive) **[JEE (Main) 2014]**
   (a) $\lambda_C = \lambda_\infty + (B)C$ (b) $\lambda_C = \lambda_\infty - (B)C$
   (c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$

5. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solution of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^-Na^+$ at room temperature. The correct assignment of the sketches is: **[JEE (Advanced) II 2016]**



   (a) **I** : KCl; **II** : CH_3OH ; **III** : $CH_3(CH_2)_{11}OSO_3^-Na^+$
   (b) **I** : $CH_3(CH_2)_{11}OSO_3^-Na^+$; **II** : CH_3OH; **III** : KCl
   (c) **I** : KCl; **II** : $CH_3(CH_2)_{11}OSO_3^-Na^+$; **III** : CH_3OH
   (d) **I** : CH_3OH; **II** : KCl; **III** : $CH_3(CH_2)_{11}OSO_3^-Na^+$

SOLUTIONS (Previous Year Problems)

1. (b) More is the size of hydrated ion ($Li^+_{aq.} > Na^+_{aq.} > K^+_{aq.}$) lesser is conductance.

2. (d) Initial conductance (Λ) of solution was due to K^+_{aq} and Cl^-_{aq}. On addition of $AgNO_{3(aq)}$, the reaction occurs
   $AgNO_{3(aq)} + KCl_{(aq)} \longrightarrow AgCl + KNO_{3(aq)}$
   $\Lambda_{KCl} = \Lambda_{KNO_3}$ till complete precipitation and then increases with further addition of $AgNO_3$.

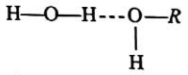
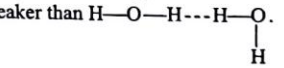
3. (a) $\kappa = \frac{1}{R}\times\frac{l}{a}$
   For given 0.2 *M* electrolyte solution
   $\kappa = 1.4\ S\ m^{-1} = 1.4\times10^{-2}\ S\ cm^{-1}$
   $\therefore \frac{l}{a} = 1.4\times10^{-2}\times50\ cm^{-1}$
   For 0.5 *M* electrolyte solution
   $$\wedge_m = \frac{\kappa\times1000}{C} = \frac{1}{R}\times\frac{l}{a}\times\frac{1000}{C}$$
   $$= \frac{1}{280}\times\frac{1.4\times10^{-2}\times50\times1000}{0.5} = 5\ S\ cm^2\ mol^{-1}$$
   $$= 5\times10^{-4}\ S\ m^2\ mol^{-1}$$

4. (c) This is called onsanger's equation.

5. (c) Substance like detergents [$CH_3(CH_2)_{11}OSO_3^-Na^+$] decreases the surface tension sharply due to micellization. Those like alcohol (*e.g.*, —CH_3OH, C_2H_5OH) lower the surface tension slightly due to their lower dielectric constant and the mixture produced acquires lower dielectric constant than water. Dielectric constant is directly proportional to surface tension.

   or

   Soluble inorganic impurities present in bulk of a liquid such as KCl slightly increase the surface tension of water. Usually ionic solute furnish ions and the solution of ions give rise to increase in molecular attraction leading to slight increase in surface tension. Addition of H_2O to CH_3OH decreases the interaction among molecules

   or
   
   bonding is weaker than
   

   A decrease in molecular attraction leads to decrease in surface tension (remember H—OH—CH_3OH shows positive deviation from Raoult's law).

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which one is correct statement?
   (a) Conductance is an additive property
   (b) Conductance order :
   $Li^+_{(aq.)} < Na^+_{(aq.)} < K^+_{(aq.)} < Rb^+_{(aq.)}$
   (c) Molar conductivity of NH_4^+ in liquid NH_3 is higher than in H_2O
   (d) At infinite dilution all the interionic attractions vanishes

2. Which relations are correct about conductances?
   (a) $K_h = \dfrac{C\Lambda_v^2}{\Lambda^\circ(\Lambda^\circ - \Lambda_v)}$
   (b) $\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$ for strong electrolytes
   (c) $\Lambda^\circ_{M\,A_XB_Y} = X\,\Lambda^\circ_{A^+} + Y\,\Lambda^\circ_{B^-}$
   (d) $\Lambda_M = \kappa \times \dfrac{1000}{M}$

3. Select the correct statements :
   (a) Λ°_M for weak electrolytes depends upon degree of dissociation of electrolyte, ionic mobility and nature of ion
   (b) Λ°_M for strong electrolytes depends upon ionic mobility and nature of ion
   (c) The SI unit of Λ_M is $S\,m^2\,mol^{-1}$
   (d) $1\ S\,m^2\,mol^{-1} = 1 \times 10^4\ S\,cm^2\,mol^{-1}$

4. A graph plotted for $\log(i-1)$ *vs.* $\log \Lambda_v$, where i is van't Hoff factor of given uni-univalent electrolyte having molar conductance Λ_v at dilution v, then which are correct?
   (a) Slope $= -\log \Lambda^\circ$; intercept $= -1$
   (b) Slope $= 1$; intercept $= -\log \Lambda^\circ_M$
   (c) Slope $= 1$; intercept $= \log \Lambda^\circ_M$
   (d) Slope $= \log \Lambda^\circ_M$; intercept $= +1$

5. Λ°_M and Λ°_E are molar and equivalent conductivity at infinite dilution and λ° is ionic conductance at infinite dilution, then for potash alum:
   (a) $\Lambda^\circ_M = 2 \times \lambda^\circ_{K^+} + 2 \times \lambda^\circ_{Al^{3+}} + 4 \times \lambda^\circ_{SO_4^{2-}}$
   (b) $\Lambda^\circ_E = \dfrac{1}{8} \times \Lambda^\circ_M$
   (c) $\Lambda^\circ_E = \dfrac{1}{4} \times \lambda^\circ_{K^+} + \dfrac{1}{4} \times \lambda^\circ_{Al^{3+}} + \dfrac{1}{2} \times \lambda^\circ_{SO_4^{2-}}$
   (d) $\Lambda^\circ_M = \lambda^\circ_{K^+} + \lambda^\circ_{Al^{3+}} + \lambda^\circ_{SO_4^{2-}}$

6. An ion travels 0.4 cm in 1 minute under the influence of 2 volt potential difference when electrodes are 3 cm apart. Which one are correct?
   (a) Speed of ion $= 6.67 \times 10^{-3}\ cm\,s^{-1}$
   (b) Ionic mobility $= 1 \times 10^{-6}\ m^2 volt^{-1} sec^{-1}$
   (c) Ionic mobility $= 1.0 \times 10^{-3}\ cm^2 volt^{-1} sec^{-1}$
   (d) Ionic mobility $= 4.44 \times 10^{-3}\ cm^2 volt^{-1} sec^{-1}$

7. The increase in ionic mobility of strong electrolytes with dilution is due to :
   (a) Increase in degree of dissociation
   (b) Increase in number of ions
   (c) Relaxation or Assymetric effect
   (d) Solution or Electrophoretic effect

8. The formula, $\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$ does not hold good for :
   (a) CH_3NH_2 (b) H_2SO_4
   (c) $HClO_4$ (d) NH_4Cl

9. In a solution of NH_4OH, at infinite dilution, which are present :
   (a) NH_4OH (b) NH_4^+
   (c) OH^- (d) None of these

10. The term infinite dilution refers for :
    (a) All interionic effect disappears
    (b) Weak electolytes are 100% dissociated
    (c) The Kohlrausch law becomes valid for weak and strong electrolytes both
    (d) Ionic mobility becomes constant

11. Which are correct for super conductors ?
    (a) possess zero resistivity
    (b) possess infinite conductivity
    (c) Metals and their alloys at 0 to 15 K
    (d) Ceramic materials and mixed oxides at 0 to 150 K

12. Which one is incorrect ?
    (a) 1 J = 1 N × 1 m
    (b) 1 J = 1 volt-coulomb
    (c) 1 J = 1 watt × 1 sec
    (d) 1 J = 1 volt × 1 ampere × 1 sec

13. Molar conductivity of NH_4^+ and NH_2^- are usually higher in liquid NH_3 than in water due to :
    (a) Grothus conductance
    (b) Auto protolysis of solvent
    (c) Higher dielectric constant of NH_3
    (d) High conducting nature of NH_3

14. Which of the following will increase the conductivity of solution :
    (a) Temperature
    (b) Dielectric constant of solvent
    (c) Decrease in viscosity of solvent
    (d) Decrease in solvation of ion

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c,d) (a) $C_T = \Sigma C_i + C_{Water}$

(b) Due to more hydration of small cation and thus size increase and conductance decreases,

(c) Due to grothus conductance. Conductance of NH_4^+ in NH_3 is more.

2. (a,c,d) $\alpha = \frac{\Lambda_v}{\Lambda^\circ}$ for weak electrolytes.

3. (a,b,c,d) These are facts.

4. (b) $\alpha = \frac{i-1}{n-1}$ $\quad n = 2$ for AB

$$\therefore \quad \frac{\lambda_v}{\Lambda^\circ_M} = \frac{i-1}{1} \quad \text{or} \quad i-1 = \frac{\Lambda_v}{\Lambda^\circ_M}$$

$$\text{or} \quad \log(i-1) = \log \Lambda_v - \log \Lambda^\circ_M$$

$$Y = mx + c$$

5. (a,b,c) Follow text of Kohlrausch law.

6. (a,b) $\text{Speed} = \frac{0.4}{60} = 6.67\times10^{-3}\ \text{cm sec}^{-1}$;

$= 6.67\times10^{-5}\ \text{m sec}^{-1}$

$$\text{Ionic mobility} = \frac{\text{Speed}}{\text{Pot. gradient}}$$

$$= \frac{6.67\times10^{-5}\times3\times10^{-2}}{2}$$

$$= 1\times10^{-6}\ \text{m}^2\text{volt}^{-1}\ \text{sec}^{-1}$$

7. (c,d) Follow Debye-Huckel theory of strong electrolytes

8. (a) The formula is valid for weak electrolytes

9. (b,c) At infinite dilution weak electrolyte is completely dissociated

10. (a,b,c,d) All are facts

11. (a,b,c,d) These are facts.

12. (a,b,c,d) –do–

13. (a,b) –do–

14. (a,b,c,d) –do–

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Electrolytes that are known as weak electrolytes on the basis of very strong dependence of conductance on concentration give quite constant concentration independent values of dissociation constant (K_a) calculated from degree of dissociation (α) values from measured conductances or from colligative properties. The partial dissociation appears to be a major factor in determining the properties of weak electrolytes and the degree of dissociation for weak electrolyte at dilution v is given by $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$. The strong electrolytes on the otherhand do not obey this relation and the variation of molar conductivity for strong electrolytes is given by $\Lambda_v = \Lambda_\infty - bc^{1/2}$.

[1] The slope of the graph $\frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)}$ *vs.* $\frac{1}{c}$, if Λ_v and Λ_∞ are molar conductivity of weak electrolyte having dissociation constant K_a at concentration c and zero respectively is:

(a) concave downwards

(b) concave upwards

(c) straight line with intercept K_a

(d) straight line with slope K_a

[2] The numerical value of Λ^∞_{ion} :

(a) is dependent of nature of ion

(b) is called molar conductivity

(c) is obtained by extrapolation of Λ_c *vs.* $\sqrt{c}$ curves to zero concentration for all electrolytes

(d) is equal to $\frac{\Lambda_v}{\alpha}$ for strong electrolytes

[3] The van't Hoff factor for weak electrolyte A_xB_y, if $(n = x + y)$ can be given as:

(a) $i = 1 - \alpha + x\alpha + y\alpha$

(b) $i = 1 + (x + y)$ at infinite dilution

(c) $i = (n-1)\frac{\Lambda_v}{\Lambda_\infty} + 1$

(d) either of these

[4] The graph plotted for $\log(i-1)$ *vs.* $\log \Lambda_v$, where i is van't Hoff factor for uni-univalent electrolyte and Λ_v is its molar conductivity at concentration c does not show the following characteristics:

(a) straight line

(b) slope equal to unity

(c) intercept equal to $\log \Lambda_\infty$

(d) intercept equal to $-\log \Lambda_\infty$

[5] Which statement is wrong about the variation of molar conductivity with dilution for a given electrolyte?

(a) Depends upon ionic mobility and degree of dissociation of all electrolytes

(b) Depends upon ionic mobility and degree of dissociation of weak electrolytes

(c) Depends upon ionic mobility for strong electrolytes

(d) Depends upon the nature of ion furnished by electrolytes on dissolution

SOLUTIONS

Comprehension 1

[1] (d) $K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_v^2}{\Lambda_\infty^2\left(1-\frac{\Lambda_v}{\Lambda_\infty}\right)}$

$$K_a = \frac{c\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)}$$

or $$\frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)} = \frac{K_a}{c}$$

$$y = m \cdot x \qquad \left(x = \frac{1}{c}\right)$$

[2] (a) Λ_∞ depends on nature of ion.

[3] (d) All are correct.

$$i = 1 - \alpha + x\alpha + y\alpha$$

$$\therefore \quad \alpha = \frac{i-1}{(x+y)-1} = \frac{i-1}{n-1}$$

or $$\frac{\Lambda_v}{\Lambda_\infty} = \frac{i-1}{n-1}$$

$$\therefore \quad i = (n-1)\frac{\Lambda_v}{\Lambda_\infty} + 1$$

[4] (c) $\because$ $n = 2$ for HA

$$\therefore \quad i = \frac{\Lambda_v}{\Lambda_\infty} + 1$$

$$\therefore \quad \log(i-1) = \log \Lambda_v - \log \Lambda_\infty$$

$\therefore$ slope = 1 and intercept = $-\log \Lambda_\infty$

[5] (a) For strong electrolytes, 'α' has no effect on Λ_M.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. **S :** A graph plotted between Λ_v *vs.* $c^{1/2}$ gives a straight line with slope equal to $-A$ and intercept equal to Λ_∞.
   E : The value of A for a given solvent and temperature depends upon the nature of electrolyte, *i.e.*, charge on cation or anion furnished by electrolyte on dissolution.
2. **S :** Conductivity of weak electrolytic solution decreases with dilution whereas equivalent conductivity, molar conductivity increases with dilution.
   E : On dilution, the ionic mobility and number of ions present in solution increases but number of ions per mL decreases.
3. **S :** The Λ^∞ for all electrolytes can be obtained by extrapolation of Λ_M curves *vs.* $\sqrt{\text{concentration}}$ to zero concentration.
   E : Λ^∞ for all electrolytes can be obtained by Kohlrausch law.
4. **S :** The ratio of speeds of cation and anions of an electrolyte under same potential gradient is 2 : 3, the fall in concentration around anodic and cathodic solution will be in the ratio 1 : 1 during the passage of current.
   E : The number of ions discharged at either electrode during electrolysis is independent of their relative speed.
5. **S :** The conductance of ions during passage of current through an electrolyte showing autoprotolysis are abnormally higher.
   E : The ions obtained during autoprotolysis show higher values due to Grotthus conductance.
6. **S :** Conductance of a solution can be obtained by designing the apparatus based on Wheatstone bridge principle.
   E : Meter bridge used to detect the resistance of metal wire can be used to read out the conductance of solutions.
7. **S :** The conductance measurement of an electrolytic solution is made by using two conductivity cells having different cell constants gives different values of conductance.
   E : The conductances of solution obtained will be different but conductivity of solution would be same.
8. **S :** Speed of ions depends upon nature of ions only.
   E : Mobility of ions depends upon mass, charge and size of ions only.

ANSWERS (Statement Explanation Problems)

1. (d) Both are facts.
2. (c) Explanation is correct reason for statement.
3. (b) $\Lambda_c vs. \sqrt{c}$ curves give Λ^∞ values on extrapolation to zero concentration for strong electrolytes only.
4. (b) The number of ions discharged on opposite electrodes is independent of their relative speed, however fall in concentration around any electrode depends upon the speed of ion moving away from it.
5. (c) Explanation is correct reason for statement.
6. (a) Some modifications such as A.C. in place of D.C., null point detector in place of galvanometer, etc., are to be made in meter bridge.
7. (d) Both are correct. The K is same in both cases because number of ions per c.c. remains same.
8. (b) Speed of ions depends upon nature of ions and potential gradient.

MATCHING TYPE PROBLEMS

Type I : More Than One Match Are Possible

1. **List A** **List B**

(A) Λ *vs* $c^{1/2}$ plots
1. $\Lambda°$ for strong electrolyte

(B) Kohlrausch law
2. Hyperbolic graph
3. Straight line graph
4. $\Lambda°$ for weak electrolyte

2. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List A. The variation in conductivity of these reactions is given in List B. Match List A with List B and select the correct using the code given below the lists : **[JEE (Advanced) II 2013]**

List A	List B
(P) $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH}$	(1) Conductivity decreases and then increases
(Q) $\underset{X}{KI(0.1M)} + \underset{Y}{AgNO_3(0.01M)}$	(2) Conductivity decreases and then does not change much
(R) $\underset{X}{CH_3COO} + \underset{Y}{KOH}$	(3) Conductivity increases and then does not change much
(S) $\underset{X}{NaOH} + \underset{Y}{HI}$	(4) Conductivity does not change much and then increases

Codes:

	P	*Q*	*R*	*S*
(a)	3	4	2	1
(b)	4	3	2	1
(c)	2	3	4	1
(d)	1	4	3	2

ANSWERS

1. A–1, 2, 3; B–1, 4
2. a

15 Thermodynamics

It involves a study of interrelation of various kinds of energy accompanying physical or chemical changes. Initially it meant for studies accompanying heat changes (*thermos* = heat, *dynamics* = flow) and interrelate heat energy with work. Now the term in broader sense involves all kinds of energy changes accompanying the process.

Terminology of Thermodynamics :

System: A specified part of universe selected for the study of effect of certain properties such as P, T, etc.

Surroundings: The adjacent part of universe outside the real or imaginary boundaries of system.

Types of Systems:

1. Homogeneous system : A system is supposed to homogeneous if it is uniform throughout, *i.e.*, all the substances present in it have only one phase.

2. Heterogeneous system : Not uniform throughout, *i.e.*, it has more than one phase.

Classification of system may also be made as;

1. Open system : A system which can exchange matter as well as energy with surroundings, *e.g.*, liquid kept in a beaker.

2. Closed system : A system which can exchange only energy with surroundings, *e.g.*, liquid in a sealed tube.

3. Isolated system : Neither exchange of matter nor exchange of energy is possible with surroundings.

State functions: The measurable properties of a system which depend only upon the state of system are known as state variables, *e.g.*, P, V, T, composition, energy, etc.

The cyclic rule: For 1 mole of an ideal gas

$$\left(\frac{\partial P}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P \times \left(\frac{\partial T}{\partial P}\right)_V = -1 \text{ or}$$

$$\left(\frac{\partial P}{\partial T}\right)_V \times \left(\frac{\partial T}{\partial V}\right)_P \times \left(\frac{\partial V}{\partial P}\right) = -1$$

State of system : The state of the system at a time signify for the fact that the variable factors, *e.g.*, P, V, T, etc. (which completely define the state of system) are known.

Properties of system : The thermodynamic properties of a system are divided as:

1. Intensive properties : Mass independent properties, *e.g.*, temperature, pressure, viscosity, density, refractive index, surface tension, chemical potential, etc.

2. Extensive properties : Mass dependent properties, *e.g.*, mass, volume, energy, heat enthalpy, entropy.

Note : An extensive property becomes intensive by specifying a unit amount of matter, *e.g.*, mass and volume are extensive but density = M/V is intensive property.

Thermodynamic process : The operations by which the changes from one state to other are made, are known as thermodynamic process. All thermodynamic properties satisfy

$$\Delta U = q + w$$

$$H = U + PV$$

$$S = \frac{q_{rev}}{T} \quad \ldots(1)$$

1. Reversible process : A reversible or quasistatic process is one in which all changes occurring at any part of the process are exactly reversed, when it is carried out in opposite direction. A reversible process involves :

(a) A slow change during investigations.

(b) Driving force is infinitesimally greater than the opposing force and *vice-versa*.

(c) The process may take place in either direction.

(d) Maximum work is obtained.

2. Irreversible process : A process whose direction cannot be reversed by small changes in variables is irreversible process. It involves :

(a) A fast change during investigation.

(b) Driving force is much different than opposing force.

(c) The unidirectional process.

(d) Net work somewhat lesser than maximum work, is obtained.

Heat and Temperature :

1. Heat is a measure of quantity of energy transferred from one body to other as a result of temperature difference between them.

2. Temperature is a measure of intensity of energy, *i.e.*, how much energetic each individual particle is.

Work : Work is expressed as the product of two factors, *i.e.*,

W = intensity factor × capacity factor

Intensity factor is measure of force against which work is done. Capacity factor is the extent for which work is done.

i.e., Mechanical work = force × displacement = $F \times d$

Gravitational work = gravitational force × height = $mg \times h$

Electrical work =

pot. difference × quantity of current = $E \times Q$

Work of expansion =

pressure × change in volume = $P \times \Delta V$

A –ve sign is given for work done by the system.

A +ve sign is given for work done on the system.

The general expression for all types of PV work can be written as

$$W = -P\Delta V$$

For expansion :

$\Delta V = V_2 - V_1 = +ve$ ($\because V_2 > V_1$) $\therefore$ $W = -ve$

For compression :

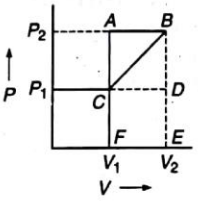
$\Delta V = V_2 - V_1 = -ve$ ($\because V_2 < V_1$) $\therefore$ $W = +ve$

Units of work : W = dyne cm or erg in C.G.S.
= newton m or joule in M.K.S.
= calorie

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg} = 4.184 \text{ J}$$

It is thus, evident that work, heat and energy have same units.

In P-V diagram as



w_{AC} = 0, since no area is covered by straight line.

w_{AB} = Area covered by square $ABEF$.

w_{BC} = Area covered by $BCEF$

= Area of square $CDEF$ + Area of triangle BCD

$$= P_1 \times (V_2 - V_1) + \frac{1}{2} \times \text{Area of square } ABCD$$

$$= P_1 \times (V_2 - V_1) + \frac{1}{2} \times (P_2 - P_1) \times (V_2 - V_1)$$

Also in a cyclic process w = –ve if clockwise and w = +ve if anticlockwise.

Internal energy : Each substance is associated with a definite amount of energy involving the energy depending upon the chemical nature of substance and the conditions of P, V, T. It includes many types of energies such as translational, vibrational, rotational, coulombic, potential energy, etc. Therefore, exact magnitude of internal energy cannot be determined. Furthermore, it is a state function and denoted by U and is independent of path. In thermodynamics we deal with the change in internal energy of two states,

$$\Delta U = U_2 - U_1$$

Heat enthalpy or heat content : Enthalpy 'H' is also a state function and independent of path. It is expressed as

$$H = U + PV$$

Like U, in thermodynamics we deal with change in heat enthalpy ΔH;

$$\Delta H = H_2 - H_1$$

Relation in between ΔH and ΔU : The two are related by

$$\Delta H = \Delta U + P\Delta V$$

at constant volume $\Delta H = \Delta U$ ($\because \Delta V = 0$)

First law of thermodynamics : According to this law, mass and energy of an isolated system remains constant. The law is expressed mathematically as

$dq = dU + (-dW)$ ...(1) (For an infinitesimal change)

where, dU = Change in internal energy

dq = Heat supplied to system

$-dW$ = Work done by the system

Also, $q = \Delta U + (-W)$ ...(2)

or $\Delta U = q + W$ (For finite change)

Some useful formulae based upon I law :

1. Isothermal process : A process in which temperature of the system remains constant throughout the studies.

$\because \Delta T = 0$ $\therefore \Delta U = 0$

$\therefore$ By Eq. (2) $q = -W$

i.e., heat given to a system is used in work done by the system.

2. Adiabatic process : A process during which no exchange of heat takes place in between system and surroundings.

$\because$ $q = 0$

$\therefore$ By Eq. (2) $+\Delta U = W$

or $-\Delta U = -W$

i.e., work is done by the system on the cost of its internal energy.

3. Cyclic process : A process in which initial state of system is regained after a series of operations.

$\because$ $\Delta U = 0$

$\therefore$ By Eq. (2) $q = -W$

4. Isochoric process : A process in which volume of the system remains constant throughout the investigations.

$\because$ $\Delta V = 0$

$\therefore$ By Eq. (2) $q_v = \Delta U$

i.e., heat given to a system under constant volume is used up in increasing internal energy.

5. Isobaric process : A process in which pressure of the system remains constant throughout the investigations.

$\because$ $\Delta P = 0$

Consider a system showing increase in volume from V_1 to V_2 at a constant pressure P, during absorption of heat q. The expansion work or work done by the system is $W = -P\Delta V$

Thus by Eq. (2) $q_p = \Delta U - (-P\Delta V)$

$= U_2 - U_1 - [-P(V_2 - V_1)]$

$= (U_2 + PV_2) - (U_1 + PV_1)$

$= H_2 - H_1 \quad (\because H = U + PV)$

$q_p = \Delta H$

i.e., heat given to a system under constant P is used up in increasing heat enthalpy of system. Work done in isobaric process $= dU - dq$

$= nC_v \cdot dT - nC_p \cdot dT = -nRdT$

$= -nR\,(T_{final} - T_{initial})$

6. Work done in irreversible isothermal process : Suppose an ideal gas expands against external pressure P and its volume changes by an amount dV then work done W can be given by

$$W = -PdV$$

(a) **Free expansion :** $W = 0$, Since, $P = 0$

(b) **Expansion or compression against external pressure P**

For a finite change V_1 or V_2,

Total work done on the system W is derived by

$$W = -P(V_2 - V_1)$$

or $$W_{irr} = -P(V_2 - V_1) \quad ...(3)$$

Also, $$\Delta U = \Delta H = 0 \quad ...(4)$$

If $V_2 > V_1$ then W_{irr} is –ve, *i.e.*, expansion work or work done by the system.

If $V_2 < V_1$ then W_{irr} is +ve, *i.e.*, compression work or work done on the system.

7. Work done in isothermal reversible process : Consider a system under isothermal condition, showing reversible expansion of an ideal gas by a volume dV, then

$\because \Delta U = 0 \quad \therefore dq = -dW = +PdV \quad (\because dW = -PdV)$

The total work done during expansion of gas from V_1 to V_2

$$\int dW = \int_{v_1}^{v_2} -P\,dV = \int_{v_1}^{v_2} -\frac{nRT}{V} \cdot dV$$

$$W_{rev} = -nRT \log_e \frac{V_2}{V_1} = -2.303\, nRT \log_{10} \frac{V_2}{V_1} \quad ...(5)$$

$(\because P \propto 1/V)$

Also, $$W_{rev} = -2.303\, nRT \log_{10} \frac{P_1}{P_2} \quad ...(6)$$

8. Work done in adiabatic reversible process : Consider a system under adiabatic conditions, showing reversible expansion of an ideal gas by a volume dV, then from I law of thermodynamics,

$(\because dq = 0)$

$$+dU = dW$$

$\because \quad dU = nC_v\,dT$ or $+C_v \cdot n \times dT = dW$

This equation reveals on further treatment within temperature limits of T_1 and T_2, reveals

$$dW = +C_v \times n \times dT$$

$$C_p - C_v = R$$

$$\frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v}$$

$$\gamma - 1 = \frac{R}{C_v}$$

$$C_v = \frac{R}{(\gamma - 1)}$$

Therefore, $$dW = +\frac{R}{(\gamma - 1)} \times n \times dT$$

$$dW = \frac{nR}{(\gamma - 1)} \cdot dT$$

on integration $$\int dW = \frac{nR}{\gamma - 1} \int_{T_1}^{T_2} dT$$

$$W_{rev} = \frac{nR}{\gamma - 1}[T_2 - T_1] \quad ...(7)$$

If $T_2 > T_1$ then W_{rev} = +ve, *i.e.*, work done on the system

If $T_2 < T_1$ then W_{rev} = –ve, *i.e.*, work done by the system

where γ is Poisson's ratio $= \frac{C_p}{C_v}$ ...(8)

Also, $$\Delta H = nC_p\,(T_2 - T_1) \quad ...(9)$$

If final temperature is not known :

$$w = -nC_vT_1\left[1 - \left(\frac{P_2}{P_1}\right)^{R/C_p}\right] \quad ...(10)$$

Some important results of adiabatic expansions

1. $PV^{\gamma} = \text{constant}$ ...(11)
2. $T^{\gamma}P^{1-\gamma} = \text{constant}$ ...(12)
3. $V^{\gamma-1}T = \text{constant}$ ...(13)

9. Work done in adiabatic irreversible expansion or compression :

(a) Expansion against vacuum or free expansion : $w = 0$

(b) Expansion or compression against external pressure :

$$w = -n \times P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right] \quad ...(14)$$

Efficiency η of Carnot cycle

(a) $$\eta = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} = \frac{Q_2 - Q_1}{Q_2} \quad ...(15)$$

where, Q_2 is the heat absorbed from the source at T_2 and $-Q_1$ is the heat lost to the sink at T_1. From Eq. (15).

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{Q_1}{Q_2}$$

Thus **"it is impossible to convert heat into equivalent amount of work without compensation."**

(b) $\eta = 1$ (100% efficiency) only when $T_1 = 0$K, (*i.e.*, –273°C) which is not practically possible.

(c) Greater the difference between T_2 and T_1 greater is the value of η. Hence, *superheated steam* (under high pressure) is used in an engine with a boiler.

Joule-Thomson Effect : *The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure through a small jet is called Joule-Thomson effect.*

(a) The temperature below which a gas becomes cooler on expansion is known as the inversion temperature T_i. Above this temperature gas shows heating effect.

$$T_i = \frac{2a}{Rb} \quad ...(16)$$

where, a and b called van der Waal's constant.

(b) Joule-Thomson effect is zero for an ideal gas in which van der Waal's forces of attraction are negligible and there is no expenditure of energy in overcoming these forces of attraction.

Joule-Thomson coefficient μ_{JT} is given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T / C_p \quad ...(17)$$

$\mu_{JT} = 0$ for an ideal gas, μ_{JT} = –ve for heating effect; μ_{JT} = +ve for cooling effect.

Entropy : Entropy (S) is a state function and is a measure of degree of disorder or randomness of system. More is the disorder in system, higher is its entropy. It is normally expressed in terms of change in entropy.

1. For a reaction entropy change (ΔS) is given by

$$\Delta S = \Sigma S_{\text{Products}} - \Sigma S_{\text{Reactants}} \quad ...(18)$$

2. $$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{W_{\text{rev}}}{T} = \frac{nRT \log_e \frac{V_2}{V_1}}{T} = nR \log_e \frac{V_2}{V_1}$$

$$= 2.303\, nR \log_{10} \frac{V_2}{V_1} \quad ...(19)$$

$$= 2.303\, nR \log_{10} \frac{P_1}{P_2} \quad ...(20)$$

where, q_{rev} is the heat supplied to a system at temperature T (K) under reversible conditions.

3. At constant P, $q_{\text{rev}} = \Delta H_{\text{rev}}$

$$\Delta S = \frac{\Delta H_{\text{rev}}}{T} \quad ...(21)$$

i.e., entropy change of fusion :

$$\Delta S_f = \frac{\Delta H_f}{T} \quad ...(22)$$

where T is freezing point

and entropy change of vaporization :

$$\Delta S_v = \frac{\Delta H_v}{T} \quad ...(23)$$

where T is boiling point

4. Entropy of one mole of a substance in pure state at one atmosphere and 25°C is termed as standard entropy, S°.

For a reaction in standard state, $A \longrightarrow B$

$$\Delta S^\circ = S^\circ_B - S^\circ_A \quad ...(24)$$

5. Entropy, S, is related to thermodynamic probability, W by the relation :

$$S = k \log_e W \text{ or } S = 2.303\, k \log_{10} W \quad ...(25)$$

where, k is Boltzmann's constant.

6. At absolute zero temperature, a solid is supposed to have highly ordered state, *i.e.*, $W = 1$ and hence $S = 0$, *i.e.*, $\lim_{T \to 0} S = 0$. This is zeroth law of thermodynamics.

Gibbs energy F or G : Free energy (F or G) is also a state function and is a measure of maximum work done. It is expressed as

$$G = H - TS \quad ...(26)$$

or $$\Delta G = \Delta H - T\Delta S \quad \text{at constant } T \quad ...(27)$$

Standard Gibbs energy change (ΔG°) :

1. $\Delta G^\circ = -2.303\, RT \log_{10} K$ ...(28)
2. At equilibrium $\Delta G = 0$.
3. The decrease in free energy ($-\Delta G$) is given as :

$$-\Delta G = W_{\text{net}} = 2.303\, nRT \log_{10} \frac{V_2}{V_1} \quad ...(29)$$

4. ΔG°_f for free elemental state = 0.
5. $\Delta G^\circ_f = G^\circ_{\text{Products}} - G^\circ_{\text{Reactants}}$ ...(30)

Conditions for spontaneity of reaction : For a spontaneous change ΔG = –ve. Thus, following results can also be evaluated for spontaneous process.

ΔH	ΔS		$\Delta H - T\Delta S$	Nature
–ve	+ve	∴	ΔG = –ve	Spontaneous
+ve	–ve	∴	ΔG = +ve	Non-spontaneous
+ve	+ve	if	$\Delta H < T\Delta S$; ΔG = –ve	Spontaneous
–ve	–ve		ΔG = –ve	Spontaneous
		if	$\Delta H > T\Delta S$	
			i.e., T is low	
			ΔG = +ve	Non-Spontaneous
		if	$\Delta H < T\Delta S$	
			i.e., T is high	

Gibbs-Helmholtz equations : It interrelates ΔG and ΔH at constant pressure :

$$\Delta G = \Delta H + T\left[\frac{\delta(\Delta G)}{\delta T}\right]_p \quad ...(31)$$

or $$\frac{\Delta G - \Delta H}{T} = \left[\frac{\delta(\Delta G)}{\Delta T}\right]_p \quad ...(32)$$

or $$-\Delta S = \left[\frac{\delta(\Delta G)}{dT}\right]_p \quad ...(33)$$

$$\Delta S = nF\left[\frac{\delta E_{\text{cell}}}{\delta T}\right]_p \quad (\because \Delta G = -nEF) \quad ...(34)$$

Thus, temperature coefficient of the emf of a cell is

$$\left[\frac{\delta E_{cell}}{dT}\right]_p = \frac{\Delta S}{nF} \quad ...(35)$$

Temperature dependence of vapour state or The Clapeyron – Clausius equation.

Variation of the vapour pressure for the liquid $\rightleftharpoons$ gas equilibrium is given by Clapeyron – Clausius equation.

$$\log P = -\frac{\Delta H_v}{2.303\,R}\left(\frac{1}{T}\right) + K \quad ...(36)$$

Eq. (36) represents the equation of a straight line. Hence, the plot of $\log P$ vs $\frac{1}{T}$ yields a straight line with slope $= -\frac{\Delta H_v}{2.303\,R}$ and intercept $= K$. This enables the evaluation of ΔH_v the **latent heat of vaporization.**

If vapour pressure P_1 and P_2 at temperatures T_1 and T_2 are known then by Eq. (36).

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad ...(37)$$

ΔH_v is latent heat of vaporisation in cal mol^{-1} or J mol^{-1}

• NUMERICAL PROBLEMS •

1. A system is provided 50 J of heat and work done on the system is 10 joule. What is the change in internal energy?
2. The work done by a system is 8 joule, when 40 joule heat is supplied to it. Calculate the increase in internal energy of system.
3. A gas occupies 2 litre at STP. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm. Calculate change in its internal energy.
4. A certain electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each second?
5. An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T. The other portion is a perfect vacuum. If a hole is opened between two portions, calculate :
   (a) the change in internal energy
   (b) the change in temperature of gas.
6. Two litre of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.
7. 2.8 g of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate $\Delta U, q$ and W for the gas.
8. Calculate the work done in open vessel at 300 K, when 92 g Na reacts with water. Assume ideal gas nature.
9. The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is + 0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.
10. Calculate the work done when a system raises a column of water of radius 5.0 mm through 10 cm.
11. Calculate the work done when 50 g of iron reacts with hydrochloric acid in (i) a closed vessel of fixed volume (ii) an open beaker at 25°C.
12. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.
13. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is 4.184 J g^{-1} K^{-1}, what is the final temperature of water?
14. A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water of temperature 290 K. Calculate final temperature of water. Specific heat of water = 4.184 J g^{-1} K^{-1}. **(Roorkee 1993)**
15. Calculate the maximum work done in expanding 16 g of oxygen at 300 K and occupying a volume of 5 dm^3 isothermally until the volume becomes 25 dm^3.
16. Calculate $q, W, \Delta U$ and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K. **(Roorkee 2000)**
17. What work is to be done on 2 mole of a perfect gas at 27°C if it is compressed reversibly and isothermally from a pressure of 1.01×10^5 Nm^{-2} to 5.05×10^6 Nm^{-2}? Also calculate the Gibbs energy change.
18. 1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume V_1 to a final volume $10V_1$ and does 10 kJ of work. The initial pressure was 1×10^7 Pa.
   (a) Calculate V_1.
   (b) If there were 2 mole of gas, what must its temperature have been? **(Roorkee 2001)**
19. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5L. Calculate $q, W, \Delta U$ and ΔH for this process. $R = 2.0$ cal K^{-1} mol^{-1}, $\log_{10} 2 = 0.30$. Atomic mass of Ar = 40. **(Roorkee 1997)**
20. At 27°C, one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate ΔU and q.
21. One mole of an ideal gas is heated at constant pressure from 0°C to 100°C.
   (a) Calculate work done.
   (b) If the gas was expanded isothermally and reversibly at 0°C from 1 atm to some other pressure P_t, what must be the final pressure if the maximum work is equal to the work involved in (a)?
22. Water is boiled under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at boiling point (373.15 K).
23. In an insulated container 1 mole of a liquid, molar volume 100 mL at 1 bar. Liquid is steeply taken to 100 bar, when volume of liquid decreases by 1 mL. find ΔH and ΔU for the process. **(IIT 2004)**
24. Calculate the standard internal energy change for the reaction;

$$OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$$

at 298 K. The standard enthalpies of formation of $OF_2(g)$, $H_2O(g)$, $HF(g)$ are +20, +250 and –270 kJ mol^{-1}.

25. Two mole of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L).

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L).

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

(i) Sketch with labels each of the processes on the same *P-V* diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the values of ΔU, ΔH and ΔS for the overall process? **(IIT 2002)**

26. 14 g oxygen at 0°C and 10 atm are subjected to reversible adiabatic expansion to a pressure of 1 atm. Calculate the work done in :

(a) Litre atm.

(b) Calorie (Given, $C_p / C_v = 1.4$).

27. A flask of 1 litre having $NH_3(g)$ at 2.0 atm and 200 K is connected with another flask of volume 800 mL having $HCl(g)$ at 8 atm and 200 K through a narrow tube of negligible volume. The two gases reacts to form $NH_4Cl(s)$ with evolution of 43 kJ mol^{-1} heat. If heat capacity of $HCl(g)$ at constant volume is 20 JK^{-1} mol^{-1} and neglecting heat capacity of flask, NH_4Cl and volume of solid NH_4Cl formed, calculate the heat produced, final temperature and final pressure in flasks. (Assume $R = 0.08$ litre-atm K^{-1} mol^{-1}).

28. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{v.m}$ for argon is 12.48 JK^{-1} mol^{-1}. **(IIT 2000)**

29. Calculate the equilibrium constant for the reaction given below at 400K, if $\Delta H^\circ = 77.2$ kJ mol^{-1} and $\Delta S^\circ = 122\ JK^{-1}\ mol^{-1}$.

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

30. A sample of ideal gas ($\gamma = 1.4$) is heated at constant pressure. If an amount of 140 J of heat is supplied to gas, find ΔU and W.

31. One mole of an ideal gas which $C_v = \frac{3}{2}R$ is heated at a constant pressure of 1 atm from 25°C to 100°C. Calculate ΔU, ΔH and the entropy change during the process.

32. Consider a class room of dimensions $5 \times 10 \times 3\ m^3$ at temperature 20°C and pressure 1 atm. There are 50 peoples in the room, each losing energy at the average of 150 watt. Assuming that the walls, ceiling, floor and furniture perfectly insulated and none of them absorbing heat, how much time will be needed for rising the temperature of air in the room to body temperature, *i.e.*, 37°C? For air $C_p = \frac{7}{2}R$. Loss of air to the outside as the temperature rises may be neglected.

33. 50 students sitting in the room of $5 \times 10 \times 3\ m^3$ dimensions. The air inside the room is at 27°C and 1 atm pressure. If each student loses 100 watt heat per second assuming the walls, ceiling, floor and all the material present inside the room is perfectly insulated as well as neglecting loss of air to the outside as the temperature is raised, how much rise in temperature will be noticed in 10 minutes? Given $C_p = \frac{7}{2}R$ for air.

34. An athlete in a gymnasium room lifts a 50 kg mass through a vertical distance of 2.0 m; $g = 9.8\ m\ s^{-2}$. The mass is allowed to fall through 2.0 m distance while coupled to an electrical generator. The electrical generator produces an equal amount of electrical work. This electrical work is used to produce aluminium by Hall's process involving the change.

$$Al_2O_3(\text{molten}) + 3C(s) \longrightarrow 2\,Al(l) + 3CO(g)$$

The reaction require standard free energy change equal to 593 kJ. How many times must the athlete lift the 50 kg mass and to drop and couple with generator to produce sufficient Gibbs free energy to produce 27 g Al?

35. An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 metre. Its engine run with pure normal octane (C_8H_{18}) has a 30% efficiency. Calculate the fuel cost of the flight, if octane sells at Rs. 3 per litre. Given density of octane = 0.705 g mL^{-1}, heat of combustion of octane = 1300 kcal mol^{-1}. ($g = 981\ cm / sec^2$)

36. A lead bullet weighing 18.0 g and travelling at 500 m/s is embedded in a wooden block of 1.00 kg. If both the bullet and the block were initially at 25.0°C, what is the final temperature of block containing bullet? Assume no temperature loss to the surroundings. (Heat capacity of wood = 0.5 kcal/kg-K; heat capacity of lead = 0.030 kcal / kg - K)

37. A mixture contains 8 g He and 14 g N_2 in a vessel at 300K. How much heat is required to increase the rms speed of these molecules to double their value? Also, calculate the final temperatures.

38. Calculate the Gibbs energy change when 1 mole of NaCl is dissolved in water at 298 K. Given,

(a) Lattice energy of NaCl = 778 kJ mol^{-1}.

(b) Hydration energy of NaCl = 774.3 kJ mol^{-1}.

(c) Entropy change at 298 K = 43 J mol^{-1}.

39. How much heat is requied to change 10 g ice at 0°C to steam at 100°C? Heat of fusion and heat of vaporization for H_2O are 80 cal/g and 540 cal/g respectively. Specific heat of water is 1 cal/g.

40. A steam boiler made up of steel weighs 900 kg. The boiler contains 400 kg of water. Assuming 70% of the heat is delivered to boiler and water, how much heat is required to raise the temperature of the whole from 10°C to 100°C? Heat capacity of steel is 0.11 kcal/kg-K and heat capacity of water is 1 kcal/kg-K.

41. Determine whether or not, it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Also calculate equilibrium constant. Given that G_f° of Al_2O_3 at 298 K $= -1582$ kJ mol^{-1}; G_f° of $Na_2O(s)$ at 298 K $= -377$ kJ mol^{-1}.

42. The vapour pressure of benzene is 1.53×10^4 Nm^{-2} at 303 K and 5.2×10^4 Nm^{-2} at 333 K. Calculate the mean latent heat of evaporation of benzene over this temperature range.

43. Calculate the change in entropy for the fusion of 1 mole of ice. The melting point of ice is 273 K and molar enthalpy of fusion for ice = 6.0 kJ mol^{-1}.

44. Molar heat capacity of CD_2O (deuterated form of formaldehyde) at constant pressure is 14 cal mol^{-1} K^{-1} at 1000 K. Calculate the entropy change associated with cooling of 3.2 g of CD_2O vapour from 1000 to 900 K.

45. Calculate entropy change for vaporization of 1 mole of liquid water to steam at 100°C, if $\Delta H_v = 40.8$ kJ mol^{-1}.

46. For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 J mol^{-1} and -105 J mol^{-1} K^{-1} respectively. Find out whether this reaction is spontaneous or not?

47. Determine the entropy change for the reaction given below;

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

at 300 K. If standard entropies of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ are 126.6, 201.20 and 68.0 J K^{-1} mol^{-1} respectively.

48. 1 mole of an ideal gas at 25°C is subjected to expand reversibly ten times of its initial volume. Calculate the change in entropy of expansions.

49. A sample of 100 g H_2O is slowly heated from 27°C to 87°C. Calculate the change in entropy during heating (Specific heat of water = 4200 J/kg-K).

50. Calculate the entropy change when 1 kg of water is heated from 27°C to 200°C forming super heated steam under constant pressure. Given specific heat of water = 4180 J / kg - K and specific heat of steam $= 1670 + 0.49T$ J/kg-K and latent heat of vaporization $= 23 \times 10^5$ J/kg.

51. Titanium metal is extensively used in aerospace industry because the metal imparts strength to structures but does not unduly add to their masses. The metal is produced by the reduction of $TiCl_4(l)$ which in turn is produced from mineral rutile $TiO_2(s)$. Can the following reaction for production of $TiCl_4(l)$ be carried out at 25°C?

$$TiO_2(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + O_2(g)$$

Given that, H_f° for $TiO_2(s)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are -944.7, -804.2, 0.0, 0.0 kJ mol^{-1}. Also S° for $TiO_2(g)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are 50.3, 252.3, 233.0, 205.1 J mol^{-1} K^{-1} respectively.

52. For a reaction $M_2O(s) \rightarrow 2M(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm. Calculate up to which temperature the reaction would not be spontaneous?

53. Calculate the temperature at which the reaction give below is at equilibrium, $Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g)$.

Given, $\Delta H = 30.5$ kJ mol^{-1} and $\Delta S = 0.066$ kJ K^{-1}mol^{-1}.

54. The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below :

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$\Delta H^\circ_{300\,K} = -41.16$ kJ mol^{-1};

$\Delta S^\circ_{300\,K} = -4.24 \times 10^{-2}$ kJ mol^{-1}

$\Delta H^\circ_{1200\,K} = -32.93$ kJ mol^{-1};

$\Delta S^\circ_{1200\,K} = -2.96 \times 10^{-2}$ kJ mol^{-1}

Calculate K_p at each temperature and predict the direction of reaction at 300 K and 1200 K, when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1$ atm at initial state.

55. One mole of CH_3COOH undergoes dimerization in vapour phase at 127°C as :

$$2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

Calculate the change in standard entropy during dimerization if dimer formation is due to two H-bonds involved in dimer, each of 33 kJ strength and the degree of dimerisation of acetic acid 98.2%.

56. Derive a relation showing reversible work of expansion from volume V_1 to V_2 by 'n' moles of a real gas obeying van der Waals' equation at temperature T where volume occupied by molecules may be taken as negligible in comparison to total volume of gas.

SOLUTIONS (Numerical Problems)

1. $q = 50\,J$

$W = +10\,J$ (work done on the system)

$\therefore \quad \Delta U = q + W = 50 + 10$

$\therefore \quad \Delta U = \mathbf{60\ J}$

2. $W = -8\,J; \quad q = 40\,J$

From I law $\quad \Delta U = q + W = 40 - 8$

$\therefore \quad = \mathbf{32\ joule}$

3. Work done $= -P \times dV = 1 \times (2.5 - 2.0)$

$= -0.5$ litre $-$ atm

$\because$ Work is carried out at constant P and thus irreversible.

$$= -\frac{0.5 \times 1.987 \times 4.184}{0.0821} \text{ joule} = -50.63\,J$$

From I law of thermodynamics

$\because \quad q = \Delta U - W$

$300 = \Delta U + 50.63 \quad \therefore \quad \Delta U = \mathbf{249.37\ joule}$

4. Energy is lost from the system as work thus W is negative.

$W = -15$ kJ

Energy is lost as heat, so $q = -2$ kJ

Therefore, by first law of thermodynamics :

$\Delta U = q + W = -2 - 15 = \mathbf{-17\ kJ}$

5. The system being thermally insulated and thus $q = 0$. The gas expands through hole in other portion to show free expansion, *i.e.*,

$w = -\int P\Delta V = 0$ (Since, $P = 0$)

Also from I law of thermodynamics

$q = \Delta U + w$

Since, $\quad q = 0; \quad w = 0 \quad \therefore \ \Delta U = \mathbf{0}$

Also internal energy $U = \frac{3}{2}RT$. Since, internal energy remains same ($\because \Delta U = 0$) and thus temperature will also remains **constant.**

6. Since, the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$\therefore \quad W = -P_{ext}(V_2 - V_1)$

$W = -1 \times (V_2 - V_1)$

Given, $\quad V_1 = 2$ litre $\quad V_2 = ? \quad T = 273$ K

$P_1 = 5$ atm $\quad P_2 = 1$ atm

$\therefore \quad P_1V_1 = P_2V_2$

$\therefore \quad V_2 = \frac{2 \times 5}{1} = 10$ litre

$\therefore \quad W = -1 \times (10 - 2) = -8$ litre-atm

$$= -\frac{8 \times 1.987}{0.0821} \text{ calorie} = -\frac{8 \times 1.987 \times 4.184}{0.0821} \text{ J}$$

$= \mathbf{810.10\ joule}$

7. Initially for N_2

$20 \times V_1 = \frac{2.8}{28} \times 0.0821 \times 300 \ \therefore \ V_1 = 0.123$ litre

Finally for N_2

$1 \times V_2 = \frac{2.8}{28} \times 0.0821 \times 300 \ \therefore \ V_2 = 2.463$ litre

$\therefore \quad W = -P \times \Delta V$ [$\because$ work is done against constant P $\therefore$ irreversible]

$= -1 \times (2.463 - 0.123)$

$= -2.340$ litre-atm

$$= -\frac{2.340 \times 1.987}{0.0821} \text{ calorie}$$

$$= -\frac{2.340 \times 1.987 \times 4.184}{0.0821} \text{ J}$$

$W = \mathbf{-236.95\ J}$

Now $\quad q = \Delta U - W$

$q = 0 + 236.95$ ($\because \Delta U = 0$ for isothermal process)

$q = \mathbf{236.95\ joule}$

8. $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

$$\text{Mole of Na} = \frac{92}{23} = 4$$

$$\text{Mole of } H_2 \text{ formed} = \frac{1}{2} \times \text{Mole of Na used} = \frac{1}{2} \times 4 = 2$$

Work is done in giving out 2 mole H_2. Thus,

$W = -P \times V_{H_2} = n_{H_2}\,RT = -2 \times 8.314 \times 300 = \mathbf{-4988.4\ J}$

The H_2 liberated pushes the atmospheric gas back and thus, does work in driving back the atmosphere. Note that in case of closed vessel $\Delta V = 0, \ \therefore \ W = 0$.

9. $\Delta H = \Delta U + P\Delta V$

Given, $\quad \Delta U = +0.21\,kJ\,mol^{-1} = 0.21 \times 10^3\,J\,mol^{-1}$,

$P = 1\,bar = 1.0 \times 10^5$ Pa

$\Delta V = V_{(aragonite)} - V_{(calcite)}$

$$= \left(\frac{100}{2.93} - \frac{100}{2.71}\right) cm^3\ mol^{-1} \text{ of } CaCO_3 = -2.77\,cm^3$$

$$= -2.77 \times 10^{-6}\ m^3$$

$\therefore \quad \Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6}$

$= \mathbf{209.72\ J = 0.20972\ kJ\ mol^{-1}}$

10. Work is given : $\quad W = -mgh$

where, $\quad m = \text{volume} \times \text{density} = \pi r^2 l \times d$

$$= \frac{22}{7} \times (0.5)^2 \times 10 \times 1$$

$g = 980\,cm\,s^{-2}$

$h = \frac{10}{2} = 5$ cm

(The centre of mass of column lies half way along its length l therefore the centre of mass is raised to a height $h = \frac{1}{2}l$)

$\therefore \quad W = -\frac{22}{7} \times (0.5)^2 \times 10 \times 1 \times 980 \times 5 = -38.5 \times 10^3$ erg

$= \mathbf{-3.85 \times 10^{-3}\ J}$

The negative sign shows that system shows a decrease in internal energy.

11. (i) Vessel is of fixed volume, hence $\Delta V = 0$. No work is done.

$W = 0$

(ii) The gas drives back the atmosphere hence.

$W = -P_{ext} \cdot \Delta V$

Also, $\Delta V = V_{final} - V_{initial} \simeq V_{final}$ $(\because V_{initial} = 0)$

$\therefore \quad \Delta V = \frac{nRT}{P_{ext}}$ or $W = -P_{ext} \cdot \frac{nRT}{P_{ext}} = -nRT$

where, n is the number of mole of H_2 gas obtained from n mole of Fe(s).

$$\underset{1\text{ mole}}{Fe(s)} + 2HCl(aq.) \longrightarrow FeCl_2(aq.) + \underset{1\text{ mole}}{H_2(g)}$$

$\therefore \quad n = \frac{50}{56} = 0.8929$ mole

$\therefore \quad W = -0.8929 \times 8.314 \times 298 = \mathbf{-2212.22\ J}$

The reaction mixture in the given system does 2.212 kJ of work driving back to atmosphere.

12. Since, work is done against constant pressure and thus, irreversible.

Given, $\Delta V = (6-2) = 4$ litre; $P = 1$ atm

$\therefore \quad W = -1 \times 4$ litre-atm $= -\frac{1 \times 4 \times 1.987}{0.0821}$ cal

(since 0.0821 litre-atm = 1.987 cal)

$= -96.81$ cal $= -96.81 \times 4.184$ J ($\because$ 1 cal = 4.184 J)

$= -405.05$ J

Now from I law of thermodynamics

$q = \Delta U - W$

$800 = \Delta U + 405.05 \quad \therefore \quad \Delta U = \mathbf{394.95\ joule}$

13. Since, work is done against constant pressure and thus irreversible.

Given, $\Delta V = (6-4) = 2$ litre; $P = 2.5$ atm

$\therefore \quad W = -P_{ext} \times \Delta V = -2.5 \times 2 = -5$ litre-atm

$= -\frac{5 \times 1.987}{0.0821}$ cal $= -\frac{5 \times 1.987 \times 4.184}{0.0821}$ J

$= -506.31$ J

Now this work is used in heating 1 mole water

$W = n \times C \times \Delta T$

$506.31 = 1 \times 4.184 \times 18 \times \Delta T \quad \left[\because C = 4.184\ J\,g^{-1}\,K^{-1} \therefore = 4.184 \times 18\ J\,mol^{-1}\right]$

$\therefore \quad \Delta T = 6.723$

$\therefore$ Final temperature $T_1 + \Delta T = 293 + 6.723 = \mathbf{299.723\ K}$

14. Since, work is done against constant P and thus, irreversible

$\Delta V = 5 - 3 = 2\,dm^3 = 2$ litre; $P = 3$ atm

$\therefore \quad W = -P.\Delta V = -3 \times 2$ litre-atm

$= -\frac{6 \times 4.184 \times 1.987}{0.0821}$ joule $= -607.57$ joule

Now this work is used up in heating water

$\therefore \quad W = n \times C \times \Delta T$

$607.57 = 10 \times 4.184 \times 18 \times \Delta T \quad \therefore \quad \Delta T = 0.81$

$\therefore$ Final temperature $T_1 + \Delta T = 290 + 0.81 = \mathbf{290.81\ K}$

15. Since, maximum work and thus, process is reversible

$n_{O_2} = \frac{w}{M} = \frac{16}{32}, \quad R = 8.314$ J, $\quad T = 300$ K,

$V_1 = 5\,dm^3, \; V_2 = 25\,dm^3$

$W = -2.303\,nRT \log_{10} \frac{V_2}{V_1}$

$= -2.303 \times \frac{16}{32} \times 8.314 \times 300 \log_{10} \frac{25}{5}$

$= \mathbf{-2.01 \times 10^3\ joule}$

16. For isothermal reversible expansion :

$W = -2.303\,nRT \log \frac{P_1}{P_2} = -2.303 \times 1 \times 8.314 \times 273 \log \frac{1.0}{0.1}$

$W = \mathbf{-5227.2\ J}$

At constant temperature, for expansion $\Delta T = 0$; Therefore, $\Delta U = \mathbf{0}$

Also, $\Delta U = 1 \times C_v \times \Delta T = 0$ (For 1 mole)

and $\Delta U = q + W \quad \therefore \quad q = -W = \mathbf{5227.2\ J}$

Also when temperature is constant $P_1V_1 = P_2V_2$ or PV is constant.

Thus, $\Delta H = \Delta U + \Delta(PV) \quad \therefore \quad \Delta H = \mathbf{0}$

17. For reversible process :

$W_{rev} = -2.303\,nRT \log \frac{P_1}{P_2}$

$= -2.303 \times 2 \times 8.314 \times 300 \log_{10} \frac{1.01 \times 10^5}{5.05 \times 10^6}$

$= \mathbf{+1.9518 \times 10^4\ joule}$

Since, W_{rev} is a measure of free energy change

$\therefore \quad -\Delta G = -W_{rev} = -W_{max}$

or $\quad \Delta G = \mathbf{1.9518 \times 10^4\ joule\ mol^{-1}}$

18. (a) $W = -2.303\,nRT \log \frac{V_2}{V_1}$

Where, W is work done by the system under isothermal reversible conditions, note that work done by the system is negative

$$-10 \times 10^3 = -2.303 \times 1 \times 8.314 \times T \log \frac{P_1}{P_2} \qquad ...(i)$$

Also, $P_1V_1 = P_2V_2$ at constant temperature

$1 \times 10^7 \times V_1 = P_2 \times 10V_1 \quad \therefore \quad P_2 = \frac{1 \times 10^7}{10} = 10^6$ Pa

$\therefore$ By Eq. (i), $-10 \times 10^3 = -2.303 \times 1 \times 8.314 \times T \log \frac{10^7}{10^6}$

$\therefore \quad T = 522.27$ K

Now, using $PV = nRT$ for 1 mole of gas;

$P = 1 \times 10^7$ Pa $= 10^7$ Nm^{-2}

$1 \times 10^7 \times V_1 = 1 \times 8.314 \times 522.27$

$V = \mathbf{4.34 \times 10^{-4}\ m^3}$

(b) If 2 mole of gas have been used, the temperature would have been

$\frac{522.27}{2} = \mathbf{261.13\ K}$

19. $W = -2.303\,nRT \log_{10} \frac{V_2}{V_1} = -2.303 \times \frac{10}{40} \times 2 \times 300 \log_{10} \frac{5}{10}$

$W = 103.991$ cal

$\Delta U = 0$

$\therefore \quad q = \Delta U - W \quad \therefore \quad q = -W = -103.991$ cal

Also when temperature is constant $P_1V_1 = P_2V_2$ or PV = constant

$\therefore \quad \Delta H = \Delta U + \Delta(PV) = 0 + 0 = \mathbf{0}$

20. $W = -2.303\, nRT \log_{10} \dfrac{P_1}{P_2}$

$W = -2.303 \times 1 \times 2 \times 300 \log_{10} \dfrac{2}{10} = +965.84$ cal

For isothermal change $\Delta U = 0$

Also $q = \Delta U - W = 0 - 965.84$ cal

$\therefore$ $q = \mathbf{-965.84\ cal}$

21. (a) Work involved in heating of gas

$W_a = -P \cdot \Delta V = -P(V_2 - V_1)$

$= -P\left(\dfrac{nRT_2}{P} - \dfrac{nRT_1}{P}\right)$

$= -nR\,(T_2 - T_1) = -1 \times 1.987(373 - 273)$

$= \mathbf{-198.7\ cal}$

(b) Now the work equivalent to 198.7 cal is used up in causing reversible isothermal expansion of gas at 0°C, then

$W_R = -2.303\, nRT \log_{10} \dfrac{P_1}{P_2}$

$\therefore$ $-198.7 = -2.303 \times 1 \times 1.987 \times 273 \log_{10} \dfrac{1}{P_t}$

$\therefore$ $P_t = \mathbf{0.694\ atm}$

22. The vaporization occurs at constant pressure therefore the enthalpy change is equal to the work done by the heater :

$\Delta H' = 0.50 \times 12 \times 300$ $(\Delta H = i \times V \times t)$

$= 1800\ \text{J} = +1.8\ \text{kJ}$

$\therefore$ Molar enthalpy of vaporization

$$\Delta H = \frac{\Delta H'}{\text{mole of } H_2O} = \frac{\Delta H}{n_{H_2O}}$$

$$= \frac{1.8}{\left(\dfrac{0.798}{18}\right)} = \mathbf{40.6\ kJ\ mol^{-1}}$$

Also, $\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_g\, RT = \Delta U + RT$

$(\because\ H_2O(l) \rightleftharpoons H_2O(g),\ \Delta n_g = 1)$

$\therefore$ ΔU = molar internal energy change

$= \Delta H - RT = 40.6 - 8.314 \times 10^{-3} \times 373.15$

$= \mathbf{37.5\ kJ\ mol^{-1}}$

23. Volume of 1 mole liquid = 100 mL at pressure 1 bar

Volume of 1 mole liquid = 99 mL at pressure 100 bar

The process is irreversible as it is steeply changed from 1 bar to 100 bar. Therefore,

$W = -P(V_2 - V_1) = -100(99 - 100)$

$= 100$ bar mL

Also, $\Delta U = q + W$

$q = 0$ since container is insulated

$\therefore$ $\Delta U = 100$ bar mL

Also, $\Delta H = \Delta U + P\Delta V = \Delta U + P_2V_2 - P_1V_1$

$= 100 + (100 \times 99 - 1 \times 100) = \mathbf{9900\ bar\ mL}$

24. $\Delta H^\circ_{\text{Reaction}} = \Sigma H^\circ_{\text{Products}} - \Sigma H^\circ_{\text{Reactants}}$

$= [2 \times H^\circ_{HF}\,(g) + H^\circ_{O_2}\,(g)] - [H^\circ_{OF_2}\,(g) + H^\circ_{H_2O}\,(g)]$

$\because$ H° of free elements = 0 $\therefore$ $H^\circ_{O_2} = 0$

$\because$ $\Delta H^\circ_f = H^\circ$, *i.e.*, standard heat of formation

= standard heat enthalpy of a compound

Also, ΔH°_f for F_2O is +ve; ΔH°_f for H_2O is −ve, because heats of combination are exothermic.

$\Delta H^\circ_R = [2 \times (-270)] + 0 - [20 + (-250)] = -310$ kJ

Now $\Delta H^\circ = \Delta U^\circ + \Delta nRT$

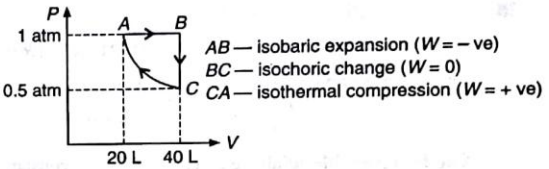
$\because$ $\Delta H^\circ_R = -310 \times 10^3$ J; $\Delta n = 3 - 2 = 1$

$R = 8.314$ J; $T = 298$ K

$\therefore$ $-310 \times 10^3 = \Delta U^\circ + 1 \times 8.314 \times 298$

$\therefore$ $\Delta U^\circ = -312477.5$ joule $\therefore$ $\Delta U^\circ = \mathbf{-312.4775\ kJ}$

25. The overall process is cyclic one, *i.e.*, initial state is regained, thus, $\Delta U = 0$; $\Delta H = 0$ and $\Delta S = 0$.



Now, total work $W = W_{A \to B} + W_{B \to C} + W_{C \to A}$

$\therefore$ $W = -P(V_B - V_A) + 0 + 2.303\ nRT \log \dfrac{V_C}{V_A}$

(work of expansion) (work of compression)

$= -1 \times (40 - 20) + 0 + 2.303 \times P_AV_A \log \dfrac{V_C}{V_A}$

$(\because P_AV_A = nRT)$

$= -20 + 2.303 \times 1 \times 20 \times \log \dfrac{40}{20}$

$= -20 + 13.87 = -6.13$ litre-atm

$= -\dfrac{6.13 \times 8.314}{0.0821}\ \text{J} = -620.77\ \text{J}$

Also, $q = -w = \mathbf{+620.77\ J}$ (For cyclic process)

26. $P_1 = 10$ atm at $T = 273$ K for $\dfrac{14}{32}$ mole O_2

$P_2 = 1$ atm at $T = T_2$ for $\dfrac{14}{32}$ mole O_2

For adiabatic expansion we have $T^\gamma \cdot P^{1-\gamma} = \text{constant}$

$\therefore$ $\left(\dfrac{T_1}{T_2}\right)^\gamma = \left(\dfrac{P_2}{P_1}\right)^{1-\gamma}$ or $\gamma \log \dfrac{T_1}{T_2} = (1 - \gamma) \log \dfrac{P_2}{P_1}$

or $1.4 \log \dfrac{273}{T_2} = (1 - 1.4) \log \dfrac{1}{10}$ $\therefore$ $T_2 = 141.4$ K

Work done in adiabatic expansion $= \dfrac{nR}{(\gamma - 1)}(T_2 - T_1)$

$$\textbf{In litre-atm} = \frac{14}{32} \times \frac{0.0821(141.4 - 273)}{(1.4 - 1)}$$

$W_{rev} = \mathbf{-11.82\ liter\text{-}atm}$

$$\textbf{In calorie} = \frac{14}{32} \times \frac{2 \times (141.4 - 273)}{(1.4 - 1)}$$

$W_{rev} = \mathbf{-287.88\ cal}$

27. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$; $\Delta H = -43.0$ kJ

Initial mole $\frac{1\times2}{0.08\times200}$ $\frac{8\times0.8}{0.08\times200}$

$= 0.125$ $= 0.4$ 0

Final mole 0 0.275 0.125

$\therefore$ Heat produced $= 0.125\times43 =$ **5.375 kJ**

The heat produced is used to increase the temperature of HCl left in flask since heat capacity of flask and $NH_4Cl = 0$

$\therefore$ $Q = n\times C_v \times \Delta T$

$5.375\times10^3 = 0.275\times20\times\Delta T$ $\therefore$ $\Delta T =$ **977.27**

$\therefore$ Final temperature $= 200 + 977.27 =$ **1177.27 K**

Also final pressure $= \frac{nRT}{V} = \frac{0.275\times0.08\times1177.27}{1.8}$

$=$ **14.39 atm**

28. $\Delta H = n\times C_p \times \Delta T$

and $C_p = C_v + R = 12.48 + 8.314 = 20.794$ JK^{-1} (R in J)

For a given sample of argon gas, mole (n)

$$n = \frac{PV}{RT} = \frac{1\times1.25}{0.0821\times300} = 0.05$$

Also for reversible adiabatic change $(TV)^{\gamma-1}$ = constant

or $T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$ or $T_2 = T_1\times\left(\frac{V_1}{V_2}\right)^{\gamma-1}$

($\gamma = 1.66$ for argon)

$$= 300\times\left(\frac{1.25}{2.50}\right)^{1.66-1} = 300\times\left(\frac{1}{2}\right)^{0.66}$$

$\therefore$ $T_2 = 189.85$ K

$\therefore$ $\Delta T = T_2 - T_1 = 189.85 - 300 = -110.15$

Thus, $\Delta H = 0.05\times20.794\times(-110.15) =$ **−114.52 J**

29. $\Delta H^\circ = 77.2$ mol^{-1}

$\Delta S^\circ = 122$ JK^{-1} mol^{-1}

$T = 400$ K

$\therefore$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = 77200 - 400\times122 = 28400$ J

Also, we have $-\Delta G^\circ = 2.303\,RT\log_{10}K_C$

where, K_C is equilibrium constant

$\therefore$ $-28400 = 2.303\times8.314\times400\log_{10}K_C$

$\therefore$ $K_C =$ **1.958×10^{-4}**

30. Gas is diatomic as $\gamma = 1.4$, thus, $C_v = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$

Given, $\Delta H = 140$ J at constant pressure

$\therefore$ $\Delta H = q_p = n\times C_p \times \Delta T$

Also, $\Delta T = \frac{140}{nC_p} = \frac{140\times2}{7n\times R} = \frac{40}{n}$

Now, $W = -nR\Delta T = -n\times2\times\frac{40}{n} =$ **− 80 J**

Also, $q_p = \Delta H = \Delta U + (-W)$

$\Delta U = \Delta H + W$

$\therefore$ $= 140 - 80$

$\Delta U =$ **60 J**

31. $\because$ $C_v = \frac{3}{2}R$ $\therefore$ $C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R$

$\therefore$ Heat given at constant pressure $= m\cdot C_p\cdot\Delta T$

or ΔH or $q_p = 1\times\frac{5}{2}\times R\times(373-298)$

or $\Delta H = 1\times\frac{5}{2}\times1.987\times75 = 372.56$ cal

Now work done in the process $= -P\Delta V$

$$W = -P(V_2 - V_1) = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$$

($\because$ $PV = nRT$)

$= -nR(T_2 - T_1) = -1\times1.987\times(373-298)$

$=$ **−149.025 cal**

$\therefore$ From I law of thermodynamics

$\Delta U = q + W = 372.56 - 149.05$ $\therefore$ $\Delta U =$ **223.51 cal**

Also, $dq_{rev} = nC_p\cdot dT$

$dS = \frac{dq_{rev}}{T}$ $\therefore$ $dS = \frac{nC_p\cdot dT}{T}$

or $\Delta S = \int_{T_1}^{T_2}\frac{nC_p\cdot dT}{T} = nC_p\log e\frac{T_2}{T_1}$

$\therefore$ $\Delta S = 2.303\,nC_p\log_{10}\frac{T_2}{T_1}$

$= 2.303\times1\times\frac{5}{2}\times R\times\log_{10}\frac{373}{298}$

$=$ **1.122 cal K^{-1} mol^{-1}**

32. Volume of air in the room

$= 5\times10\times3 = 150\ m^3 = 150\times10^6\ cm^3$

$\therefore$ Mole of air $= n = \frac{PV}{RT} = \frac{1\times150\times10^6}{10^3\times0.0821\times293} = 6.236\times10^3$

Also, $\left(\frac{\delta H}{\delta T}\right)_p = C_p = \frac{\Delta H}{\Delta T}$ (for 1 mole)

$\therefore$ $\Delta H = n\cdot C_p\cdot\Delta T$ (for n mole)

$= 6.236\times10^3\times\frac{7}{2}\times8.314\times(310-293)$

$= 3.085\times10^6$ J

Thus, heat needed to heat the room to 37°C $= 3.085\times10^6$ J

Also, heat released by 50 peoples

$= 150\times50$ J/sec $= 7500$ J/sec

7500 J heat is provided in 1 sec

$\therefore$ 3.085×10^6 J heat will be provided in $\frac{1\times3.085\times10^6}{7500}$

$=$ **411.3 second**

33. Volume of the room $5\times10\times3 = 150\ m^3 = 1.5\times10^4\ l$

Mole of air in the room at 27°C and 1 atm P,

$$n = \frac{PV}{RT} = \frac{1\times15\times10^4}{0.0821\times300}$$

$= 6.1\times10^3$

Heat produced per sec by 50 students

$= 100\times50 = 5000$ watt/sec

Heat produced in 10 minutes

$= 5000\times10\times60$ watt $= 3\times10^6$ watt or Js^{-1}

$\therefore$ Change in enthalpy of air, $\Delta H = n \times C_p \times \Delta T$

$$3\times10^6 = 6.1\times10^3 \times \frac{7}{2}\times 8.314 \times \Delta T \quad \therefore \quad \Delta T = \mathbf{16.90}$$

Thus, a rise in 16.90°C will be noticed in air temperature.

34. ΔG° needed for 54 g Al = 593 kJ

$\therefore$ ΔG° needed for 27 g Al $= \frac{593}{2}$ kJ

Heat produced when 50 kg mass falls from 2 m is Q.

Then, $Q = mgh = 50\times 9.8\times 2 = 980$ J

Thus, number of lifting and fall $n = \frac{\Delta G^\circ}{Q} = \frac{593\times10^3}{2\times980}$

$= \mathbf{302.6}$

Thus, athlete should go for 303 lifting.

35. Mass of the plane $= 6.3\times10^7$ g

Height of the plane $= 8\times10^5$ cm

$\therefore$ Work required to lift it to this height = mgh

$= 6.3\times10^7 \times 981\times 8\times10^5$ erg $= 4.9442\times10^{16}$ erg

$= \frac{4.9442\times10^{16}}{4.18\times10^7}$ cal $= 1.1828\times10^9$ cal

$\because$ Efficiency of fuel is 30%

$\therefore$ Work obtained by 1 mole fuel $= \frac{1300\times30}{100}$ kcal

$\because$ $\frac{1300\times30}{100}$ kcal work is obtained by 1 mole fuel

$\therefore$ 1.1828×10^6 kcal work is obtained by 1 mole fuel

$$= \frac{1.1828\times10^6\times100}{30\times1300} = 3.033\times10^3 \text{ mol}$$

$$= 3.033\times10^3 \times 114 \text{ g} = 3.46\times10^5 \text{ g}$$

$\therefore$ Volume of fuel $= \frac{3.46\times10^5}{d} = \frac{3.46\times10^5}{0.705}$ mL

$= 4.908\times10^5$ mL $= 4.908\times10^2$ litre

$\therefore$ Cost of fuel $= 490.8\times3 = \mathbf{1472.4\ Rs.}$

36. Kinetic energy of bullet is converted into heat.

$$\text{KE} = \frac{1}{2}mu^2 = \frac{1}{2}\times18\times10^{-3}\times(500)^2 = 2.25\times10^3 \text{ J}$$

$$= \frac{2.25\times10^3}{4.184\times10^3} \text{ kcal} = 0.538 \text{ kcal}$$

Also, $q = \text{KE} = mS\Delta T \quad \therefore \quad \Delta T = \frac{\text{KE}}{mS}$

$mS = mS$ for bullet + mS for wooden block

$$= (18\times10^{-3}\times0.030 + 1\times0.50)$$

$$\Delta T = \frac{0.538}{(18\times10^{-3}\times0.030 + 1\times0.500)}$$

$$= 1.08 \text{ K} = 1.08^\circ\text{C}$$

$\therefore$ Final temperature $= (25.0 + 1.08) = \mathbf{26.08^\circ C}$

37. Mole of He $= \frac{8}{4} = 2$

Mole of $N_2 = \frac{14}{28} = 0.5$

KE of He at 300 K $= \frac{3}{2}\times2\times8.314\times300 = 7.4833\times10^3$ J

KE of N_2 at 300 K $= \frac{3}{2}\times0.5\times8.314\times300 = 1.871\times10^3$ J

Now, since KE $= \frac{1}{2}M(U_{rms})^2$

On doubling U_{rms}, kinetic energy will becomes four times of initial value

$\therefore$ New KE of He $= 4\times7.483\times10^3$ J $= 2.99\times10^4$ J

New KE of N_2 $= 4\times1.871\times10^3$ J $= 7.484\times10^3$ J

Thus, for He $4\times7.483\times10^3 = \frac{3}{2}RT\times n$

(T is new temperature)

$$= \frac{3}{2}\times2\times8.314\times T$$

$\therefore$ $T = \mathbf{1200\ K}$

Now, heat given at constant volume to gases to heat them from 300 K to 1200 K is

$$\Delta H_{He} = n\times C_v \times \Delta T = n\times\frac{3}{2}R\times\Delta T$$

$$= 2\times\frac{3}{2}\times8.314\times(1200-300)\left[C_v \text{ for He} = \frac{3}{2}R\right]$$

$$= 22447.8 \text{ J}.$$

$$\Delta H_{N_2} = 0.5\times\frac{5}{2}\times8.314\times(1200-300) = 9353.25 \text{ J}$$

$$\left[C_v \text{ for } N_2 = \frac{5}{2}R\right]$$

$\therefore$ Heat provided $= 22447.8 + 9353.25 = 31801.05$ J

$$= 3.18\times10^4 \text{ J}$$

38. $\Delta H_{\text{dissolution}} = \Delta H_{\text{(ionisation)}} + \Delta H_{\text{(hydration)}} = 778 - 774.3$

$= 3.7$ kJ mol^{-1} $= 3700$ J mol^{-1}

$\Delta S_{\text{dissolution}} = 43$ J mol^{-1}

$\therefore$ $\Delta G_{\text{dissolution}} = \Delta H - T\Delta S = 3700 - 298\times43 = -9114$ J

$\Delta G = \mathbf{-9.114\ kJ}$

39. $\Delta H_{\text{total}} = \Delta H_{\text{fusion}} + \Delta H_{\text{heating}} + \Delta H_{\text{vaporization}}$

$= 10\times80 + 10\times1\times100 + 10\times540 = \mathbf{7200\ cal}$

40. ΔH required for heating $= \underset{\text{(boiler)}}{mS\Delta T} + \underset{\text{(water)}}{mS\Delta T}$

$= 0.11\times900\times90 + 1\times400\times90 = 44910$ kcal

Since, only 70% of heat given is used up to do so.

Thus, actual heat required $= \frac{44910\times100}{70} = \mathbf{64157\ kcal}$

41. The given reaction is :

$$Al_2O_3(s) + 6Na(s) \longrightarrow 3Na_2O(s) + 2Al(s)$$

Hence, $\Delta G^\circ = 3\times G_f^\circ(Na_2O) - G_f^\circ(Al_2O_3)$

(G° for Na and Al = 0)

$$= 3\times(-377) - (-1582) = +451 \text{ kJ mol}^{-1}$$

The reaction cannot occur since $\Delta G^\circ(298\text{ K})$ is positive.

Also, $\Delta G^\circ = -2.303RT\log_{10}K$

$$451 = -2.303\times8.314\times10^{-3}\times298\log_{10}K$$

$\therefore$ $\text{Log } K = -79.04$

$K = \mathbf{9.1\times10^{-80}}$

42. Using Clausius-Clapeyron equation :

$$2.303 \log_{10} \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

$$\Delta H_v = \frac{2.303 R T_1 T_2}{(T_2 - T_1)} \log_{10} \frac{P_2}{P_1}$$

We have $\Delta H_v = \frac{2.303 \times 8.314 \times 303 \times 333}{(333-300)} \log_{10} \frac{5.2 \times 10^4}{1.53 \times 10^4}$

$= 31.1 \times 10^3 \text{ J} = \mathbf{31.1 \text{ kJ}}$

43. For entropy change of fusion, $\Delta S_f = \frac{\Delta H_f}{T}$

Given, $\Delta H_f = 6 \times 10^3$ J; $T = 273$ K

$\therefore \quad \Delta S_f = \frac{6 \times 10^3}{273} = \mathbf{21.97 \text{ JK}^{-1} \text{ mol}^{-1}}$

44. ΔH for cooling $CD_2O = mS\Delta T = \frac{3.2}{32} \times 14 \times 100 = 140$ cal

$\because$ Cooling is exothermic $\Delta H = -140$ cal.

Now, $\Delta S = \frac{\Delta H}{T} = -\frac{140}{900} = \mathbf{-0.1555 \text{ cal deg}^{-1}}$

45. For entropy change of vaporization, $\Delta S_v = \frac{\Delta H_v}{T}$

Given, $\Delta H_v = 40.8 \times 10^3$ J; $T = 373$ K

$\therefore \quad \Delta S_v = \frac{40.8 \times 10^3}{373} = \mathbf{109.38 \text{ JK}^{-1} \text{ mol}^{-1}}$

46. Given, $\Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$

$\Delta S = -105 \text{ J mol}^{-1} \text{ K}^{-1}$

$T = 298$ K

$\therefore \quad \Delta G = \Delta H - T\Delta S$

$= -11700 - 298 \times (-105) = 19590$ J

$= \mathbf{+19.59 \text{ kJ}}$

Since, $\Delta G = +$ ve $\quad \therefore$ reaction is not spontaneous.

47. $\Delta S_{\text{Reaction}} = \Sigma S_{\text{Product}} - \Sigma S_{\text{Reactants}}$

$= 2 \times S_{H_2O} - [2 \times S_{H_2} + S_{O_2}]$

$= 2 \times 68 - [2 \times 126.6 + 201.20]$

$\Delta S = \mathbf{-318.4 \text{ JK}^{-1}}$

48. We have, $\Delta S = \frac{q_1}{T} = \frac{2.303 nRT \log_{10} \frac{V_2}{V_1}}{T}$

Given, $n = 1$, $R = 8.314$ J, $T = 298$ K, $V_1 = V$, $V_2 = 10V$

$\therefore \Delta S = 2.303 \times 1 \times 8.314 \log_{10} \frac{10V}{V} = \mathbf{19.15 \text{ JK}^{-1} \text{mol}^{-1}}$

49. $\Delta S = 2.303 \times m \times C_p \times \log \frac{T_2}{T_1}$

$= 2.303 \times \frac{100}{1000} \times 4200 \log \frac{360}{300} = \mathbf{76.59 \text{ J}}$

50. $\Delta S = 2.303 m \times C_p \times \log \frac{T_2}{T_1}$

[where m in kg and C_p in J/kg]

Entropy change for heating water from 27° to 100°C.

$\Delta S = 2.303 \times 4180 \log \frac{373}{300} = 910.55$ J

Entropy change for heating 1 kg H_2O to 1 kg steam at 100°C.

$\Delta S = \frac{\Delta H_v}{T} = \frac{23 \times 10^5}{373} = 6166.21$ J

Entropy change for heating 1 kg steam from 373 to 473 K, m in kg.

$$\Delta S = \int_{373}^{473} \frac{nC_p \cdot dT}{T} = m \int_{373}^{473} \frac{(1670 + 0.49T) dT}{T}$$

$$= m \int_{373}^{473} \frac{1670 dT}{T} + m \int_{373}^{473} 0.49 \, dT$$

$$= m \times 1670 \times 2.303 [\log T]_{373}^{473} + m \times 0.49 [T]_{373}^{473}$$

$$= 1 \times 1670 \times 2.303 \log \frac{473}{373} + 1 \times 0.49 \times 100$$

$= 396.73 + 49 = 445.73$ J

$\therefore$ Total entropy change $= 910.55 + 6166.21 + 445.73$

$= \mathbf{7522.50 \text{ J}}$

51. ΔH° for reaction

$$= \left[H^\circ_{TiCl_4}(l) + H^\circ_{O_2}(g) - H^\circ_{TiO_2} - H^\circ_{Cl_2} \times 2 \right]$$

$= [-804.2 + 0.0 - (-944.7) - 0.0] = 140.5$ kJ

Also, ΔS° for reaction

$$= \left[S^\circ_{TiCl_4}(l) + S^\circ_{O_2}(g) - S^\circ_{TiO_2}(s) - S^\circ_{Cl_2}(g) \times 2 \right]$$

$= [252.3 + 205.1 - 50.3 - 2 \times 233.0]$

$= -58.9 \text{ J} = -0.0589$ kJ

Now, $\Delta G^\circ = \Delta H^\circ - T\Delta S$

$= 140.5 - 298.15 \times (-0.0589) = \mathbf{158.06 \text{ kJ}}$

Positive value of ΔG° suggests that reaction is not possible.

52. Given, for the change

$\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$

$\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$

For a non-spontaneous reaction $\Delta G = +$ ve

Since, $\Delta G = \Delta H - T\Delta S \quad \therefore \quad \Delta H - T\Delta S$ should be +ve

or $\Delta H > T\Delta S \quad$ or $\quad T < \frac{\Delta H}{\Delta S}$

$< \frac{30 \times 10^3}{70}$

$\mathbf{T < 428.57 \text{ K}}$

53. $\because \quad \Delta G = \Delta H - T\Delta S$

Also, ΔG at equilibrium $= 0 \quad \therefore \quad \Delta H = T\Delta S$

$30.5 = T \times 0.066 \quad \therefore \quad T = \frac{30.5}{0.066} = \mathbf{462.12 \text{ K}}$

54. At equilibrium : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\therefore \quad \Delta G^\circ_{300\text{ K}} = -41.16 - 300 \times (-4.24 \times 10^{-2}) = \mathbf{-28.44 \text{ kJ}}$

and

$\Delta G^\circ_{1200\text{ K}} = -32.93 - 1200 \times (-2.96 \times 10^{-2}) = \mathbf{+2.59 \text{ kJ}}$

Thus, at 300 K, reaction will proceed in forward direction and at 1200 K in backward direction.

Also, $\Delta G^\circ = -2.303 RT \log K_p$

At, 300 K, $-28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log K_p$

$\therefore \quad K_p = 8.94 \times 10^4$

Similarly, at 1200 K, $K_p = 0.77$

55. $\underset{1-0.982}{\overset{1}{2CH_3COOH(g)}} \rightleftharpoons \underset{\frac{0.982}{2}}{\overset{0}{(CH_3COOH)_2(g)}}$

$$K^\circ = \frac{(CH_3COOH)_2}{(CH_3COOH)^2} = \frac{0.982}{2 \times (0.018)^2} = 1515.4$$

Now, ΔH° for dimerization $= -2 \times 33$ kJ $= -66$ kJ

Thus, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-2.303 RT \log K^\circ = \Delta H^\circ - T\Delta S^\circ$

$-2.303 \times 8.314 \times 400 \times \log (1515.4) = -66 \times 10^3 - 400 \times \Delta S^\circ$

$-24359.2 = -66000 - 400\,\Delta S^\circ$

$\therefore \quad \Delta S^\circ = -\frac{41640.8}{400} = -104.102$ **J / mol**

56. For a real gas, $\left[P + \frac{n^2 a}{V^2}\right][V - nb] = nRT$

If $nb << V$, (as given), then

$$\left[P + \frac{n^2 a}{V^2}\right] V = nRT \text{ or } P = \frac{nRT}{V} - \frac{n^2 a}{V^2}$$

Now work done in reversible expansion is

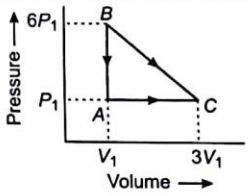
$$w = -\int P\,dV = -\int_{V_1}^{V_2} \frac{nRT\,dV}{V} + \int_{V_1}^{V_2} \frac{n^2 a}{V^2}\,dV$$

$$= -nRT \log \frac{V_2}{V_1} - \left[\frac{n^2 a}{V_2} - \frac{n^2 a}{V_1}\right]$$

$$= -nRT \log \frac{V_2}{V_1} - n^2 a \left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

• SINGLE INTEGER ANSWER PROBLEMS •

1. 6 kJ heat is provided to a system as well as work equivalent to 2 kJ is done on the system. The total change in internal energy during these operations in kJ is .....
2. Specific heat at constant volume of a monoatomic gas is 0.075 cal/g. 1 mole of this gas requires 3 cal of heat to raise the temperature of 1 mole gas. The heat required to raise the temperature through 1°C of 1 mole gas at constant pressure is ..... cal.
3. Exactly 3.0 g of carbon was burned to CO_2 in copper calorimeter. The mass of calorimeter is 1.5 kg and the mass of water in calorimeter is 2 kg. The initial temperature was 20°C and final temperature was 31.5°C. If specific heat of copper is 0.0826 cal/g-K, the heat value to closest integer of carbon in kcal/g is .....
4. A new element E forms a compound with chlorine which contains 1.455 g Cl per g E. The specific heat of E was found 0.05 cal/g. If eq. mass of element is 24, what is x in ECl_x?
5. The enthalpy of transition of crystalline boron to amorphous boron at 1500°C is 0.4 kcal mol^{-1}. Assuming atomic mass of boron 10, the change in enthalpy of transition 50 g boron from crystalline to amorphous form is .....
6. If ΔG and ΔS for the reaction : $A_{(g)} + B_{(g)} \longrightarrow P_{(g)}$ at 300 K are – 600 cal and –10 cal/K. The ΔU for the reaction in kcal is .....
7. At 0°C, if enthalpy of fusion of ice is 1365 kcal/mol. The molar entropy change for melting of ice at 0°C is ..... kcal.
8. A certain number of mole of gas is allowed to heat from 300 K to 500 K at constant P. By doing so gas is expanded to do work on boundries equivalent to 9.9768 kJ. How many mole of gas were used ?
9. 'a' mole of Na reacts with sufficient water in an open vessel at 300 K. The work done by the liberated gas H_2 is equivalent to 4988.4 J. What is a ?
10. A reversible reaction is carried out at 500 K, where its equilibrium constant is unity. If ΔH° at 500 K is 4.0 kJ, the value of ΔS° is equal to .....
11. A reaction becomes spontaneous only at 500 K. If ΔH at 500 K is 3.0 kJ, the change in entropy at 500 K.
12. A certain amount of gas ($P = 5$ atm, $V = 2$L, $T = 500$ K) in state A is compressed to state B ($P = 2$ atm, $T = 100$ K, $V = ?$). The final volume of state B in litre is :
13. One mole of monoatomic ideal gas at $P = 2$ bar and $T = 273$ K is compressed to 4 bar pressure following a reversible path obeying P/V = constant. Assume $C_v = 12.5$ J mol^{-1} K^{-1}. The value of $\frac{\Delta U}{W}$ for this process is minus.
14. How much of the following are intensive properties?
    Vapour pressure, Molarity, Refractive index, Dielectric constant, Osmotic pressure, Molarity, Specific gravity, Molar volume
15. Out of the following properties how many are path functions?
    Heat enthalpy, Internal energy, Temperature, Work, Heat, Specific heat
16. Out of the following properties how many are state functions?
    Heat enthalpy, Internal energy,Temperature, E_{cell}, Work, Heat, Specific heat, Resistance
17. Out of the following properties how many are extensive properties?
    Resistance, Electromotive force, Ionic mobility, Dipole moment, Heat capacity, Specific heat, Density, Specific volume
18. How many of the following are intensive properties?
    Vapour pressure, Molarity, Refractive index, Dielectric constant, Osmotic pressure, Molality, Specific gravity, Molar volume
19. An ideal gas shows the cyclic process $ABCA$ as represented by figure. The net work done during the cycle is $a\,PV$. The value of a is .....



20. The work done in kJ on decomposition of 6.8 g H_2O_2 in open vessel at 27°C is approximately -2.50×10^a J. The value of a is .....
21. The average molar heat capacity (in cal) at constant volume of a gaseous mixture containing 2 mole of gas $A\left(C_v = \frac{3}{2}R\right)$ and 2 mole of gas $B\left(C_v = \frac{5}{2}R\right)$ is .....
22. If a gas expands adiabatically at constant pressure such that $T \propto V^{-1/2}$. The value of $C_p : C_v$ for it is a:2. The value of a is.....
23. Two mole of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = \text{constant}$. The gas expands from 1 litre to 3 litre starting from initial temperature of 300 K and the value of ΔH for the expansion in kcal is .....

24. The degree of freedom for a triatomic gas is .....

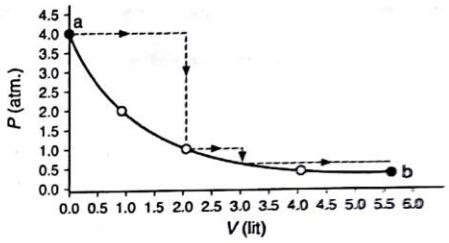
25. An ideal engine operates in a carnot cycle between 327°C and 127°C. It absorbs 9 kcal of heat at high temperature. The amount of heat in kcal rejected to sink is .....

26. Following gases are placed at same temperature and pressure and expanded adiabatically to double their original volume.

$$O_2, N_2, Ar, Ne, SO_2, O_3, H_2O_2, Cl_2$$

How much of these gases will require the greatest quantity of heat isochorically to restore their original temperature.

27. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and dashed line as shown in graph below. If the work done along the solid line is w_s



and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is ..... **(IIT 2010)**

ANSWERS

1. Eight	2. Five	3. Eight	4. Five	5. Two	6. Three	7. Five	8. Six	9. Four	10. Eight	11. Six	12. One
13. Three	14. Seven	15. Three	16. Three	17. Three	18. Seven	19. Nine	20. Two	21. Four	22. Three	23. Two	24. Six
25. Six	26. Two (Ar, Ne)		27. Two								

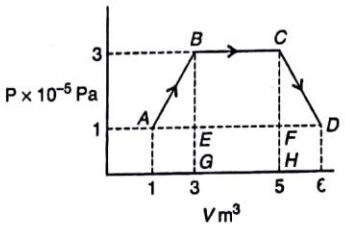
OBJECTIVE PROBLEMS (One Answer Correct)

1. An equilibrium $\text{Hexane}_{(l)} \rightleftharpoons \text{Hexane}_{(v)}$ exists at 300 K. If 29 kJ energy is absorbed for conversion of 1 mole $\text{hexane}_{(l)}$ to hexane vapours at 300 K, the change in entropy during the conversion of 1 g $\text{hexane}_{(l)}$ to 1 g hexane vapours is :
   (a) $96.67\ \text{JK}^{-1}$ (b) $1.124\ \text{JK}^{-1}$
   (c) $0.097\ \text{JK}^{-1}$ (d) $1.124\times10^{-3}\ \text{JK}^{-1}$

2. If for the reaction at 300 K : $2\text{Mg}_{(s)} + \text{O}_{2(g)} \longrightarrow 2\text{MgO}_{(s)}$; $\Delta_r H = -1202\ \text{kJ mol}^{-1}$ and $\Delta_r S = -217.0\ \text{JK}^{-1}\ \text{mol}^{-1}$. The total entropy change $(\Delta S)_T$ and Gibbs energy change during the course of reaction $(\Delta_r G)$ are respectively :
   (a) 3.79×10^3 J, -1136.9 kJ
   (b) 3.79×10^3 J, $+1000$ J
   (c) $+1000$ J, 3.79×10^3 J
   (d) -1136.9 kJ, 3.79×10^3 J

3. Given,
   $2\text{Fe}_2\text{O}_{3(s)} \longrightarrow 4\text{Fe}_{(s)} + 3\text{O}_{2(g)}$; $\Delta_r G_1^\circ = +1487\ \text{kJ mol}^{-1}$
   $6\text{CO}_{(g)} + 3\text{O}_{2(g)} \longrightarrow 6\text{CO}_{2(g)}$; $\Delta_r G_2^\circ = -1543.2\ \text{kJ mol}^{-1}$
   Select the correct statement :
   (a) $\Delta_r G^\circ$ for reduction of iron oxide by CO is + 56.2 kJ mol^{-1}
   (b) Fe_2O_3 can be reduced by CO spontaneously
   (c) Fe_2O_3 cannot be reduced by CO spontaneously
   (d) The reduction of Fe_2O_3 takes part in higher part of blast furnace.

4. The net work done through a series of changes reported in figure for an ideal gas is :



   (a) -6×10^5 J (b) -7×10^5 J
   (c) -12×10^5 J (d) $+12\times10^5$ J

5. For adiabatic expansion of a perfect gas $\frac{dP}{P}$ is :
   (a) $\frac{dV}{V}$ (b) $\gamma.\frac{dV}{V}$
   (c) $-\gamma\frac{dV}{V}$ (d) $-\gamma^2\frac{dV}{V}$

6. Specific heat at constant pressure of a diatomic gas having molar mass M is approximately equal to :
   (a) $\frac{\gamma R}{M(\gamma-1)}$ (b) $\frac{\gamma}{RM}$
   (c) $\frac{M}{R(\gamma-1)}$ (d) $\frac{\gamma RM}{\gamma+1}$

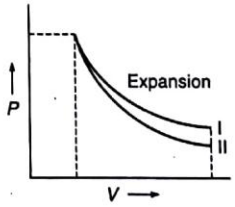
7. Which of the following is incorrect for the change shown below ?

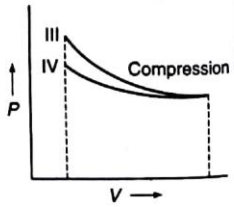
$$\underset{(298\ \text{K})}{aA+bB} \xrightarrow{\Delta_r S_1^\circ} \underset{(298\ \text{K})}{cC+dD}$$
$$\Delta_r S_2^\circ \downarrow \qquad \uparrow \Delta_r S_4^\circ$$
$$\underset{(0\ \text{K})}{aA+bB} \xrightarrow{\Delta_r S_3^\circ} \underset{(0\ \text{K})}{cC+dD}$$

   (a) $\Delta_r S_1^\circ = cS_C^\circ + dS_D^\circ - (aS_A^\circ + bS_B^\circ)$
   (b) $\Delta_r S_2^\circ = -[aS_A^\circ + bS_B^\circ]$
   (c) $\Delta_r S_3^\circ = 0$
   (d) $\Delta_r S_4^\circ = -[cS_C^\circ + dS_D^\circ]$

8. In a thermodynamic process helium gas obeys the law $\frac{T}{P^{2/5}} = \text{constant}$. The heat given to n mole of He in order to raise the temperature from T to $2T$ is :
   (a) $8\,RT$ (b) $4\,RT$
   (c) $16\,RT$ (d) zero.

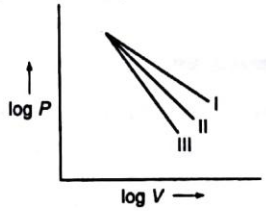
9. Which of the following figures given below shows adiabatic process ?





   (a) II, III (b) I, III
   (c) II, IV (d) I, IV

10. The following curves represents adiabatic expansions of gases He, O_2 and O_3 not necessarily in order. Which curve represents for O_3 :



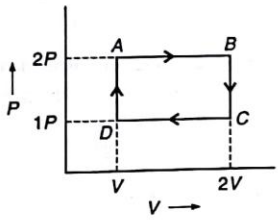
   (a) I (b) II
   (c) III (d) any one of these

11. During an adiabatic expansion a gas obeys VT^3 = constant. The gas must be :
(a) monoatomic (b) diatomic
(c) polyatomic (d) either of these

12. He, N_2 and O_3 are expanded adiabatically and their expansion curves between log P and log V are plotted under similar conditions. About the ratio of the slopes, which one is not correct ?
(a) The ratio of slopes of log P *vs* log V curves for He and O_3 is 1.25
(b) The ratio of slopes of log P *vs* log V curves for He and N_2 is 1.20
(c) The ratio of slopes of log P *vs* log V curves for N_2 and O_3 is 1.05
(d) The slope of He is least steeper and for O_3 is most steeper

13. Which expansion will produce more change in entropy during reversible and isothermal process ?
(a) 1 mole H_2 at 300 K from 2 litre to 20 litre
(b) 1 mole N_2 at 400 K from 1 litre to 10 litre
(c) 1 mole O_3 at 500 K from 3 litre to 30 litre
(d) All have same ΔS

14. An ideal monoatomic gas follows the path *ABCD*. The work done during the complete cycle is :



(a) $-PV$ (b) $-2PV$
(c) $-\frac{1}{2}PV$ (d) zero

15. Molar heat capacity of a gas at constant temperature and pressure is :
(a) $\frac{3}{2}R$ (b) $\frac{5}{2}R$
(c) depends on gas (d) infinity

16. The maximum change in entropy is observed during mixing of :
(a) 8.6 g hexane + 10.0 g heptane
(b) 8.6 g hexane + 5.0 g heptane
(c) 4.3 g hexane + 10.0 g heptane
(d) 1 g hexane + 10.0 g heptane

17. Heat of neutralisation of strong acid and strong base under 1 atm and 25°C is –13.7 kcal. If standard Gibbs energy change for dissociation of water to H^+ and OH^- is –19.14 kcal, the change in standard entropy for dissociation of water in cal K^{-1} mol^{-1} is :
(a) 18.25 (b) 110.2
(c) –18.25 (d) None of these

18. C_p and C_v for a gas are 0.125 cal/g and 0.075 cal/g respectively. Which one of the gas has these values?
(a) He (b) O_2
(c) Ar (d) Ne

19. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statement is correct?
(a) $(T_f)_{irrev.} > (T_f)_{rev.}$
(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(c) $(T_f)_{rev.} = (T_f)_{irrev.}$
(d) $T_f = T_i$ for both reversible and irreversible process

20. The W/Q of a carnot engine is 1/6. When temperature of sink is reduced by 62°C, this ratio becomes twice, therefore the initial temperature of the sink and source are:
(a) 33°C, 67°C (b) 37°C, 99°C
(c) 67°C, 33°C (d) 97 K, 97 K

21. A scientist says that the efficiency of his heat engine which works at source temperature 127°C and sink temperature (27°C) is 26%, then :
(a) it is impossible
(b) it is possible
(c) it is possible but less probable
(d) data is incomplete

22. In a closed insulated container, a liquid is stirred with a paddle to increase the temperature, then which of the following is true:
(a) $\Delta U = w \neq 0, q = 0$ (b) $w = 0, \Delta U = q \neq 0$
(c) $\Delta U = 0, w = q \neq 0$ (d) $\Delta U = w = q \neq 0$

23. An ideal gas heat engine operates in a carnot cycle between 227°C and 127°C. It absorbs 6 kcal at the higher temperature. The amount of heat converted into work in kcal is equal to:
(a) 4.8 (b) 3.5
(c) 1.6 (d) 1.2

24. On the basis of reaction : $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$; $\Delta G = -827\,kJ\,mol^{-1}$ of O_2, the minimum emf required to carry out electrolysis of Al_2O_3 is:
(a) 6.42 V (b) 8.56 V
(c) 2.14 V (d) 4.28 V

25. The densities of graphite and diamond are 2 and 3 g/mL at 298 K respectively. If the $\Delta H - \Delta U$ for the change $C_G \rightarrow C_D$ is equal to 100 J mol^{-1}, the pressure at which graphite will be transformed into diamond is:
(a) 5×10^7 Pa (b) 9.92×10^5 Pa
(c) 9.92×10^{10} Pa (d) 9.92×10^8 Pa

26. One mole of an ideal gas at an initial temperature T K, does $6R$ J of work adiabatically. If the ratio of specific heats of this gas at constant P and V respectively is 5/3, the final temperature of gas will be:
(a) $(T+2.4)$ K (b) $(T-2.4)$ K
(c) $(T+4)$ K (d) $(T-4)$ K

27. Considering entropy(s) as the thermodynamic parameter, the criterion for the spontaneity of any process is:
(a) $\Delta S_{sys}+\Delta S_{surr}>0$ (b) $\Delta S_{sys}-\Delta S_{surr}>0$
(c) Only $\Delta S_{sys}>0$ (d) Only $\Delta S_{surr}>0$

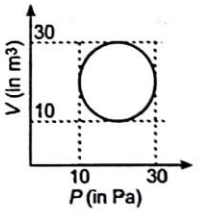
28. The molar specific heat at constant pressure for an ideal gas is $\frac{7}{2}R$. Which of the following is correct:
(a) $\gamma=1.44$, and atomicity = 3
(b) $\gamma=1.33$, and atomicity = 3
(c) $\gamma=1.66$, and atomicity = 1
(d) $\gamma=1.44$, and atomicity = 2

29. The enthalpy and entropy change for the reaction:
$$Br_{2(l)}+Cl_{2(g)}\rightarrow 2BrCl_{(g)}$$
are 30 kJ mol^{-1} and 105 JK^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is:
(a) 450 K (b) 300 K
(c) 285.7 K (d) 273 K

30. If Q, U and W denotes respectively the heat added, change in internal energy and work done in a closed cycle process, then:
(a) $\Delta U=0$ (b) $Q=0$
(c) $W=0$ (d) $Q=W=0$

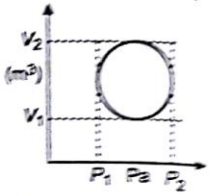
31. For the reaction : $PCl_{5(g)}\rightarrow PCl_{3(g)}+Cl_{2(g)}$, which one is true ?
(a) $\Delta H=-ve$; $\Delta S=+ve$
(b) $\Delta H=+ve$; $\Delta S=+ve$
(c) $\Delta H=+ve$; $\Delta S=0$
(d) $\Delta H=+ve$; $\Delta S=-ve$

32. A system works under cyclic process as shown in figure. Heat absorbed during the process is:
(a) $\frac{22}{7}\times10^2$ J
(b) $\frac{22}{7}\times10^3$ J
(c) $\frac{22}{7}\times10^4$ J
(d) $\frac{22}{7}\times10^5$ J

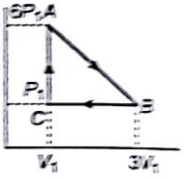


33. For two mole of an ideal gas:
(a) $C_p-C_v=2R$ (b) $C_p-C_v=R$
(c) $C_p-C_v=\frac{R}{2}$ (d) none of these

34. The PV diagram shown in figure is in circle for a cyclic process. The work done during the process can not be given by:
(a) $\frac{\pi}{4}\times(P_2-P_1)^2$
(b) $\frac{\pi}{4}\times(V_2-V_1)^2$
(c) $\pi(P_2-P_1)\times(V_2-V_1)$
(d) $\frac{\pi}{4}(P_2-P_1)(V_2-V_1)$



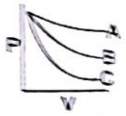
35. An ideal gas shows $P-V$ work done in cyclic process as shown in figure. The net work done by the gas during the cycle is:
(a) $12P_1V_1$
(b) $6P_1V_1$
(c) $9P_1V_1$
(d) $5P_1V_1$



36. The work done by 3.4 g $H_2O_{2(l)}$ on decomposition to $H_2O_{(l)}$ and $O_{2(g)}$ against a pressure of 1 atm at 25°C:
(a) -3.2×10^2 J (b) $+3.2\times10^2$ J
(c) 1.24×10^2 J (d) -1.24×10^2 J

37. During an adiabatic process pressure of the gas $=T^5$. The Poison's ratio for gas is:
(a) $\frac{3}{2}$ (b) $\frac{5}{3}$
(c) $\frac{7}{2}$ (d) $\frac{4}{3}$

38. Plots of P vs V are made during adiabatic process of three gases as shown in figure. Which of the statement is correct:
(a) C is for monoatomic gas
(b) B is for diatomic gas
(c) A is for polyatomic gas
(d) All of these



39. In the pressure-volume diagram given below, the isochoric, isothermal, isobaric and isoentropic process are respectively:
(a) BA, AD, DC, CB
(b) DC, CB, BA, AD
(c) AB, BC, CD, DA
(d) CD, DA, AB, BC



40. A sample of an ideal gas is expanded from $1\,m^3$ to $3\,m^3$ in a reversible process for which $P=KV^{-2}$ having $K=6$ bar m^{-6}. Work done by the gas in (bar m^3) is:
(a) 5.2 (b) 15.6
(c) 52 (d) 55

41. 100 mole of an ideal gas at 8.21 atm is heated to show a linear graph between $\log V$ and $\log T$. The slope of the line is:
(a) 1/2 (b) 1
(c) 1/3 (d) 1/4

42. An ideal gas at 27°C is compressed adiabatically to 8/27 of its original volume if $\gamma=\frac{5}{3}$, then rise in temperature is:

(a) 405 K (b) 225 K
(c) 375 K (d) 305 K

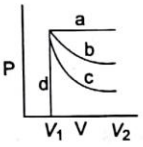
43. The pressure(P) and density(ρ) of a diatomic gas $\left(\gamma=\frac{7}{5}\right)$ changes from $P_1\rho_1$ to $P_2\rho_2$. If $\frac{\rho_1}{\rho_2}=32$, the value of $\frac{P_1}{P_2}$ is :

(a) 32 (b) $\frac{1}{32}$
(c) 128 (d) 164

44. An ideal gas expands isothermally from a volume V_1 to V_2 and then compressed to original volume V_1 adiabatically. Initial pressure was P_1 and final pressure was P_3. The total work done is w, then:

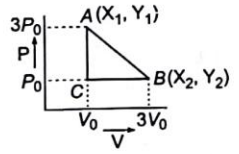
(a) $P_3 > P_1$, w = +ve (b) $P_3 < P_1$, w = −ve
(c) $P_3 > P_1$, w = −ve (d) $P_3 = P_1$, $w = 0$

45. In which of the following graphs work done is maximum ?



(a) a
(b) b
(c) c
(d) d

46. n mole of an ideal gas undergo a process ABC as shown in figure. Maximum temperature of the gas during the process AB is:



(a) $\frac{4P_0V_0}{nR}$
(b) $\frac{P_0V_0}{nR}$
(c) $\frac{2P_0V_0}{nR}$
(d) $\frac{3P_0V_0}{nR}$

47. Molar heat capacity of water in equilibrium with ice at constant pressure is:

(a) zero (b) infinite
(c) 40.45 kJ K^{-1} mol^{-1} (d) 75.48 kJ K^{-1} mol^{-1}

48. Assuming complete dissociation of 1 mole each of H_2, N_2, O_2 and Cl_2 into respective atoms *i.e.*, in monoatomic gaseous atoms under identical conditions of P, V and T, which will show greater entropy ?

(a) Cl (b) O
(c) N (d) H

49. One mole of an ideal gas is compressed isothermally to half of its initial volume and then heated to twice of its temperature under isochoric condition, the change in entropy is :

(a) $C_v \ln 2$ (b) $C_p \ln 2$
(c) $R \ln 2$ (d) $(C_v - R)\ln 2$

50. A gas expands adiabatically such that its temperature $T \propto \frac{1}{\sqrt{V}}$. The value of poisson's ratio (γ) for gas is :

(a) 1.30 (b) 1.50
(c) 1.70 (d) 2

51. A sample of an ideal gas at pressure P and volume V proceed for an isothermal process showing an entropy change of ΔS. The work done by the gas is :

(a) $-\frac{PV\Delta S}{nR}$ (b) $-nR\Delta S$
(c) $-PV$ (d) $-\frac{P\Delta S}{nRV}$

52. Given :

$$Fe_2O_3(s) + \underset{1\text{ mole}}{3CO} \rightleftharpoons \underset{1\text{ mole}}{2Fe(s)} + 3CO_2 \; ; \; \Delta G_{25^\circ C} = -10 \text{ kJ}$$

What is the value of $\Delta G_{25^\circ C}$ for

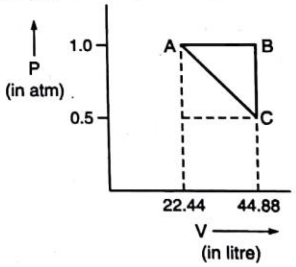
$$\underset{2\text{ mole}}{2Fe(s) + 3CO_2} \rightleftharpoons Fe_2O_3(s) + \underset{2\text{ mole}}{3CO}$$

(a) + 10 kJ (b) + 11.717 kJ
(c) 8.28 kJ (d) 9.45 kJ

53. How many times a diatomic gas should be expanded adiabatically to reduce its root mean square speed to half?

(a) 16 (b) 40
(c) 32 (d) 8

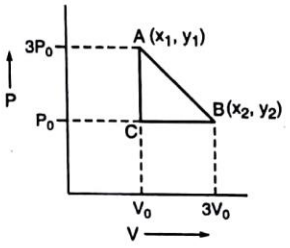
54. One mole sample of a monoatomic ideal gas is allowed to proceed for a given cycle as shown in the figure :



The temperatures at A, B and C (in K) are respectively :

(a) 273, 546, 273 (b) 546, 273, 273
(c) 273, 273, 273 (d) 546, 546, 273

55. n mole of an ideal gas undergo a process ABC as shown in figure. Maximum temperature of the gas during the process AB is :

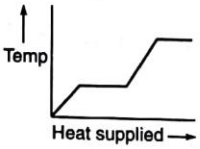


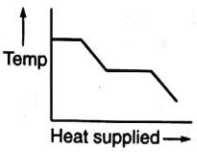
(a) $\frac{4P_0V_0}{nR}$ (b) $\frac{P_0V_0}{nR}$

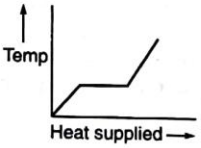
(c) $\frac{2P_0V_0}{nR}$ (d) $\frac{3P_0V_0}{nR}$

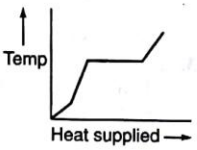
56. Molar heat capacity of water in equilibrium with ice at constant pressure is :
(a) zero (b) infinite
(c) 40.45 kJ $K^{-1}mol^{-1}$ (d) 75.48 kJ $K^{-1}mol^{-1}$

57. A block of ice at –10°C is slowly heated and converted to steam at 100°C. Which of the following curves represents the phenomenon correctly.

(a) 

(b) 

(c) 

(d) 

58. Select the incorrect statement :
(a) during adiabatic change specific heat is zero
(b) during isothermal change specific heat is infinite
(c) the ratio of the slopes of adiabatic and isothermal change is equal to γ
(d) a room can be cooled by opening the door of a running refrigerator in a closed room

59. Select the incorrect statement :
(a) work can be completely converted into heat
(b) heat can be completely converted into work
(c) chemical energy a part of internal energy can be converted into kinetic energy
(d) during condensation, kinetic energy remains constant

60. A mixture contains n_1 moles of monoatomic gas and n_2 moles of diatomic gas. If $\gamma = 1.50$ for mixture, the ratio of $n_1 : n_2$ is :
(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) 2 : 3

61. For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, the signs of ΔH and ΔS respectively are :
(a) +, – (b) + , +
(c) –, – (d) –, +

62. What is ΔG for the reaction $X_2O_4(l) \longrightarrow 2XO_2(g)$; at 27°C Given ΔU and ΔS are 2.1 k cal mol^{-1} and 20 cal $K^{-1}mol^{-1}$:
(a) 2.7 k cal (b) 1.5 k cal
(c) 3.3 k cal (d) 4.4 k cal

63. Which process is isothermal and adiabatic both ?
(a) Free expansion of ideal gas
(b) Work done by gas at constant temperature
(c) Work done on gas at constant temperature
(d) Cyclic process

64. For water $\Delta H_{vap} = 540$ cal g^{-1}. ΔS for water at its boiling point 100°C in cal $K^{-1}mol^{-1}$ is :
(a) 540 (b) 1.45
(c) 26.06 (d) 35.60

65. The efficiency of an engine operating between 110°C and an unknown temperature T is 23.3%. What is T?
(a) 394 K (b) 294 K
(c) 194 K (d) 494 K

66. Enthalpy of vaporisation of a certain liquid is 24.914 kJ mol^{-1} and the entropy of vaporisation is 94.684 $JK^{-1}mol^{-1}$. The temperature at which both the phases coexist is :
(a) 263.12 K (b) 363.12 K
(c) 10 K (d) 110 K

67. The enthalpy of a system increases by 50 kJ when its internal energy is increased by 113 kJ. What is the pressure in k Nm^{-2} of the system if the volume of gas is reduced by 10 m^3 at constant pressure ?
(a) 16.13 (b) 6.3
(c) 5 (d) 30.2

68. The reaction between H_2 and O_2 to produce water vapour is given by the equation : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$
The work done at STP is :
(a) –2.27 J (b) +2.27 J
(c) –2.27 kJ (d) +2.27 kJ

69. The molar heat capacity of a diatomic gas at constant pressure is :
(a) 8.314 $JK^{-1}mol^{-1}$ (b) 20.8 $JK^{-1}mol^{-1}$
(c) 29.1 $JK^{-1}mol^{-1}$ (d) 28.0 $JK^{-1}mol^{-1}$

70. Select the correct statement about
$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$
(a) work is done on surroundings
(b) work done is negative
(c) work done is positive
(d) no work is done

71. The change in internal energy (in J mol^{-1}) of 1 mole of a diatomic gas when its temperature increases by 15°C.
(a) 75 (b) 311.75
(c) 41.59 (d) 83.14

72. Select the correct statement :
(i) standard Gibb's energy has no effect on equilibrium constant
(ii) standard Gibb's energy is proportional to logarithm of equilibrium constant
(iii) equilibrium constant can be obtained from standard Gibb's energy
(iv) only K_p can be obtained from standard Gibb's energy
(a) (i) and (iv) (b) (ii) and (iii)
(c) (i) and (ii) (d) (iii) and (iv)

73. For a given reaction $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$ JK^{-1}mol^{-1}. The reaction is spontaneous at :
(Assume that ΔH and ΔS do not vary with temperature)
(a) T < 425 K (b) T > 425 K
(c) all temperatures (d) T > 298 K

74. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joule will be :
(a) 1136.25 J (b) –500 J
(c) –505 J (d) +505 J

SOLUTIONS (One Answer Correct)

1. (b) $\Delta S_v = \frac{\Delta H_v}{T} = \frac{29\times10^{+3}}{300} = 96.67\ \text{JK}^{-1}\ \text{mol}^{-1}$

$= \frac{96.67}{86} = 1.124\ \text{JK}^{-1}\ \text{g}^{-1}$

2. (a) $\Delta G = \Delta H - T\Delta S$

$= -1202 - (-217\times10^{-3}\times300) = -1136.9$ kJ

Heat released will be absorbed by the surroundings to increase the entropy of surroundings.

$\Delta S_{\text{surr.}} = +\frac{1202\times10^3}{300} = +4.01\times10^3\ \text{J mol}^{-1}$

$\therefore\ \Delta S_{\text{total}} = -217 + 4.01\times10^3 = +3793\ \text{J mol}^{-1}$

3. (b) $\Delta_r G^\circ$ for $2Fe_2O_3 + 6CO \longrightarrow 4Fe + 6CO_2$

$= \Delta_r G_1^\circ + \Delta_r G_2^\circ$

$= +1487 - 1543.2 = -56.2\ \text{kJ mol}^{-1}$

The reduction occurs spontaneously in lower part of blast furnace.

4. (b) Net work done = Area covered by PV curve

= Area of ΔABE + Area of square $BCEF$ + Area of ΔCDF

$= -\left[\frac{1}{2}(3\times10^{+5} - 1\times10^5)\times2\right]$

$+3\times10^5\times2 + \frac{1}{2}[(1\times10^5 - 3\times10^5)\times1]$

$= -[2\times10^5 + 6\times10^5 - 1\times10^5] = -7\times10^5$ J

5. (c) For adiabatic expansion PV^γ = constant

On differentiating $P\cdot\gamma\cdot V^{\gamma-1}dV + V^\gamma dP = 0$

$-P.\gamma.V^{\gamma-1}dV = V^\gamma dP$ or $\frac{dP}{P} = -\gamma\cdot\frac{V^{\gamma-1}}{V^\gamma}dV = -\gamma\cdot\frac{dV}{V}$

6. (a) $C_p - C_v = R$

$c_p - c_v = \frac{R}{M}$

$\frac{c_p}{c_v} = \gamma$

$\therefore\ c_p - \frac{c_p}{\gamma} = \frac{R}{M}$

$\therefore\ c_p\frac{(\gamma-1)}{\gamma} = \frac{R}{M}$

$\therefore\ c_p = \frac{R\gamma}{(\gamma-1).M}$

7. (d) $\Delta_r S_4^\circ = \Sigma S_P - \Sigma S_R = cS_C^\circ + dS_D^\circ - 0 - 0$

8. (d) $T = K\times P^{2/5}$

$\because PV = RT = R.K.P^{2/5}$ or $P^{3/5}\times V = K'$ or $PV^{5/3} = K'$

or $PV^\gamma = K'$ (γ for He = 5/3)

$\therefore$ Process is adiabatic and $\Delta H = 0$.

9. (a) Adiabatic slope are more steeper than isothermal
Slope of adiabatic process = $\gamma\times$ slope of isothermal process

10. (a) PV^γ = constant or $\log P = -\gamma\log v$

γ is slope for $P - V$ plots for He, O_2 and O_3, *i.e.*, $\frac{5}{3}, \frac{7}{5}$ and $\frac{4}{3}$ respectively.

11. (c) VT^3 = constant,
Also, $V^{\gamma-1}.T$ = constant for adiabatic expansion

$\therefore\ V.T^{\frac{1}{\gamma-1}}$ = constant or $\frac{1}{\gamma-1} = 3$

$\gamma = \frac{4}{3}$, *i.e.*, polyatomic gas.

12. (d) Ratio of slope = $\frac{\gamma\text{ for gas I}}{\gamma\text{ for gas II}}$; slope for He, N_2 and O_3 are 5/3, 7/5 and 4/3 respectively.

13. (d) $\Delta S = 2.303\,nR\log\frac{V_2}{V_1} = 2.303\times1\times8.314\log10$

$= 19.15\ \text{J K}^{-1}\ \text{mol}^{-1}.\left(\frac{V_2}{V_1} = 10\text{ for all}\right)$

14. (a) Net work done during the complete cycle is equal to area under the cycle (–ve if cycle is clockwise, *i.e.*, work done by the gas and +ve when cycle is anticlockwise, *i.e.*, work done on the gas)

$w = -P\times V = -(2P - P)\times(2V - V) = -PV$

15. (d) $\left(\frac{\delta H}{\delta T}\right)_P = \infty$ $\therefore\ C_P = \infty$

(δT is zero at constant P and T)

16. (a) Mole of hexane = $\frac{8.6}{86} = 0.1$,

Mole of heptane = $\frac{10}{100} = 0.1$

Also, $\Delta S = R\,\Sigma X\cdot\ln X$, when X is mole fraction.

17. (b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ΔH° for

$H_2O \rightleftharpoons H^+ + OH^-$ is + 13.7 kcal

$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{+13.7 + 19.14}{298}$

$= 0.1102\ \text{kcal K}^{-1}\text{mol}^{-1} = 110.2\ \text{cal K}^{-1}\ \text{mol}^{-1}$

18. (c) $C_p - C_v = \frac{R}{M}$ $\therefore$ $M = 40$, *i.e.*, gas is Argon.

19. (a) Work done in (–ve) reversible process is maximum. Thus, in reversible process $T_{f\ \text{rev.}} << T_{f\ \text{irrev.}}$

20. (b) $\eta_1 = \frac{T_2 - T_1}{T_2} = \frac{1}{6}$

$$\eta_2 = \frac{T_2 - (T_1 - 62)}{T_2} = 2 \times \frac{1}{6} = \frac{1}{3}$$

$\therefore T_1 = 372\text{K} = 99^\circ\text{C}$

$T_2 = 310\text{K} = 37^\circ\text{C}$

21. (a) Efficiency $= 1 - \frac{T_{\text{sink}}}{T_{\text{source}}}$

$$= 1 - \frac{300}{400} = 25\%$$

22. (a) $q = 0$ for insulated container.

23. (d) $\eta = \frac{W}{Q} = 1 - \frac{T_2}{T_1}$

(T_1, T_2 are temperature of source and sink respectively)

$\therefore$ $\frac{W}{6\times10^3} = 1 - \frac{400}{500}$

$\therefore$ $W = 1.2 \times 10^3$ cal $= 1.2$ kcal

24. (c) $\Delta G = -nEF$ $\qquad 4e + (O^0)_2 \rightarrow 2O^{-2}$

$-827 \times 10^3 = -4 \times E \times 96500$

$\therefore$ $E = \frac{827\times10^3}{4\times96500} = 2.14$ V

25. (a) $C_{(G)} \rightarrow C_D$ $\qquad \begin{bmatrix} V_D = \frac{12}{3}\text{mL} \\ V_G = \frac{12}{2}\text{mL} \end{bmatrix}$

$\Delta H = \Delta U + P_2V_2 - P_1V_1$

$\Delta H - \Delta U = P \times (V_D - V_G)$

$-10^2\ \text{J} = P \times \left[\frac{12}{3} - \frac{12}{2}\right] \times 10^{-6}$

$P = \frac{10^{+2}}{10^{-6} \times 2} = 5 \times 10^7\ \text{Nm}^{-2}$

26. (d) Work done by gas adiabatic process

$$= \frac{nR}{\gamma - 1}[T_i - T_f] = \frac{R \times (T_i - T_f)}{\frac{5}{3} - 1} = 6R$$

$\therefore$ $T_f - T_i = -4$

$T_f = [T_i - 4]$ K

27. (a) For irreversible process which are spontaneous $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$.

28. (d) $C_p = \frac{7}{2}R$ $\qquad \therefore C_v = \frac{7}{2}R - R = \frac{5}{2}R$

$\therefore$ $\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.44$, *i.e.*, diatomic gas.

29. (c) At eq. $\Delta G = 0$

$\therefore$ from $\Delta G = \Delta H - T\Delta S$

$T = \frac{\Delta H}{\Delta S} = \frac{30\times10^3}{105} = 285.7$ K

30. (a) For a cyclic process change in internal energy ΔU is zero.

31. (b) Decomposition of PCl_5 is endothermic process. Also formation of two gas results increase in disorder.

32. (a) For cyclic process $dU = 0$, on absorbing heat work is done by the system

$\therefore$ $q = dU + (-w)$

$\therefore$ $q = -w =$ area occupied by circle

$$= \pi r^2 = \frac{22}{7} \times 10^2 = \frac{22}{7} \times 10^2\ \text{J}$$

33. (b) $C_p - C_v = R$ as the value of C_p and C_v are expressed for 1 mole.

No doubt the difference in molar heat capacity, *i.e.*, $2C_p - 2C_v = 2(C_p - C_v) = 2R$

34. (c) For cyclic process ; $q = -w =$ area occupied by circle

$$= \pi \times \left(\frac{P_2 - P_1}{2}\right)\left(\frac{V_2 - V_1}{2}\right)$$

$$= \frac{\pi}{4}(P_2 - P_1) \times (V_2 - V_1)$$

$$= \frac{\pi}{4}(P_2 - P_1)^2 = \frac{\pi}{4}(V_2 - V_1)^2$$

$\because$ $P_2 - P_1 = V_2 - V_1$ for circle

35. (d) Net work done $= w_{AB} + w_{BC} + w_{CA}$ (All are clockwise)

(w_{AB} is expansion work, w_{BC} is compression work and $w_{CA} = 0$

$$= \left[-\frac{1}{2}(P_2 + P_1)(V_2 - V_1)\right] + P_2(V_2 - V_1) + 0$$

$$= \left[-\frac{1}{2}(6P_1 + P_1)(3V_1 - V_1)\right] + P_1(3V_1 - V_1)$$

$$= -7P_1V_1 + 2P_1V_1 = -5P_1V_1$$

36. (d) $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

Mole of $H_2O_2 = \frac{3.4}{34} = 0.1$

$\therefore$ Mole of O_2 formed $= 0.05$

$\therefore$ Work done by the gas $O_2 = -P \times \Delta V$

$$= \Delta nRT = -0.05 \times 298 \times 8.314$$

$$= -123.86\ \text{J}$$

37. (a) For adiabatic process $T^{\frac{\gamma}{1-\gamma}} \cdot P = \text{constant}$

$P \propto T^3$ $\qquad \therefore$ $PT^{-3} = \text{constant}$

or $\frac{\gamma}{1-\gamma} = -3$ $\qquad \therefore$ $\gamma = \frac{3}{2}$

38. (d) For adiabatic expansion

$PV^\gamma = \text{constant}$

$\gamma PV^{\gamma-1}dV + V^\gamma dP = 0$

$\gamma PdV + VdP = 0$

Slope $= \frac{dP}{dV} = -\frac{\gamma P}{V}$

For mono atomic slope $= -\frac{1.67P}{V}$

For diatomic slope $= -\frac{1.4P}{V}$

For polyatomic slope $= -\frac{1.33P}{V}$

39. (d) CD is isochoric as V remains constant.

40. (c) $\int dw = -\int Pdv$

$$= -\int 6V^2 dv = -6\left[\frac{V_2^3}{3} - \frac{V_1^3}{2}\right]$$

$$= -6\left[\frac{3^3}{3} - \frac{1^3}{3}\right] = -6\times\frac{26}{3} = 52 \text{ bar m}^3$$

41. (b) $V = \frac{nRT}{P} = \frac{100\times 0.0821\times T}{8.21} = T$

$\therefore \log V = \log T$

or slope of line is 1.

42. (c) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $(\because T\gamma^{1-\gamma} = \text{constant})$

$$\frac{T_2}{T_1} = \left(\frac{27}{8}\right)^{\frac{5}{3}-1} = \frac{9}{4}$$

$\therefore T_2 = \frac{9}{4}\times 300 = 675 \text{ K}$

$\therefore$ rise in temperature = 675 – 300 = 375 K

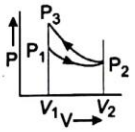
43. (c) $P_1V_1^\gamma = P_2V_2^\gamma$

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^\gamma = \left(\frac{\rho_1}{\rho_2}\right)^\gamma = (32)^{7/5} \qquad \left[\because V \propto \frac{1}{\rho}\right]$$

$$= (2^5)^{7/5} = 2^7 = 128$$

44. (c) Slope of isothermal curve is lesser than adiabatic and thus PV work done in compression is lesser than PV work done in expansion, *i.e.*, net work is done by gas or $w = -$ve.

45. (a) Work done = Area under P-V curve between volume V_1 and V_2.



46. (a) Equation of line AB is

$$Y - Y_1 = \frac{Y_1 - Y_2}{X_1 - X_2}(X - X_1)$$

$$P - 3P_0 = \frac{3P_0 - P_0}{V_0 - 3V_0}(V - V_0) \qquad ...(i)$$

$$\frac{nRT}{V} - 3P_0 = -\frac{P_0}{V_0}(V - V_0)$$

or $nRT = 3P_0V - \frac{P_0}{V_0}\cdot V^2 + P_0V$ ...(ii)

Differentiating w.r.t. V

$$\frac{nRdT}{dV} = 3P_0 - \frac{2P_0}{V_0}\cdot V + P_0 = 4P_0 - \frac{2P_0}{V_0}\cdot V$$

For max. value of T, $\frac{dT}{dV} = 0$

$\therefore P^0\left[4 - \frac{2V}{V_0}\right] = 0$ or $V = 2V_0$

Now from (ii)

$$nRT_{max} = 6P_0\cdot V_0 - \frac{P_0}{V_0}\cdot 4V_0^2 + P_0\cdot 2V_0 = 4P_0V_0$$

$\therefore T_{max} = \frac{4P_0V_0}{nR}$

47. (b) $\Delta C_p = \frac{\Delta H}{\Delta T}$ At equilibrium $\Delta T = 0$

48. (d) Due to low molar mass, H-atom will move more fastly and thus show more disorder.

49. (d) During compression for isothermal process

$$\Delta S = nR\ln\frac{V_2}{V_1} = -R\ln 2 \qquad \left(V_2 = \frac{V_1}{2}\right)$$

During heating for isochoric process

$$\Delta S = nC_v \ln\frac{T_2}{T_1} = C_v \ln 2 \qquad (T_2 = 2T_1)$$

Thus, total change in entropy $= C_v \ln 2 - R\ln 2$

$$= (C_v - R)\ln 2$$

50. (b) For adiabatic process $TV^{\gamma-1} = \text{constant}$

Given $T(V)^{1/2} = \text{constant}$

$\therefore \quad \gamma - 1 = \frac{1}{2}$

or $\gamma = \frac{3}{2} = 1.5$

51. (a) $-\Delta S = \frac{dq}{T} = \frac{\text{Work done by the gas } (W)}{T}$

$$W = -\Delta S\times T = \frac{-\Delta S\times PV}{nR}$$

52. (a) Initial equilibrium

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$-10 = \Delta G^\circ + RT\ln\frac{(1)^3}{(1)^3}$$

$\therefore \quad \Delta G^\circ = -10$ kJ

Thus, ΔG° for the reverse reaction $= +10000$ J

$$\underset{2 \text{ mole}}{2Fe(s)} + 3CO_2 \rightleftharpoons Fe_2O_3(s) + \underset{2 \text{ mole}}{3CO}\ ;$$

$\Delta G^\circ = 10000$ J

Also, $\Delta G = \Delta G^\circ + 2.303RT\log_{10}\frac{(2)^3}{(2)^3}$

$= 10000 + 0$

$= 10000$ J

53. (c) $\frac{u_{rms_1}}{u_{rms_2}} = \sqrt{\frac{T_1}{T_2}}$

$$\frac{2\times u}{u} = \sqrt{\frac{T_1}{T_2}} \qquad \left(u_{rms_2} = \frac{u_{rms_1}}{2}\right)$$

or $\frac{T_1}{T_2} = 4$

i.e., $T_2 = \frac{T_1}{4}$

From $TV^{\gamma-1} = \text{constant}$ for adiabatic expansion

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

or $\left[\frac{V_1}{V_2}\right]^{\gamma-1} = \frac{T_2}{T_1} = \frac{1}{4}$

$$\therefore \quad \left(\frac{V_1}{V_2}\right)^{1.4-1} = \frac{1}{4}$$

or $$\frac{V_2}{V_1} = 32$$

54. (a) At A : $T_1 = \frac{PV}{nR} = \frac{1\times 22.44}{1\times 0.0821} = 273\ \text{K}$

At B : $T_2 = \frac{PV}{nR} = \frac{1\times 44.88}{1\times 0.0821} = 546\ \text{K}$

At C : $T_3 = \frac{PV}{nR} = \frac{0.5\times 44.88}{1\times 0.0821} = 273\ \text{K}$

55. (a) Equation of line AB is $Y - Y_1 = \frac{Y_1 - Y_2}{X_1 - X_2}(X - X_1)$

$$P - 3P_0 = \frac{3P_0 - P_0}{V_0 - 3V_0}(V - V_0) \qquad \ldots (i)$$

$$\frac{nRT}{V} - 3P_0 = -\frac{P_0}{V_0}(V - V_0)$$

or $$nRT = 3P_0V - \frac{P_0}{V_0}V^2 + P_0V \qquad \ldots (ii)$$

Differentiating w.r.t. V

$$\frac{nRdT}{dV} = 3P_0 - \frac{2P_0}{V_0}V + P_0 = 4P_0 - \frac{2P_0}{V_0}V$$

For max. value of T, $\frac{dT}{dV} = 0$

$$\therefore \quad P^0\left[4 - \frac{2V}{V_0}\right] = 0 \quad \text{or} \quad V = 2V_0$$

Now from (ii)

$$nRT_{max} = 6P_0V_0 - \frac{P_0}{V_0}4V_0^2 + P_0 2V_0 = 4P_0V_0$$

$$\therefore \quad T_{max} = \frac{4P_0V_0}{nR}$$

56. (b) $$\Delta C_p = \frac{\Delta H}{\Delta T} \qquad \text{At equilibrium } \Delta T = 0$$

57. (a) At f.pt. and b.pt., curves become parallel to x-axis during phase transition.

58. (d) Rest all are correct.

59. (b) It is against the 2nd law of thermodynamics.

60. (a) $$C_{v_m} = \frac{n_1 \times \frac{3R}{2} + n_2 \times \frac{5R}{2}}{n_1 + n_2} = \frac{3Rn_1 + 5Rn_2}{2(n_1 + n_2)}$$

$$C_{p_m} = \frac{n_1 \times \frac{5}{2} + n_2 \times \frac{7R}{2}}{n_1 + n_2} = \frac{5Rn_1 + 7Rn_2}{2(n_1 + n_2)}$$

$$\therefore \quad \frac{C_{p_m}}{C_{v_m}} = 1.50 = \frac{5R \times n_1 + 7R \times n_2}{3R \times n_1 + 5R \times n_2}$$

or $$4.50Rn_1 + 7.5Rn_2 = 5Rn_1 + 7Rn_2$$

$$0.5Rn_2 = 0.5Rn_1$$

$$\therefore \quad \frac{n_1}{n_2} = 1$$

61. (c) Formation of bond releases energy *i.e.*, ΔH = – ve. Also entropy decreases during association *i.e.*, ΔS = –ve.

62. (a) $$\Delta H = \Delta U + \Delta nRT$$
$$= 2100 + 2 \times 2 \times 300$$
$$= 3300\ \text{cal/mol}$$
$$\Delta G = \Delta H - T\Delta S$$
$$= 3300 - 300 \times 20$$
$$= 2700\ \text{cal}$$

63. (a) For free expansion $P_{ext} = 0; dw = 0; dq = 0;$

$\therefore$ $du = 0$ and so $dT = 0$

64. (c) $$\Delta S = \frac{\Delta H}{T} = \frac{540\times 18}{373}\ \text{cal mol}^{-1}$$
$$= 26.06\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

65. (b) $$\eta = \frac{T_2 - T_1}{T_2}$$

$$\frac{23.3}{100} = \frac{383 - T}{383}$$

$\therefore$ $T = 294\ \text{K}$

66. (a) For : $\text{Liquid} \rightleftharpoons \text{Vapour}$ $\Delta G = 0$

$\therefore$ $\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{24.914\times 10^3}{94.684} = 263.12\ \text{K}$$

67. (b) $\Delta H = \Delta U + P\Delta V$

$\therefore$ $$P = \frac{\Delta H - \Delta U}{\Delta V} = \frac{50 - 113}{-10} = 6.3\ \text{k Nm}^{-2}$$

68. (c) $w = P(V_2 - V_1)$

At STP, $P = 101325\ \text{Nm}^{-2}$

Initial volume $= 3 \times 22.4\ \text{dm}^3$
$= 67.2\ \text{dm}^3 = 67.2\times 10^{-3}\ \text{m}^{-3}$

Final volume $= 2 \times 22.4\ \text{dm}^3$
$= 44.8\ \text{dm}^3 = 44.8\times 10^{-3}\ \text{m}^{-3}$

$\therefore$ $w = 101325\times[44.8\times 10^{-3} - 67.2\times 10^{-3}]$
$= -101325 \times 22.4 \times 10^{-3}$
$= -2.27\ \text{kJ}$

69. (c) $$C_p = \frac{5}{2}R + R = \frac{7}{2}R = \frac{7\times 8.314}{2}$$
$$= 29.1\ \text{JK}^{-1}\text{mol}^{-1}$$

70. (d) $\Delta n = 0$

71. (b) $$\Delta U = n \times C_v \times \Delta T = 1\times\frac{5}{2}\times 8.314\times 15 = 311.75$$

72. (b) $\Delta G^\circ = 2.303RT \log K_p$

73. (b) For a spontaneous reaction, ΔG = –ve, Thus from

$$\Delta H < T\Delta S$$
$$T > \frac{\Delta H}{\Delta S} = \frac{35.5\times 1000}{83.6} = 425\ \text{K}$$

74. (c) $q = 0$ (For insulated systems)

From I law $q = \Delta U + (-W)$ Work done by the system

$\Delta U = +W$

$\therefore$ $\Delta U = W = -P_{ext} \times \Delta V$
$= -2.5\times(4.5 - 2.5)$
$= -5\ \text{L-atm}$
$= -5 \times 101 = -505\ \text{J}$

PREVIOUS YEARS PROBLEMS

1. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1 atm litre^{-1}. What is the molar heat capacity of gas? **(IIT 2006)**
   (a) $\frac{4R}{2}$ (b) $\frac{3R}{2}$
   (c) $\frac{5R}{2}$ (d) 0

2. Which one of the following statement is false? **(IIT 2001)**
   (a) Work is a state function
   (b) Temperature is state function
   (c) Change in the state is completely defined when initial and final states are specified
   (d) Work appears at the boundary of the system

3. In thermodynamics, a process is called reversible when : **(IIT 2001)**
   (a) surroundings and system changes into each other
   (b) there is no boundary between system and surroundings
   (c) the surroundings are always in equilibrium with system
   (d) the system changes into the surroundings spontaneously

4. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) when a change in internal energy $\Delta U = 30.0$ L - atm. The change in enthalpy (ΔH) of the process is L-atm is : **(IIT 2002)**
   (a) 40.0
   (b) 42.3
   (c) 44.0
   (d) not defined because pressure is not constant

5. Two mole of an ideal gas expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is : **(IIT 2004)**
   (a) 11.4 (b) –11.4
   (c) 0 (d) 4.8

6. The enthalpy of vaporisation of a liquid is 30 kJ mol^{-1} and entropy of vaporisation is 75 J mol^{-1} K^{-1}. The boiling point of the liquid at 1 atm is : **(IIT 2004)**
   (a) 250 K (b) 400 K
   (c) 450 K (d) 600 K

7. When one mole of monoatomic ideal gas T K undergoes reversible adiabatic change under a constant external pressure of 1 atm changes volume from 1 litre to 2 litre. The final temperature in kelvin would be : **(IIT 2005)**
   (a) $\frac{T}{(2)^{2/3}}$ (b) $T + \frac{2}{3 \times 0.081}$
   (c) T (d) $T - \frac{3}{2 \times 0.0821}$

8. The direct conversion of A to B is difficult, hence it is carried out as :
   $A \longrightarrow C \longrightarrow D \longrightarrow B$
   Given, $\Delta S_{(A \to C)} = 50\, eU$; $\Delta S_{(C \to D)} = 30\, eU$; $\Delta S_{(B \to D)} = 20\, eU$; where eU is entropy unit. Thus change in entropy in $(A \to B)$ is : **(IIT 2006)**
   (a) 100 eU (b) 60 eU
   (c) – 100 eU (d) – 60 eU

9. For the reaction : $H_2O_{(l)}$ (1 bar, 373 K) $\longrightarrow$ $H_2O_{(g)}$ (1 bar, 373 K), the correct set of thermodynamic parameters is: **(IIT 2007)**
   (a) $\Delta G = 0, \Delta S = +$ ve (b) $\Delta G = 0, \Delta S = -$ ve
   (c) $\Delta G = +$ ve, $\Delta S = 0$ (d) $\Delta G = -$ ve, $\Delta S = +$ ve

10. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be : ($R = 8.314$ J/mol K) (In 7.5 = 2.01) **[JEE (Main) 2013]**
    (a) $q = -208$ J, $w = +208$ J (b) $q = +208$ J, $w = +208$ J
    (c) $q = +208$ J, $w = -208$ J (d) $q = -208$ J, $w = -208$ J

11. For the process
    $H_2O(l) \longrightarrow H_2O(g)$
    at $T = 100°C$ and 1 atmosphere pressure, the correct choice is : **[JEE (Advanced-II) 2014]**
    (a) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} > 0$
    (b) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} < 0$
    (c) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} > 0$
    (d) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} < 0$

12. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is : (1 L atm = 101.3 J) **[JEE (Advanced) I 2016]**
    (a) 5.763 (b) 1.013
    (c) – 1.013 (d) – 5.763

13. ΔU is equal to : **[JEE (Main) 2017]**
    (a) Isochoric work (b) Isobaric work
    (c) Adiabatic work (d) Isothermal work

14. The standard state Gibbs free energies of formation of C (graphite) and C (diamond) at $T = 298$ K are
    $\Delta_f G°$ [C (graphite)] = 0 kJ mol^{-1}
    $\Delta_f G°$ [C (diamond)] = 2.9 kJ mol^{-1}
    The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is :

[JEE (Advanced) II 2017]

[Useful information : 1 J = 1 kg $m^2 s^{-2}$; 1 Pa = 1 kg $m^{-1} s^{-2}$; 1 bar = 10^5 Pa]

(a) 14501 bar (b) 29001 bar
(c) 58001 bar (d) 1450 bar

SOLUTIONS (Previous Year Problems)

1. (a) $\left(\frac{\delta H}{\delta T}\right)_P = \left(\frac{\delta U}{\delta T}\right)_P + P\left(\frac{\Delta V}{\Delta T}\right)_P$

Now $PV = RT$

or $(V \times 1) \cdot V = RT \quad \left[\because \frac{P}{V} = 1\, l\,\text{atm}^{-1}\right]$

or $V^2 = RT$

or $2V\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{1}$

or $\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{2V \times (1\,\text{atm}\, l^{-1})}$

$\therefore \quad C_P = C_v + \frac{P \times R}{2V} = \frac{3}{2}R + \frac{R}{2} = 2R \qquad \left(\because \frac{P}{V} = 1\right)$

2. (a) Work is not a state function. State functions are P, T, V, U, H, S, etc. State functions are path independent.

3. (c) During reversible process, the internal equilibrium is disturbed only infinitesimally small and in the limit, it is not disturbed at all. Thus, system and surroundings remain in equilibrium.

4. (c) $H = U + PV$

$\Delta H = \Delta U + \Delta(PV)$

$= \Delta U + P_1(V_2 - V_1) + V_2(P_2 - P_1)$

$= 30 + 2(5-3) + 5 \times (4-2)$

$= 44$ L-atm

5. (c) For 1 mole $\Delta H = \Delta U + P\Delta V$

$= C_v(T_2 - T_1) + R(T_2 - T_1)$

$\Delta H = (C_v + R)(T_2 - T_1)$

$= (C_v + R)\Delta T$

$\because \quad \Delta T = 0 \qquad \therefore \Delta H = 0$

6. (b) $\Delta S = \frac{\Delta H_{\text{vap.}}}{T}$

$\therefore \quad T = \frac{\Delta H_{\text{vap.}}}{\Delta S} = \frac{30 \times 10^3}{75} = 400\,\text{K}$

7. (a) $TV^{\gamma-1} = K$

$\therefore \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad \left(\gamma = \frac{5}{3}\right)$

$T_1 V_1^{2/3} = T_2 V_2^{2/3}$

or $T_1 (1)^{2/3} = T_2 (2)^{2/3}$

or $T_2 = \frac{T_1}{(2)^{2/3}} = \frac{T}{(2)^{2/3}}$

8. (b) $\Delta S_{A \to B} = \Delta S_{A \to C} + \Delta S_{C \to D} + \Delta S_{D \to B}$

$= 50 + 30 - 20 = 60\, eU$

$(\Delta S_{B \to D} = 20, \ \therefore \ \Delta S_{D \to B} = -20)$

9. (a) $S_{(g)} > S_{(l)}$ and the process is spontaneous at 100°C and is in equilibrium. Thus $\Delta G = 0$

10. (c) The given process is isothermal, hence $\Delta U = 0$

$\therefore \quad q = -w$

$\because \quad q = 208\,\text{J}$

$\therefore \quad w = -208\,\text{J}$ (*i.e.* work done by the system)

11. (b) At 100°C and 1 atmosphere pressure, water shows equilibrium in two phases as $H_2O(l) \rightleftharpoons H_2O(g)$ and thus for equilibrium $\Delta S_{\text{total}} = 0$ and

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

For change of liquid to gases state, ΔS_{sys} is + ve and therefore $\Delta S_{\text{surr.}}$ will be − ve.

$\therefore \quad \Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$

12. (c) $\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{q_{\text{sys}}}{T} = \frac{W_{\text{sys}}}{T}$

($\because$ Isothermal expansion $\Rightarrow \Delta U = 0$)

$\Delta S_{\text{surr}} = \frac{-P_{\text{ext}}(V_f - V_i)}{T} = \frac{-3(2-1)}{300}\,\text{L atm K}^{-1}$

$= -0.01\,\text{L atm K}^{-1} = -0.01 \times 101.3\,\text{JK}^{-1}$

$= -1.013\,\text{JK}^{-1}$

Note : The temperature of surroundings has been assumed to be 300 K.

13. (c) For adiabatic process, $q = 0$

From 1st law of thermodynamics, $\Delta U = W$

14. (a) $\Delta G^\circ = \Delta V \cdot \Delta P$

$= 2 \times 10^{-6} \Delta P$

or $\Delta P = \frac{\Delta G^\circ}{\Delta V} = \frac{2.9 \times 10^3 \times 10^6}{2}\,\text{Pa}$

$\Delta P = 1.45 \times 10^9\,\text{Pa} = \frac{1.45 \times 10^9}{10^5}\,\text{bar}$

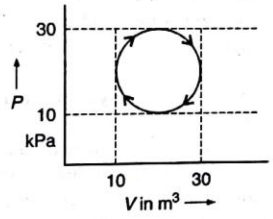
$= 1.45 \times 10^4\,\text{bar}$

$P_F - 1 = 14500\,\text{bar}$

or $P_F = 14501\,\text{bar}$

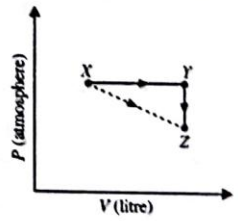
OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Select the correct statement :
   (a) There is a natural asymmetry between converting work to heat and converting heat to work.
   (b) No process is possible in which the sole results is the absorption of heat from a reservoir and its complete conversion into work.
   (c) For every chemical reaction at equilibrium standard change in Gibbs free energy is zero.
   (d) A constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
2. Which of the following are intensive properties?
   (a) Heat capacity (b) Refractive index
   (c) Specific volume (d) Entropy
3. Which of the following are extensive properties?
   (a) Elevation in b. pt. (b) b. pt.
   (c) f.pt. (d) E° of cell
4. Which one is not correct for a cyclic process as shown in figure?



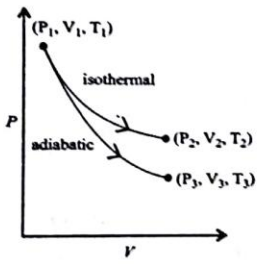
   (a) $dU = 0$ (b) $q = -w$
   (c) 314 J (d) 31.4 J
5. If w_1, w_2, w_3 and w_4 are work done in isothermal, adiabatic, isobaric and isochoric reversible expansion for an ideal gas then :
   (a) $w_3 > w_1$ (b) $w_1 > w_2$
   (c) $w_2 > w_4$ (d) $w_4 > w_2$
6. Average value of poisson's ratio for a mixture of 2 mole of each gas A and B is 1.66, then :
   (a) gases are monoatomic
   (b) gases are diatomic
   (c) average molar heat capacity at constant volume is 4 cal
   (d) average molar heat capacity at constant V is 3 cal
7. A reaction attains equilibrium state under standard conditions, then :
   (a) equilibrium constant $K = 0$
   (b) equilibrium constant $K = 1$
   (c) $\Delta G^\circ = 0$ and $\Delta H^\circ = T\Delta S^\circ$
   (d) $\Delta G = 0$ and $\Delta H = T\Delta S$
8. The poisson's ratio for O_2 is 1.4. Which are correct for O_2?
   (a) $C_v = 5$ cal (b) $c_v = 0.156$ cal
   (c) $C_p = \frac{R\gamma}{\gamma - 1}$ (d) $C_v = \frac{R}{(\gamma - 1)}$
9. Select the correct statements :
   (a) The magnitude of work involved in an intermediate irrversible expansion is less than that involved in reversible expansion
   (b) Heat absorbed during intermediate reversible expansion is more than that in intermediate reversible expansion
   (c) The magnitude of work involved in an intermediate reversible compression is more than that involved in intermediate irreversible compression
   (d) Heat released during intermediate irrversible compression is more than that in intermediate reversible compression
10. Select the correct statements for the equilibrium under standard conditions
    $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$; ΔS_1°
    $H_2O_{(l)} \rightleftharpoons H_2O_{(v)}$; ΔS_2°
    $H_2O_{(s)} \rightleftharpoons H_2O_{(v)}$; ΔS_3°
    (a) $\Delta S_1^\circ > \Delta S_2^\circ$ (b) $\Delta S_2^\circ >>> \Delta S_1^\circ$
    (c) $\Delta S_3^\circ > \Delta S_2^\circ$ (d) $\Delta S_3^\circ > \Delta S_1^\circ$
11. A cyclic process is completed by process 1 and process 2. If ΔQ and ΔW represent heat supplied and work done respectively. ΔU_1 and ΔU_2 are the changes in internal energy of two process then:
    (a) $\Delta U_1 = \Delta U_2$ (b) $\Delta U_1 = -\Delta U_2$
    (c) $\Delta Q = \Delta W$ (d) $\Delta Q = -\Delta W$
12. For a reaction to be spontaneous in neither direction regarding the closed system:
    (a) $(\Delta G)_{T,P} = 0$ (b) $(\Delta G)_{T,P} = -$ve
    (c) $(\Delta S)_{U,V} = 0$ (d) $(\Delta S)_{U,V} = +$ve
13. Which of the following are not path dependent:
    (a) Work (b) Internal energy
    (c) Heat change (d) Entropy
14. Identify the intensive quantities from the following:
    (a) Enthalpy (b) Temperature
    (c) Volume (d) Refrative index
15. Among the following, the state function(s) is (are) : **(IIT 2009)**
    (a) Internal energy
    (b) Irreversible expansion work
    (c) Molar enthalpy
    (d) Reversible expansion work
16. Among the following the intensive property (properties) are: **(IIT 2010)**
    (a) Molar conductivity (b) Electromotive force
    (c) Resistance (d) Heat capacity

17. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done] **(IIT 2012)**



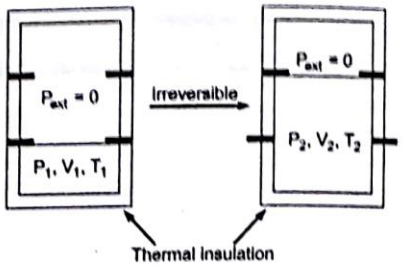
(a) $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$
(b) $w_{x\to z} = w_{x\to y} + w_{y\to z}$
(c) $w_{x\to y\to z} = w_{x\to y}$
(d) $\Delta S_{x\to y\to z} = \Delta S_{x\to y}$

18. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? **(IIT 2012)**



(a) $T_1 = T_2$
(b) $T_3 > T_1$
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

19. An ideal gas in a thermally insulated vessel at internal pressure $= P_1$, volume $= V_1$ and absolute temperature $= T_1$ expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion,



[JEE (Advanced-I) 2014]

(a) $q = 0$ (b) $T_2 = T_1$
(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

20. An ideal gas is expanded from (P_1, V_1, T_1) to (P_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are): **[JEE (Advanced-I) 2017]**

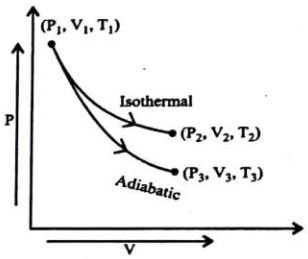
(a) The work done on the gas is maximum when it is compressed irreversibly from (P_2, V_2) to (P_1, V_1) against constant pressure P_1
(b) The work done on the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions
(c) The change in internal energy of the gas (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$
(d) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

21. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by: **[JEE (Advanced-II) 2017]**

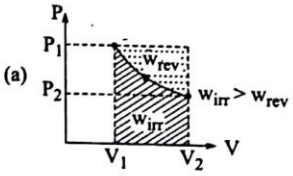
(a) with increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
(b) with increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
(c) with increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
(d) with increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative

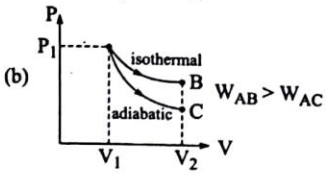
SOLUTIONS (More Than One Answer Correct)

1. (b,d) $\Delta G = -$ ve for spontaneous process and $\Delta G^\circ \neq 0$ at equilibrium. Statement (b) represents carnot theorem.
2. (b,c,d) Mass independent properties are intensive.
3. (a) Mass dependent properties are extensive.
4. (a,b,c) For a cyclic process $dU = 0$
   $\therefore\ q = \Delta U + (-w), \qquad q = -w$
   Also, w = area covered by sphere
   $$= \pi r^2 = \pi \times \left[\frac{(V_2 - V_1)}{2}\right]^2 = \frac{\pi \times (20)^2}{2^2}$$
   $$= 100\pi = 100 \times 3.14 = 314 \text{ J}$$
5. (a,b,c) The correct order is : $w_3 > w_1 > w_2 > w_4$
6. (a,d) γ for monoatomic is 1.66 $\therefore\ C_v = \frac{3R}{2}, C_p = \frac{5}{2}R$
   $$C_{vM} = \frac{2\times\frac{3R}{2} + 2\times\frac{3R}{2}}{4} = \frac{3}{2}R \quad \therefore \quad C_v = 3\text{cal}$$
   $$\therefore\ C_{pM} = \frac{2\times\frac{5R}{2} + 2\times\frac{5R}{2}}{4} = \frac{5}{2}R \quad \therefore \quad C_p = 5\text{cal}$$
7. (b,c,d) $\Delta G^\circ = 0$ at equilibrium under standard state. Also, at eq. $\Delta G = 0$
   $\therefore \qquad \Delta H^\circ - T\Delta S^\circ = 0$
   Also, $\qquad \Delta G^\circ = 2.303\, RT \ln K$
   $\therefore \qquad K = 1$
8. (a,b,c,d) $\qquad \frac{C_p}{C_v} = 1.4 = \gamma$
   $$C_p - C_v = R$$
   $\therefore \gamma C_v - C_v = R\ \therefore C_v = \frac{R}{\gamma - 1}$ and similarly $C_p - \frac{C_p}{\gamma} = R$
   $\therefore \qquad C_v = \frac{2}{0.4} = 5\text{cal}\ \therefore\ C_p \frac{\gamma . R}{(\gamma - 1)}$
   Also, $\qquad c_v = \frac{2}{0.4 \times 32} = 0.156\text{cal}$
9. (a,b,c,d) These are mathematically established facts. For details consult **Concepts of Physical Chemistry by Dr. P. Bahadur,** Prakash Publications Muzaffarnagar.
10. (b,c,d) $H_2O_{(s)}$ has more ordered arrangement. Also,
    $$\Delta S_2^\circ = S^\circ_{H_2O_{(l)}} - S^\circ_{H_2O_{(l)}}$$
    $$\Delta S_0^1 = S^\circ_{H_2O_{(l)}} - S^\circ_{H_2O_{(s)}}$$
    $\therefore\ S^\circ_{H_2O_{(l)}}$ is maximum and this $\Delta S_2^\circ >>> \Delta S_1^\circ$
11. (a, c) For a cyclic process $\Delta U = 0 \qquad \therefore\ \Delta U_1 = -\Delta U_2$
    and $\quad \Delta Q = \Delta U + \Delta w$
    $\therefore \qquad \Delta Q = \Delta w$
12. (a, c) For a reaction to be spontaneous in neither direction $(\Delta G)_{T,P}, (\Delta S)_{U,V}$ and $(\Delta U)_{S,V}$ should be zero.
13. (b, d) Internal energy and entropy are path independent.
14. (b, d) These are mass independent.
15. (a,c) Work is not state function.
16. (a,b) An intensive property is one for which a system in fixed state is divided into two parts, the property of each part in that state shows same value. These are mass independent. Resistance and heat capacity are mass dependent.
17. (a,c) $\Delta S_{x-z} = \Delta S_{x\to y} + \Delta S_{y\to z}$ [entropy (S) being a state function, and thus additive property]
    $W_{x\to y\to z} = W_{x\to y}$ (work done in $Y \to Z$ is zero because it is an isochoric process)
18. (a,c,d)



    $T_1 = T_2$ because process is isothermal.
    Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.
    In adiabatic process work of expansion is done on the cost of internal energy hence it decrease while in isothermal process temperature remains constant and thus no change in internal energy. Therefore $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$
19. (a,b,c)
    For thermally insulated container, $q = 0$ and for free expansion, $W = 0$ and $\Delta U = 0$
    So, $\qquad T_1 = T_2$
    Also, $\qquad P_1V_1 = P_2V_2$
20. (a,b,d)





(c) (i) $\Delta U = nC_v\Delta T = 0$ (isothermal hence $\Delta T = 0$)

(ii) $\Delta U = q + w = -\text{ve}$ ($q = 0, w$ is negative, as work done by the system $\Delta U = nC_v\Delta T$, ΔU can be negative only when $\Delta T = -\text{ve}$

(d) $q = 0$ (adiabatic), $w = 0$ (free expansion)
$\Delta U = 0$ and $\Delta T = 0$ (isothermal)

21. (b,c)

$\because \quad \Delta G = \Delta H - T\Delta S$

at equilibrium $\Delta G = 0$

$\therefore \quad \Delta S = T\Delta S$

$$\Delta S_{\text{Surr}} = +\frac{\Delta H_{\text{Surr}}}{T_{\text{Surr}}}$$

For endothermic reaction ($\Delta H_{sys} = +\text{ve}$) and $\Delta H_{\text{Surr}} = -\text{ve}$, if T_{Surr} increases, $\Delta S_{Surr} = -\text{ve}$ or entropy of surrounding decreases *i.e.*, unfavourable change.

For exothermic reaction ($\Delta H_{sys} = -\text{ve}$), if T_{surr} increases, $\Delta S_{surr} = +\text{ve}$ or entropy of surrounding increases. Thus, favourable change

Also, for $\Delta S_{sys} = \dfrac{\Delta H_{sys}}{T_{sys} \text{ or } T_{surr}}$ (in equilibrium)

For exothermic reaction $\Delta H_{sys} = -\text{ve}$

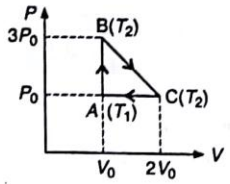
$\therefore \quad \Delta S_{sys} = -\text{ve}$

For endothermic reaction $\Delta H_{sys} = +\text{ve}$

$\therefore \quad \Delta S_{sys} = +\text{ve}$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : One mole of an ideal monoatomic gas is taken round cyclic process $ABCA$ as shown in figure. Calculate.



[1] The work done by the gas.
(a) P_0V_0 (b) $-P_0V_0$
(c) $2P_0V_0$ (d) $-2P_0V_0$

[2] The heat rejected by the gas in the path CA the heat absorbed by the gas in the path AB respectively.
(a) $\frac{5}{2}P_0V_0, 3P_0V_0$ (b) $3P_0V_0, \frac{5}{2}P_0V_0$
(c) $5P_0V_0, 3P_0V_0$ (d) $3P_0V_0, 5P_0V_0$

[3] The net heat absorbed by the gas in the path BC.
(a) $\frac{P_0V_0}{3}$ (b) $\frac{P_0V_0}{2}$
(c) P_0V_0 (d) $2P_0V_0$

[4] The maximum temperature attained by the gas during the cycle.
(a) $3T_1$ (b) $2T_1$
(c) $4T_1$ (d) $5T_1$

Comprehension 2: The change in internal energy (U) can be brought about in two ways :

(i) Either by allowing the heat to flow into the system or out of the system

(ii) By doing work on the system or the work done by the system

Using the symbol q to represent heat transferred to system and using work done by the system $-w$, we can represent the internal energy change of a system Δu, as :

$$q = \Delta U + (-w)$$ (First law of thermodynamics)

If the reaction is carried out in a closed container with constant volume, so that $\Delta V = 0$

Hence, $q_v = \Delta U$

On the other hand, if a reaction is carried out in open vessel that keeps the pressure constant and allows the volume of the system to change freely. In such case, $\Delta V \neq 0$ and $-w = P \cdot \Delta V$.

Hence, $q_p = \Delta U + P\Delta V$

Also $q_p = q_v + \Delta n_g RT$

As reactions carried out at constant pressure are so common, the heat change for such process is given a special symbol ΔH, called the enthalpy change of the reaction. The enthalpy (H) of the system is the name given to the quantity ($U + PV$).

[1] In which of the following cases ΔH and ΔU are not equal to each other?
(a) The reaction involves no gaseous reactant and product
(b) The number of mole of gaseous reactants and gaseous products are not equal to each other
(c) The number of mole of gaseous reactants and gaseous products are equal to each other
(d) The process is carried out in closed vessel

[2] The latent heat of vaporization of liquid at 500 K and 1 atmospheric pressure is 10.0 kcal/mol. What will be the change in internal energy of 3 mole of the liquid at the same temperature and pressure?
(a) 27.0 kcal (b) 13.0 kcal
(c) –27.0 kcal (d) –13.0 kcal

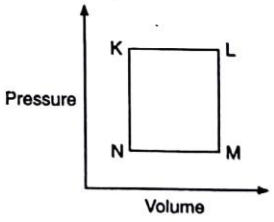
[3] A mixture of 2 mole of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If ΔH is the enthalpy change and ΔU is the change in internal energy, then :
(a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$
(c) $\Delta H = \Delta U$ (d) Not definite

[4] A piston exerting a pressure of 1.0 atmosphere rests on the surface of water at 100°C. The pressure is reduced to smaller extent and as a result 10 g of water evaporates and absorbs 22.2 kJ of heat. The change in internal energy is :
(a) 18.24 kJ (b) 20.477 kJ
(c) 22.05 kJ (d) 23.923 kJ

[5] A system is provided 50 kJ energy and work done on the system is 100 J. The change in internal energy is :
(a) 150 J (b) 50 kJ
(c) 50.1 kJ (d) 49.9 kJ

[6] One mole of a gas is allowed to expand freely in vacuum at 300 K. The work done during the process is :
(a) 300 J (b) 300 kJ
(c) zero (d) nothing can be said

Comprehension 3 : A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



[1] The pair of isochoric processes among the transformation of states is : **[JEE (Advanced) 2013]**

(a) K to L and L to M (b) L to M and N to K
(c) L to M and M to N (d) M to N and N to K

[2] The succeeding operations that enable this transformation of states are :

(a) Heating, cooling, heating, cooling
(b) Cooling, heating, cooling, heating
(c) Heating, cooling, cooling, heating
(d) Cooling, heating, heating, cooling

[JEE (Advanced) II 2013]

SOLUTIONS

Comprehension 1

Path AB is isochoric ($w_1 = 0$), path BC is isothermal ($w_2 = -ve$), path CA is isobaric ($w_3 = +ve$)

[1] (b) Total work done by gas $(w) = w_1 + w_2 + w_3$

$$= 0 - \frac{1}{2}[(P_B + P_C) \times (V_C - V_B)] + P_A(V_C - V_A)$$

$$= 0 - \frac{1}{2}[4P_0 \times V_0] + P_0(2V_0 - V_0)$$

$$= -2P_0V_0 + P_0V_0 = -P_0V_0$$

Also, $w_2 = -2P_0V_0$

and $w_3 = P_0V_0$

[2] (a) Also, **For the path AB, i.e., isochoric**

$$q_1 = n \times C_v \times (T_B - T_A) = 1 \times \frac{3}{2}R\left[\frac{P_BV_B - P_AV_A}{R}\right]$$

$$= \frac{3}{2}[3P_0V_0 - P_0V_0] = +3P_0V_0$$

For the path CA, i.e., isobaric

$$q_3 = n \times C_p(T_A - T_B) = 1 \times \frac{5}{2}R\left[\frac{P_AV_A - P_BV_B}{R}\right]$$

$$= \frac{5}{2}[P_0V_0 - 2P_0V_0]$$

$$q_3 = -\frac{5}{2}P_0V_0$$

[3] (b) Also net heat absorbed $= 3P_0V_0 - \frac{5}{2}P_0V_0 = \frac{P_0V_0}{2}$

$$\therefore \quad q_{net} = \frac{P_0V_0}{2}$$

[4] (a) Also, $\frac{P_0V_0}{T_1} = \frac{3P_0V_0}{T_2} \quad \therefore \quad T_2 = 3T_1$

Comprehension-2

[1] (b) If $\Delta n_g = 0$ then only $\Delta H = \Delta U$

[2] (a) $3H_2O(l) \longrightarrow 3H_2O(g)$; $\Delta n_g = 3$

$$\Delta H = \Delta U + \Delta n_gRT$$

$$\therefore \quad \Delta U = \Delta H - \Delta n_gRT$$

$$= 10 \times 3 - 3 \times 2 \times 10^{-3} \times 500 = 27 \text{ kcal}$$

[3] (b) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

$$\Delta n_g = 2 - 3 = -1$$

$$\Delta H = \Delta U + \Delta n_gRT = \Delta U - RT$$

Hence, $\Delta H < \Delta U$

[4] (b) $\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_gRT$

$$\therefore \quad \Delta U = \Delta H - \Delta n_gRT$$

$$= 222 - \frac{10}{18} \times 8.314 \times 10^{-3} \times 373$$

$$= 220.477 \text{ kJ}$$

[5] (c) $q = \Delta U + (-W)$

or $\Delta U = q + (W)$ where W is work done on the system

$$= 50 \times 10^{-3} + 100 = 50.100 \text{ J} = 50.1 \text{ kJ}$$

[6] (c) $W = -P_{ext}(V_2 - V_1) = -0 \times (V_2 - V_1) = 0$

($P_{ext} = 0$ if expansion in vacuum)

Comprehension-3

[1] (b) For a given mass of gas (constant n) volume increases from K to L at constant P due to heating *i.e.* isobaric process. Pressure decreases from L to M at constant V due to cooling *i.e.* **isochoric process.** Volume decreases from M to N at constant P due to cooling *i.e.* **isobaric process.** Pressure increases from N to K at constant V due to heating *i.e.* **isochoric process.** Thus isochoric process (constant V) are L to M and N to K.

[2] (c) Follow answer 1.

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. S : Work and internal energy are not state functions.
   E : The sum of $q + w$ is state function.
2. S : Internal energy of a system is an extensive property.
   E : The internal energy of a system depends upon the amount and physical state of the substance.
3. S : The change in internal energy and change in heat enthalpy does not depend upon the path by which changes are brought in.
   E : Both ΔU and ΔH are path independent as U and H are state functions.
4. S : Both work and heat are manifested by an effect on the surroundings.
   E : Work done by/on the system and ΔH appear only at the boundary of system.
5. S : The zeroth law of thermodynamics was known before I law of thermodynamics.
   E : The zeroth law concerning thermal equilibrium was appeared after three laws (I, II and III) of thermodynamics and thus was named as zeroth law.
6. S : The entropies of CO, NO, N_2O, $Cl_2(s)$ are not zero at absolute zero.
   E : These are exceptions to III law of thermodynamics.
7. S : Phase transition involves change in internal energy only.
   E : Phase transition occurs at constant pressure.
8. S : The change in entropy during melting of ice is negligible in comparison to change in entropy during vaporisation.
   E : The volume occupied by solid and liquid is too less in comparison to volume occupied by gas.
9. S : The SI unit of entropy is $JK^{-1}mol^{-1}$.
   E : $\Delta S = \frac{q_{rev}}{T}$.
10. S : Whole of work can be converted to heat but whole heat cannot be converted to work.
    E : Conversion of work into heat by friction and II law of thermodynamics are respectively responsible for statement.
11. S : For $H_2(g) + O_2(g) \longrightarrow H_2O_2(l)$; $\Delta H = -187.6$ kJ mol^{-1}, the word stability for H_2O_2 represents energetic stability and not kinetic stability.
    E : The reaction does not occur spontaneously.
12. S : $\Delta_f H°$ for white phosphorus has been taken to be zero, whereas black phosphorus is most stable allotrope of phosphorus and this is only exception.
    E : The reference standard state of white phosphorus is taken despite the fact that this form not being the most stable allotrope but simply the most reproducible form of phosphorus.
13. S : Two bodies at thermal equilibrium may or may not have equal heat.
    E : Two bodies at thermal equilibrium have same temperature.
14. S : Energy can neither be created nor destroyed.
    E : Total energy of the universe is constant.
15. S : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
    E : The volume occupied by the molecules of an ideal gas is zero.
16. S : A non-spontaneous endothermic reaction at room temperature may be spontaneous at high temperature.
    E : At high temperature $T\Delta S$ becomes more than ΔH.
17. S : Neither q nor W is state function but $q + W$ is state function.
    E : ΔU is state function.
18. S : Fall of water as rain drops from clouds is spontaneous.
    E : During the process entropy increases.
19. S : There is a natural asymmetry between converting work to heat and converting heat to work.
    E : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. **[IIT 2008]**

ANSWERS (Statement Explanation Problems)

1. (d) w and q are state functions, whereas $\Delta U = q + w$ is state function.
2. (c) Reason is correct explanation for statement.
3. (c) Reason is correct explanation for statement.
4. (c) —do—
5. (b) The reason is also an explanation for the name Zeroth law.
6. (d) Both are facts.
7. (b) Phase transition occurs at constant P and thus change is referred as ΔH.
8. (c) Reason is correct explanation for statement. $\Delta S_{vap} = S_{vap} - S_{liq}$ and $\Delta S_{fus} = S_{(L)} - S_{(S)}$ $\Delta S_{vap} >>> \Delta S_{fus}$. Gaseous state has more disordered system.
9. (c) $\Delta S = \frac{q_{rev}}{T}$, thus, unit is $J\ K^{-1} mol^{-1}$.
10. (c) Reason is correct explanation for statement.
11. (c) —do—
12. (c) —do—
13. (d) Both are facts.
14. (d) Both are facts.
15. (d) $q = \Delta U - W$. For isothermal expansion $\Delta U = 0$. Also $W = 0$, because $W = P \times \Delta V$ and $P = 0$; Also volume occupied by molecules is zero for ideal gas. Thus, both assertion and reason are correct, but this is not an explanation for assertion.
16. (c) For a spontaneous reaction $\Delta G = -ve$ and $\Delta G = \Delta H - T\Delta S$, if $\Delta H = +ve, \Delta G$ will be negative when $T\Delta S > \Delta H$.
17. (c) Explanation is correct reason for statement.
18. (c) Explanation is correct reason for statement.
19. (c) Statement represents II law of thermodynamics which is an arguement for statement.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List A	List B
A. Kirchoff's equation	(a) $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)$
B. Claussues Clapeyron equation	(b) $\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$
C. van't Hoff isochore	(c) $\frac{d \ln P}{dT} = \frac{\Delta H^\circ}{RT^2}$
D. Gibbs Helmholtz equation	(d) $\frac{\partial(\Delta G)}{\partial T} = \Delta C_p$

Type II : More Than One Match Are Possible

2.

List A	List B
A. $H_2O(l) \xrightarrow{1\text{ atm, }20\text{ K}} H_2O(s)$	1. $\Delta rG = +ve$
B. $H_2O(l) \xrightarrow{1\text{ atm, }363\text{ K}} H_2O(g)$	2. $\Delta rS = +ve$
C. $H_2O(l) \xrightarrow{1\text{ atm, }373\text{ K}} H_2O(g)$	3. $\Delta rH = -ve$
D. $H_2O(g) \xrightarrow{1\text{ atm }273\text{ K}} H_2O(l)$	4. $\Delta rH = +ve$

3.

List A	List B
A. Work	1. Boundary phenomenon
B. Heat	2. Path function
C. Temperature	3. Intensive property
D. $q + w$	4. Extensive property

4.

Reaction	At equilibrium
A. $H_2O(l) \rightleftharpoons H_2O(v)$	a. $\Delta G = 0$
B. $H_2O(s) \rightleftharpoons H_2O(v)$	b. $\Delta S_{Total} = 0$
C. $H_2O(s) \rightleftharpoons H_2O(l)$	c. $Q = K_p$
	d. $\Delta H = +ve$
	e. $\Delta H = -ve$
	f. $\Delta V = +ve$
	g. $\Delta V = -ve$

5.

List A	List B
(A) Cyclic rule	1. $-P_{ext} \times \Delta V$
(B) Work done in reversible isothermal process	2. $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$
(C) Work done in isobaric process	3. $nRT \ln \frac{P_1}{P_2}$
(D) Work done during free expansion	4. $nRT \ln \frac{V_1}{V_2}$
(E) Work done in adiabatic reversible process	5. $-nR(T_{final} - T_{initial})$
(F) Work done in adiabatic irreversible process	6. Zero
	7. $\frac{nR}{r-1}(T_{final} - T_{initial})$
	8. $-nC_v \cdot T_{initial}\left[1 - \left(\frac{P_2}{P_1}\right)^{R/C_p}\right]$
	9. $-P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right]$

6.

Thermodynamic Functions	Dependent
A. Internal energy	(a) Temperature
B. Heat enthalpy	(b) Mass
C. Entropy	(c) Pressure
D. Gibbs energy	(d) Volume
E. Work	(e) State

7.

List A	List B
A. Raw egg → Boiled egg	(a) $\Delta S_T = +ve$
B. $Pd + H_2 \rightleftharpoons$ absorbed gas	(b) $\Delta S = -ve$
C. $Water_{(l)} \underset{1\text{ atm}}{\overset{373\text{ K}}{\rightleftharpoons}} Water_{(g)}$	(c) $\Delta G^\circ = -ve$
D. $Water_{(s)} \underset{1\text{ atm}}{\overset{0^\circ C}{\rightleftharpoons}} Water_{(l)}$	(d) $\Delta G = 0$

8. Match the thermodynamic processes given under Column-I with the expressions given under Column-II.

Column-I	Column-II
(A) Freezing of water at 273 K and 1 atm	(P) $q=0$
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q) $w=0$
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R) $\Delta S_{sys}<0$
(D) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm	(S) $\Delta U=0$
	(T) $\Delta G=0$

[JEE (Advanced I) 2015]

Type III : Only One Match From Each List

9.

List A	List B	List C
1. Trouton's rule	a. $\Delta S^{\circ}_{vap}=\frac{\Delta H^{\circ}_{V}}{T_b}$	(i) Entropy of vaporisation
2. Kirchoff's equation	b. $\left(\frac{\partial \Delta_H}{\partial T}\right)_P=C_p$	(ii) Reaction enthalpy
3. Joule-Thomson effect	c. $\left(\frac{\partial T}{\partial P}\right)_H=\mu$	(iii) Inversion temperature
4. Polymeri-sation	d. $\overline{M}_n=\frac{\Sigma n_i m_i}{\Sigma n_i}$	(iv) Glass transition temperature
5. Ideal gas	e. $\left(\frac{\partial E}{\partial V}\right)_T=0$	(v) Hypothetical concept
6. Sublimation of ice	f. $\Delta H_{sub}=\Delta H_f+\Delta H_V$	(vi) Hoar frost

ANSWERS

1. A – d; B – c; C – b; D – a
2. A – 3; B – 1, 2, 4; C – 2,4; D – 2,4
3. A – 1, 2, 4; B – 1, 2, 4; C – 3; D – 3
4. A – a, b, c, d, f; B – a, b, c, d, f; C – a, b, c, d, g
5. A – 2; B – 1, 3, 4; C – 1, 5; D – 1, 6; E – 1, 7, 8; F – 1, 5, 9
6. A – a, b, d, e; B – a, b, c, e; C – a, b, c, d, e; D – a, b, c, d, e; E – a, c, d
7. A – a, c; B – b, c, d; C – a, c, d; D – b, c, d
8. A – R, T; B – P, Q, S; C – P, Q, S; D – P, Q, S, T
9. 1 – a – i; 2 – b – ii; 3 – c – iii; 4 – d – iv; 5 – e – v; 6 – f – vi

16 Thermochemistry

The chapter deals with thermal as well as chemical changes during the course of reaction.

The thermochemical equation : 1. A thermochemical equation represents the thermal changes as well as chemical changes taking place during the course of reaction, *e.g.*,

$$C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.3 \text{ kcal}$$

2. A thermochemical equation is treated as an algebraic equation for all practical purposes, *e.g.*, it may be added, subtracted, multiplied or divided as the case may be.

3. A thermochemical equation should always be written in mole and never in g.

Exothermic and Endothermic reactions

For a given chemical change

$$A + B \longrightarrow C + D$$

Change in internal energy during reaction (ΔU)
= Internal energy of products – Internal energy of reactants

i.e., $\Delta U = \Sigma U_P - \Sigma U_R$

if ΔU = +ve; the reaction is endothermic

if ΔU = –ve; the reaction is exothermic

The exothermic and endothermic nature are expressed as

Exothermic : $C + O_2 \longrightarrow CO_2; \qquad \Delta U = -94.3$ kcal

or $C + O_2 \longrightarrow CO_2 + 94.3$ kcal

Endothermic : $C + 2S \longrightarrow CS_2; \qquad \Delta U = +22$ kcal

or $C + 2S \longrightarrow CS_2 - 22$ kcal

Heat of reaction : It is defined as,

—the amount of heat absorbed or released (*i.e.*, the change in internal energy or the change in heat enthalpy)

during the complete course of reaction as represented by balanced chemical equation *e.g.*,

$$C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.3 \text{ kcal}$$

i.e., 12 g C reacts with 32 g O_2 to give 44 g CO_2 along with 94.3 kcal of heat evolution,

$$C + 2S \longrightarrow CS_2; \qquad \Delta H = +22 \text{ kcal}$$

i.e., 12 g C reacts with 64 g S to give 76 g CS_2 along with 22.0 kcal of heat absorption.

Factor's influencing heat of reaction

1. Condition of constant *P* or *V* :

Heat changes at constant volume are expressed in ΔU.

Heat changes at constant pressure are expressed in ΔH.

Also, for a change $\Delta H = \Delta U + P\Delta V$ ...(1)

where, P is the pressure and ΔV is change in volume.

Also, ΔH and ΔU are related together as

$$\Delta H = \Delta U + \Delta n \cdot RT \qquad ...(2)$$

Δn = Mole of products – Mole of reactants

R = Molar gas constant

T = Temperature in kelvin.

Note : While using Eq. (2) for numericals one should keep in mind that for Δn

(1) Count only gaseous phase molecules.

(2) If $\Delta n = 0$; $\Delta H = \Delta U$.

(3) Δn may be +ve, –ve, integer or fraction.

(4) Put R in the same units in which ΔH and ΔU are given.

(5) Normally reactions are carried out at constant pressure and therefore, heat changes are to be taken as ΔH unless stated otherwise.

2. Physical nature of reactants and products :

For reactants : If $C_{Diamond}$ and $C_{Amorphous}$ are allotropic forms of C.

$$C_{Diamond} + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -94.3 \text{ kcal}$$

$$C_{Amorphous} + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -97.6 \text{ kcal}$$

For products :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -68.3 \text{ kcal}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \qquad \Delta H = -57.0 \text{ kcal}$$

3. Temperature : The variation of ΔH or ΔU with temperature is expressed in terms of Kirchhoff's equation.

$$\Delta H_2 - \Delta H_1 = \Delta C_p\ (T_2 - T_1)$$

$$\Delta U_2 - \Delta U_1 = \Delta C_v\ (T_2 - T_1)$$

where ΔH_2 and ΔU_2 are heats of reaction at temperature T_2

ΔH_1 and ΔU_1 are heats of reaction at temperature T_1

$\Delta C_p = C_p$ of products $- C_p$ of reactants

$\Delta C_v = C_v$ of products $- C_v$ of reactants

C_p and C_v are molar specific heats at constant P and V respectively.

Other terms used for heats of reactions :

Heat of formation : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of a substance is formed from its **initial components,** *e.g.*,

CO_2 has C and O-atoms therefore, heat of formation of CO_2 is

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H(f) = -94.3 \text{ kcal}$$

H_2SO_4 has H, S and O-atoms therefore, heat of formation of H_2SO_4 is

$$H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(l); \qquad \Delta H(f) = q$$

and not $\quad H_2O + SO_3 \longrightarrow H_2SO_4; \qquad \Delta H = q$

Heat of combustion : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of a substance is **completely oxidized** in air (O_2), *e.g.*,

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -94.3 \text{ kcal} \quad ...(1)$$

Heat of combustion of C is given by Eq. (1) and not by $C + \frac{1}{2}O_2 \rightarrow CO$, since C is not completely oxidized in this case.

Also, $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$; $\Delta H = -115$ kcal but heat of combustion of H_2 is –115/2, *i.e.*, since 1 mole H_2 be taken

Also, $Mg + \frac{1}{2}O_2 \longrightarrow MgO$; ΔH = Heat of combustion

$$3Mg + N_2 \longrightarrow Mg_3N_2;$$

ΔH = Not heat of combustion since oxidation is not by O_2.

Note : (1) Heats of combustions are always exothermic except oxidation of N as :

$$N_2 + \frac{1}{2}O_2 \longrightarrow N_2O; \qquad \Delta H = +\text{ ve}$$

$$N_2 + O_2 \longrightarrow 2NO; \qquad \Delta H = +\text{ ve}$$

$$N_2 + 2O_2 \longrightarrow 2NO_2; \qquad \Delta H = +\text{ ve}$$

(2) In $F_2 + \frac{1}{2}O_2 \rightarrow F_2O$; $\Delta H = +$ ve; here O_2 is oxidized and not F_2, which is reduced.

Heat of solution : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of the solute is dissolved in **excess of solvent** so that further dilution does not bring any heat change.

Further on dissolution of an electrolyte in water;

(1) Heat of ionisation (ΔH_i) is required to separate ions from each other, *i.e.*, $\Delta H_i = +$ ve.

(2) Heat of hydration is given out during hydration of ions, *i.e.*, $\Delta H_h = -$ ve.

Therefore, $\Delta H_s = \Delta H_i + \Delta H_h$

$\Delta H_i > \Delta H_h$ then $\Delta H_s = +$ ve

if $\Delta H_i < \Delta H_h$ then $\Delta H_s = -$ ve

Note : Remember in thermochemical equations

(1) $n \times aq. = aq.$, where n is any no.

(2) $aq. = nH_2O$ or $aq. = -nH_2O$

Heat of neutralization : It is defined as the change in heat enthalpy or change in internal energy when **1 g equivalent of an acid** reacts completely with **1 g equivalent of base** in dilute solution. Dilute solution refers for complete ionisation of acids and bases in it, *i.e.*,

$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O; \qquad \Delta H = -13.7 \text{ kcal}$$

In dilute solutions

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O; \qquad \Delta H = -13.7 \text{ kcal}$$

or $\quad H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.7$ kcal

i.e., heat of neutralization is also defined as heat of formation of water from H^+ and OH^- ions.

In case of weak acids or weak bases the observed value is little lower because a part of it is used in dissociating weak acid or weak base which is not at all completely ionised at dilute solution conditions. These are, however, completely ionised at infinite dilution, *e.g.*,

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O; \qquad \Delta H = -13.2 \text{ kcal}$$

$$CH_3COO^- + H^+; \ \Delta H = q \ ; Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O; \Delta H = -13.2 \text{ kcal}$$

$\therefore \quad H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.2 - q$

$\therefore \quad -13.2 - q = -13.7$

$\therefore \quad q = 0.5$ kcal

where q is heat of dissociation of weak acid.

Bond energy : The change in heat enthalpy when a bond is broken into (or produced from), isolated gaseous atoms.

$$O{-}H \longrightarrow O(g) + H(g); \qquad \Delta H = +X$$

$$O(g) + H(g) \longrightarrow O{-}H; \qquad \Delta H = -X$$

Thus, bond energy is +ve when bond is broken up and bond energy is –ve when bond is formed.

Note : (1) Bond energy values are normally given +ve sign for breaking up of bond unless given otherwise.

(2) Bond energy data is normally expressed per mole.

(3) For like atoms bonds

H_2 or $H{-}H \longrightarrow 2H(g); \qquad \Delta H = BE$

and $\quad \frac{1}{2}H_2 \longrightarrow H(g); \qquad \Delta H_f = \frac{BE}{2}$

ΔH_f is heat of formation of H-atom $= \frac{BE}{2}$

(4) For solving bond energy numericals say

$H_2 + Cl_2 \longrightarrow 2HCl$

ΔH = BE data of formation of bond + BE data of dissociation of bond

$= -2\ BE_{[H-Cl]} + BE_{[H-H]} + BE_{[Cl-Cl]}$

Since, bond formation is always exothermic.

(5) In some cases bond energy represents for average bond energy, *e.g.*,

$CH_4 \longrightarrow C(g) + 4H(g)$; Heat of dissociation = ΔH

Average bond energy of C—H

$$= \frac{\text{Heat of dissociation of } CH_4}{\text{No. of bonds broken}} = \frac{\Delta H}{4}$$

Standard heat of formation and heat enthalpy :

(1) Standard heat enthalpy H° of a substance is its heat enthalpy at 25°C and 1 atm P.

(2) Consider formation of a substance say CO_2 from its components at 25°C and 1 atm P.

$$C(s) + O_2(g) \longrightarrow CO_2(g): \quad \Delta H_f^\circ = -94.3 \text{ kcal}$$

$$\Delta H_f^\circ = H_{CO_2}^\circ - [H_C^\circ(s) + H_{O_2}^\circ(g)]$$

$$\Delta H_f^\circ = H_{CO_2}^\circ$$

Since, H° values for pure elements has been assumed to be zero

$$\therefore \quad H_C^\circ(s) = 0; \; H_{O_2}^\circ(g) = 0$$

i.e., standard heat of formation of a substance = standard heat enthalpy of that substance

Laws of thermochemistry :

(1) Lavoisier and Laplace law : The heat enthalpy change or internal energy change in a chemical reaction is equal but opposite to that of heat change, when reaction is reversed, *e.g.*,

$C + O_2 \longrightarrow CO_2$; $\quad \Delta H = -94.3$ kcal

or $\quad CO_2 \longrightarrow C + O_2$; $\quad \Delta H = +94.3$ kcal

(2) Hess's law of constant heat summation : Whether a reaction is made by one method or by other, in one step or in several steps, the total change in heat enthalpy or internal energy remains constant throughout the complete course of reaction, *e.g.*,

I Method	**II Method**	
$A \longrightarrow$ Products, $\Delta H = Q_1$	$A \longrightarrow B$	$\Delta H = q_1$
	$B \longrightarrow C$	$= q_2$
	$C \longrightarrow$ Products	$= q_3$
	$A \longrightarrow P$;	
	$\Delta H = q_1 + q_2 + q_3 = Q_2$	

Therefore, according to Hess's law,

$$Q_1 = Q_2$$

The law has been verified theoretically, however, experimental verification is not possible.

• NUMERICAL PROBLEMS •

1. Heat of reaction for,
$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(v)$$
at constant pressure is – 651 kcal at 17°C. Calculate the heat of reaction at constant volume at 17°C.

2. The reaction,
$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$
is carried out in a bomb calorimeter and the heat liberated during the course of reaction was found to be –742.7 kJ mol^{-1} at 25°C. Calculate the heat of reaction at constant pressure at 25°C.

3. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured at constant volume and at 27°C. Calculate heat of combustion of benzene at constant pressure at 27°C. ($R = 8.3$ J mol^{-1} K^{-1}) **(Roorkee 1996)**

4. Two mole of CO and one mole of O_2 are taken in a container of volume 1 litre to form 2 mole of CO_2 according to eq.
$$2\,CO + O_2 \longrightarrow 2\,CO_2; \qquad \Delta H = -560 \text{ kJ}$$
The pressure in the vessel changes from initial pressure of 70 atm to 40 atm. Find out the magnitude of absolute value of ΔU at 500 K. The gases deviates appreciably from ideal nature. (1 L-atm = 0.1 kJ) **(IIT 2006)**

5. Determine the value of ΔH and ΔU for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water vapours behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1}.
($R = 2$ cal mol^{-1} K^{-1}) **(Roorkee 1998)**

6. When 1 mole of ice melts at 0°C and at constant pressure of 1 atm, 1440 cal of heat are absorbed by the system. The molar volume of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔU.

7. Standard heat of formation of HgO(s) at 298 K and at constant pressure is –90.8 kJ mol^{-1}. If excess of HgO(s) absorbs 41.84 kJ of heat at constant volume, calculate the amount of Hg that can be obtained at constant volume and 298 K. (At. wt. of Hg = 200).

8. When 1 mole of ice at 0°C and 4.6 mm of Hg is converted to water vapours at a constant temperature and pressure. Find ΔH and ΔU, if the latent heat of fusion of ice is 80 cal/g and latent heat of vaporisation of liquid water at 0°C is 536 cal/g. The volume of ice in comparison to volume of vapours may be neglected.

9. Calculate the heat of transition for carbon from the following :
$$C_{Diamond} + O_2 \longrightarrow CO_2(g); \qquad \Delta H = -94.3 \text{ kcal}$$
$$C_{Amorphous} + O_2 \longrightarrow CO_2(g); \qquad \Delta H = -97.6 \text{ kcal}$$
Also calculate the heat required to change 1g of $C_{Diamond}$ to $C_{Amorphous}$.

10. Calculate the enthalpy of vaporisation for water from the following :
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \qquad \Delta H = -57.0 \text{ kcal}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \qquad \Delta H = -68.3 \text{ kcal}$$
Also calculate the heat required to change 1g $H_2O(l)$ to $H_2O(g)$.

11. The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heats of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°C?

12. The heat of reaction for $N_2 + 3H_2 \longrightarrow 2NH_3$ at 27°C is –91.94 kJ. What will be its value at 50°C? The molar heat capacities at constant P and 27°C for N_2, H_2 and NH_3 are 28.45, 28.32 and 37.07 joule respectively.

13. Calculate the standard internal energy change for the reaction $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$ at 298 K. Given standard enthalpies of formation in kJ mol^{-1} are
$OF_2(g) = +20$; $H_2O(g) = -250$ and $HF(g) = -270$.

14. The molar heats of combustion of $C_2H_2(g)$, $C_{(Graphite)}$ and $H_2(g)$ are 310.62, 94.05 and 68.32 kcal respectively. Calculate heat of formation of C_2H_2.

15. From the standard enthalpies of combustion given below in (kJ mol^{-1}) and standard enthalpy of acetylene, find the standard enthalpy change when acetylene is hydrogenated to ethane.
($C = -394$, $H_2 = -286$, $C_2H_6 = -1560$, $C_2H_2 = +227$)

16. The molar heat of formation of $NH_4NO_3(s)$ is –367.54 kJ and those of $N_2O(g)$, $H_2O(l)$ are 81.46 and –285.8 kJ respectively at 25°C and 1 atmosphere pressure. Calculate ΔH and ΔU of the reaction $NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$.

17. At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ and $H_2O(l)$ are – 408, – 393 and –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.31$ J mol^{-1} K^{-1})
(Roorkee 1995)

18. Given below are some standard heats of reaction;
(a) Heat of formation of water = – 68.3 kcal
(b) Heat of combustion of acetylene = – 310.6 kcal
(c) Heat of combustion of ethylene = – 337.2 kcal
Calculate the heat of reaction for the hydrogenation of acetylene at constant volume at 25°C.

19. When 2 mole of $C_2H_6(g)$ are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $C_2H_6(g)$. ΔH_f for $CO_2(g)$ and $H_2O(l)$ are – 395 and $-286\,kJ\,mol^{-1}$ respectively.

20. The standard heats of formation for $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are – 25.5, – 57.8, – 94.1 and –22.1 kcal respectively. Calculate $\Delta H_{(298)}$ for the reaction,

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

21. The standard enthalpy of combustion at 25°C of H_2, C_6H_{10} and cyclohexane (C_6H_{12}) are –241, –3800 and $-3920\,kJ\,mol^{-1}$ respectively. Calculate heat of hydrogenation of cyclohexene (C_6H_{10}).

22. Calculate standard heat of formation of CS_2. Given that standard heat of combustion of C, S and CS_2 are –393.3, –293.72 and $-1108.76\,kJ\,mol^{-1}$.

23. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene(g) are –393.5, –285.8 and $20.42\,kJ\,mol^{-1}$ respectively. The enthalpy of isomerisation of cyclopropane to propene is $-33.0\,kJ\,mol^{-1}$. **(IIT 1998)**

24. Determine enthalpy change for,

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$$

at 25°C using heat of combustion values under standard conditions.

Compounds	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	$C_{(Graphite)}$
$\Delta H°$ in kJ/mol	–285.8	–890.0	–1560.0	–393.5

The standard heat of formation of $C_3H_8(g)$ is $-103.8\,kJ\,mol^{-1}$. **(IIT 1992)**

25. Standard heat of formation of CH_4, CO_2 and $H_2O(g)$ are -76.2, -394.8 and $-241.6\,kJ\,mol^{-1}$ respectively. Calculate the amount of heat evolved by burning $1\,m^3$ of CH_4 measured under normal conditions. **(Roorkee 1990)**

26. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane :

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s); \quad \Delta H = -1273\,kJ \quad ...(1)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -286\,kJ \quad ...(2)$$

$$H_2O(l) \longrightarrow H_2O(g); \quad \Delta H = 44\,kJ \quad ...(3)$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \quad \Delta H = 36\,kJ \quad ...(4)$$

(IIT 2000)

27. Calculate heat of formation of KOH(s) using the following equations.

$$K(s) + H_2O(l) + aq. \longrightarrow KOH(aq.) + \frac{1}{2}H_2(g); \quad \Delta H = -48.0\,kcal \quad ...(1)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -68.4\,kcal \quad ...(2)$$

$$KOH(s) + aq. \longrightarrow KOH(aq.); \quad \Delta H = -14.0\,kcal \quad ...(3)$$

28. Calculate ΔH_f° for chloride ion from the following data :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \quad \Delta H_f^\circ = -92.4\,kJ$$

$$HCl(g) + nH_2O \longrightarrow H^+(aq.) + Cl^-(aq.); \quad \Delta H° = -74.8\,kJ$$

$\Delta H_f^\circ H^+(aq.) = 0.0\,kJ$ **(Roorkee 1992)**

29. Benzene burns in O_2 according to the equation :

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 3H_2O(g) + 6CO_2(g)$$

If standard heat enthalpy of $C_6H_6(l)$, $H_2O(g)$ and $CO_2(g)$ are 11.7, – 68.3 and – 94.0 kcal respectively, calculate the amount of heat liberated by burning 1 kg benzene.

30. The heat evolved on combustion of 1 g starch $(C_6H_{10}O_5)_n$ into CO_2 and $H_2O(l)$ is $17.49\,kJ\,g^{-1}$. Compute the enthalpy of formation of 1g starch. Given ΔH_f of $H_2O(l) = -285.85\,kJ\,mol^{-1}$, ΔH_f of $CO_2 = -293.7\,kJ\,mol^{-1}$.

31. The heat of combustion of ethane gas is 368 kcal/mol. Assuming that 60% of the heat is useful, how many m^3 of ethane measured at STP must be burnt to supply enough heat to convert 50 kg of water at 10°C to steam at 100°C? Specific heat of water is 1 cal/g. Heat of vaporisation of H_2O is 540 cal/g.

32. ΔH for combustion of ethane and ethyne are –341.1 and –310.0 kcal respectively. Which is better gas welder and why?

33. The combustion of 5.0 g of coke raised the temperature of 1.0 kg of water from 10 to 47°C. Calculate the fuel value of coke. Specific heat of H_2O is 1 cal/g.

34. A cooking gas cylinder is assumed to contain 11.2 kg isobutane having heat of combustion $-2658\,kJ\,mol^{-1}$. If a family needs 15×10^3 kJ energy per day for cooking, how long a cylinder can last. Also if 30% heat is lost due to incomplete combustion, then how long would it take to last.

35. An athlete is given 100 g glucose of energy equivalent to 1560 kJ. He utilize 50% of this gained energy in an event. In order to avoid storage of energy in body, calculate the mass of water he would need to perspire. Enthalpy of H_2O for evaporation is $44\,kJ\,mol^{-1}$.

36. The enthalpy change involved in the oxidation of glucose is $-2880\,kJ\,mol^{-1}$. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is

the maximum distance that a person will be able to walk after eating 120 g of glucose? **(IIT May 1997)**

37. An athlete takes 20 breaths per minute at room temperature. The air inhaled in each breath is 200 mL which contains 20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all the oxygen consumed if used for converting glucose into CO_2 and $H_2O(l)$, how much glucose will be burnt in the body in one hour and what is the heat produced? (Room temperature = 27°C and enthalpy of combustion of glucose is –2822.5 kJ mol^{-1} at 0°C)

38. Calculate the ΔH for $NO_2(g) \longrightarrow NO(g) + O(g)$ if heat of formation of O-atoms is 249 kJ/mol and

$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$; $\Delta H = -200$ kJ

$3O_2(g) \longrightarrow 2O_3(g)$; $\Delta H = 285.4$ kJ

39. Calculate the heat of dissociation of N_2O_4 into NO_2 from the data :

$N_2 + O_2 \longrightarrow 2NO$; $\Delta H = +43.10$ kcal ...(1)

$N_2 + 2O_2 \longrightarrow N_2O_4$; $\Delta H = -1.870$ kcal ...(2)

$2NO_2 \longrightarrow 2NO + O_2$; $\Delta H = +26.10$ kcal ...(3)

40. 3.67 litre of ethylene and methane gaseous mixture on complete combustion at 25°C produces 6.11 litre of CO_2. Find out the amount of heat evolved on burning one litre of gaseous mixture. The heats of combustion of C_2H_4 and CH_4 are –1423 and –891 kJ mol^{-1} at 25°C.

(IIT 1991)

41. An intimate mixture of Fe_2O_3 and Al is used in solid fuel rocket. Calculate the fuel value per g and per mL of mixture.

$\Delta H_{Al_2O_3} = 399.0$ kcal, $\Delta H_{Fe_2O_3} = 199.0$ kcal

density of Fe_2O_3 and Al are 5.2 g/mL and 2.7 g/mL respectively.

42. The heat of solution of anhydrous $CuSO_4$ is –15.9 kcal and that of $CuSO_4 \cdot 5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

43. Calculate the integral heat of solution for

$H_2SO_4 + 3H_2O \longrightarrow H_2SO_4 \cdot 3H_2O$

and $H_2SO_4 \cdot 3H_2O + 5H_2O \longrightarrow H_2SO_4 \cdot 8H_2O$

Given that integral heat of solution for H_2SO_4 is given by : $\frac{75.6 \times n}{n + 1.8}$ kJ where n is number of water molecules associated with H_2SO_4.

44. The dissolution of 1 mole of NaOH (s) in 100 mole of $H_2O(l)$ give rise to evolution of heat as – 42.34 kJ. However if 1 mole of NaOH(s) is dissolved in 1000 mole of $H_2O(l)$ the heat given out is 42.76 kJ. What would be enthalpy change when 900 mole of $H_2O(l)$ are added to a solution containing 1 mole of NaOH(s) in 100 mole of H_2O?

45. Calculate heat of dissociation for acetic acid from the following data :

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$; $\Delta H = -13.2$ kcal

$H^+ + OH^- \longrightarrow H_2O$; $\Delta H = -13.7$ kcal

Also, calculate heat of dissociation for NH_4OH if,

$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$; $\Delta H = -12.27$ kcal

46. Calculate the heat of neutralization from the following data. 200 mL of 1 M HCl is mixed with 400 mL of 0.5 M NaOH. The temperature rise in calorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is 1 cal/mL – degree for solution.

47. Calculate ΔH° for $2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$ given that standard heat enthalpy of Fe_2O_3 and Al_2O_3 are –196.5 and –399.1 kcal.

48. Calculate the enthalpy change when 6.80 g of NH_3 is passed over heated CuO. The standard heat enthalpies of $NH_3(g)$, $CuO(s)$ and $H_2O(l)$ are – 46.0, –155.0 and –285.0 kJ mol^{-1} respectively and the change is

$$NH_3 + \frac{3}{2}CuO \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l) + \frac{3}{2}Cu(s).$$

49. Calculate the enthalpy change when infinitely dilute solutions of $CaCl_2$ and Na_2CO_3 are mixed. ΔH_f° for $Ca^{2+}(aq.)$, $CO_3^{2-}(aq.)$ and $CaCO_3(s)$ are –129.80, –161.65 and –288.50 kcal mol^{-1} respectively.

50. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation for HCl gas.

51. Calculate the C—C bond energy from the following data :

(a) $C(s) \longrightarrow C(g)$; $\Delta H = 170.9$ kcal

(b) $\frac{1}{2}H_2 \longrightarrow H(g)$; $\Delta H = 52.1$ kcal

(c) Heat of formation of ethane = –20.3 kcal

(d) C—H bond energy = 99.0 kcal

52. Heat of combustion of n-propane and n-butane are $-a$ kcal and $-b$ kcal per mole respectively. Calculate approximate value of heat of combustion of n-decane.

53. The enthalpy change for the following reaction at 25°C are given below :

$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)$;

$\Delta H = -10.06$ kcal ...(1)

$H_2(g) \longrightarrow 2H(g)$; $\Delta H = 104.18$ kcal ...(2)

$O_2(g) \longrightarrow 2O(g)$; $\Delta H = 118.32$ kcal ...(3)

Calculate OH bond energy in hydroxyl radical.

54. Using bond energy data, calculate heat of formation of isoprene.

$$5\,C(s) + 4H_2(g) \longrightarrow H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle H}{\underset{|}{C}}{=}CH_2$$

Given, C — H = 98.8 kcal, H — H = 104 kcal

C — C = 83 kcal, C = C = 147 kcal

and $C(s) \longrightarrow C(g) = 171$ kcal

55. The dissociation energy of CH_4 is 360 kcal/mol and of ethane is 620 kcal/mol. Calculate C—C bond energy.

56. The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 and H_2O are 94.38 and 68.38 kcal respectively, calculate C≡C bond energy. Given that heat of atomisation of C and H are 150.0 and 51.5 kcal respectively and C—H bond energy is 93.64 kcal.

57. Calculate enthalpy change of the following reaction :
$H_2C=CH_2(g)+H_2(g)\longrightarrow H_3C-CH_3(g)$
The bond energy of C—H, C—C, C=C, and H—H are 414, 347, 615 and 435 kJ mol^{-1} respectively.
(Roorkee 1985)

58. Heat of atomisation of NH_3 and N_2H_4 are x kcal mol^{-1} and y kcal mol^{-1} respectively. Calculate average bond energy of N—N bond.

59. Using the data (all values in kcal mol^{-1} at 25°C) given below, calculate bond energy of C—C and C—H bonds.

$$C(s)\longrightarrow C(g);\qquad \Delta H=172$$
$$H_2\longrightarrow 2H;\qquad \Delta H=104$$
$$H_2+\frac{1}{2}O_2\longrightarrow H_2O(l);\qquad \Delta H=-68.0$$
$$C(s)+O_2\longrightarrow CO_2;\qquad \Delta H=-94.0$$

Heat of combustion of $C_2H_6=-372.0$
Heat of combustion of $C_3H_8=-530.0$ **(IIT 1990)**

60. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are −156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexane (l) at 25°C is −119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene. **(IIT 1996)**

61. Calculate the resonance energy of N_2O from the following data : ΔH_f° of N_2O is 82 kJ mol^{-1}.

N≡N	946 kJ mol^{-1}
N=N	418 kJ mol^{-1}
O=O	498 kJ mol^{-1}
N=O	607 kJ mol^{-1} **(Roorkee 1991)**

62. Compute the heat of formation of liquid methyl alcohol in kilojoule per mol, using the following data. Heat of vaporisation of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.
Average bond energies : C—H, 415 kJ/mol; C—O, 356 kJ/mol; O—H, 463 kJ/mol. **(IIT July 1997)**

63. Estimate ΔH for $2C_4H_{10}\longrightarrow C_8H_{18}+H_2$. Given bond energy of C—C, C—H are 347.3 and 414.2 kJ mol^{-1}. The heat of formation of H-atom is 217.55 kJ mol^{-1}.

64. Calculate the resonance energy of C_6H_6 using Kekule formula for C_6H_6 from the following data.
(1) ΔH_f° for $C_6H_6=-358.5$ kJ mol^{-1}
(2) Heat of atomisation of C = 716.8 kJ mol^{-1}
(3) Bond energy of C—H, C—C, C=C and H—H are 490, 340, 620 and 436.9 kJ mol^{-1} respectively.

65. Assume that for a domestic hot water supply 150 kg of water per day must be heated from 10°C to 65°C and gaseous fuel propane C_3H_8 is used for this purpose. What mole and volume of propane in litre at STP would have to be used for heating domestic water? ΔH for combustion of propane is −2050 kJ and specific heat of water is 4.184×10^{-3} kJ/g.

66. The temperature of a bomb calorimeter was found to rise by 1.617 K when a current of 3.20 ampere was passed for 3 seconds from a 12.0 V source. 100 g sample of a liquid (molar mass = 40) is now placed in this calorimeter and a passage of 0.5 ampere current for 3 minutes from a 1.50 V source gave a temperature rise of 0.8°C. What is molar heat capacity of liquid?

67. A slice of banana mass 2.502 g was burnt in a bomb calorimeter producing a temperature rise of 3.05°C. The combustion of 0.316 g of benzoic acid in the same calorimeter produced a temperature rise of 3.24°C. The heat of combustion of benzoic acid at constant volume is −3227 kJ mol^{-1}. If average banana mass is 125 g, how many calories can be obtained from one average banana?

68. The commercial production of water gas utilizes the reaction under standard conditions : $C+H_2O(g)\rightarrow H_2+CO$. The heat required for this endothermic reaction may be supplied by adding a limited amount of air and burning some carbon to CO_2. How many g of carbon must be burnt to CO_2 to provide enough heat for the water gas conversion of 100 g carbon? Neglect all heat losses to the environment. Also ΔH_f° of CO, $H_2O(g)$ and CO_2 are −110.53, −241.81 and −393.51 kJ/mol respectively.

69. The specific heat at constant volume for a gas 0.075 cal/g and at constant pressure is 0.125 cal/g. Calculate :
(i) the molar mass of gas
(ii) atomicity of gas
(iii) No. of atoms of gas in its 1 mole.

70. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner, which has been adjusted for methane as fuel (with X litre/hour of CH_4 and $6X$ litre/hour of O_2), is to be readjusted for butane C_4H_{10}. In order to get same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion, etc., are the same for both fuels and that gases behave ideally. Heats of combustion $CH_4=809$ kJ mol^{-1}; $C_4H_{10}=2878$ kJ mol^{-1}. **(IIT 1993)**

71. From the following data of ΔH, of the following reactions,

$$C(s)+\frac{1}{2}O_2(g)\longrightarrow CO(g); \qquad \Delta H=-110\text{ kJ}$$

$$C(s)+H_2O(g)\longrightarrow CO(g)+H_2(g); \qquad \Delta H=132\text{ kJ}$$

Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping temperature constant.

72. A person inhales 640 g of O_2 per day. If all the O_2 is used for converting sugar into CO_2 and H_2O, how much sucrose ($C_{12}H_{22}O_{11}$) is consumed in the body in one day and what is the heat evolved? $\Delta H_{\text{Combustion of sucrose}}=-5645\text{ kJ mol}^{-1}$.

73. When 12.0 g of carbon reacted with oxygen to form CO and CO_2 at 25°C and constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen needed for it and the mole of CO and CO_2 formed. Given, $\Delta H_f\,CO_2=-94.05$ and $\Delta H_f\,CO=-26.41\text{ kcal mol}^{-1}$.

74. 1.0 g magnesium atoms in vapour phase absorbs 50.0 kJ of energy to convert all Mg into Mg ions. The energy absorbed is needed for the following changes :

$$Mg(g)\longrightarrow Mg^+(g)+e; \qquad \Delta H=740\text{ kJ mol}^{-1}$$

$$Mg^+(g)\longrightarrow Mg^{2+}(g)+e; \qquad \Delta H=1450\text{ kJ mol}^{-1}$$

Find ou. the % of Mg^+ and Mg^{2+} in final mixture.

75. Estimate the average S—F bond energy in SF_6. The standard heat of formation values of $SF_6(g)$, $S(g)$ and $F(g)$ are : −1100, 275 and 80 kJ mol^{-1} respectively.

(IIT 1999)

76. Consider the following reactions :

$$Au(OH)_3+4HCl\longrightarrow HAuCl_4+3H_2O;\ \Delta H=-28\text{ kcal}$$

$$Au(OH)_3+4HBr\longrightarrow HAuBr_4+3H_2O;\ \Delta H=-36.8\text{ kcal}$$

If 1 mole of $HAuBr_4$ was mixed with 4 mole of HCl, 0.44 kcal heat was absorbed, what fraction of $HAuBr_4$ was converted into $HAuCl_4$? Also report the percentage conversion.

77. The enthalpies of neutralisation of a strong acid *HA* and weak acid *HB* by NaOH are −13.68 kcal/eq. and −2.9kcal / eq., respectively. If one equivalent of *HA* and one equivalent of *HB* are mixed with one equivalent of NaOH, the enthalpy change was found to be − 6.9 kcal / eq., calculate the distribution of NaOH to neutralise *HA* and *HB*.

78. The standard enthalpy of formation of FeO and Fe_2O_3 is −65 kcal mol^{-1} and −197 kcal mol^{-1} respectively. If a mixture containing FeO and Fe_2O_3 in 2 : 1 mole ratio on oxidation is changed into 1: 2 mole ratio, how much of thermal energy will be released per mole of the initial mixture?

79. Ethanol undergoes decomposition to form two sets of products.

$$C_2H_5OH(g)\xrightarrow{1} C_2H_4(g)+H_2O(g);\ \Delta H^\circ=-45.54\text{ kJ}$$

$$C_2H_5OH(g)\xrightarrow{2} CH_3CHO(g)+H_2(g);\ \Delta H^\circ=-68.91\text{ kJ}$$

If the products molar ratio of C_2H_4 to CH_3CHO formed are in the ratio of 8 : 1 in a set of product gas, determine the energy involved in the decomposition of 1 mole of ethanol.

80. Calculate the enthalpy change for the reaction :

$$XeF_4\longrightarrow Xe^+ + F^- + F_2 + F; \qquad \Delta H$$

The average Xe — F bond energy is 34 kcal/mol. IE_1 of Xe is 279 kcal/mol and electron affinity of F is 85 kcal / mol and bond dissociation energy of F_2 is 38 kcal / mol.

81. In a constant volume calorimeter, 3.5 g of a gas with molar mass 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas is kJ mol^{-1} is. **(IIT 2009)**

SOLUTIONS (Numerical Problems)

1. We know, $\Delta H = \Delta U + \Delta nRT$

Given, $\Delta H = -651\times10^3$ cal; $R = 2$ calorie

$T = 290$ K; $\Delta n = 6+6-6 = 6$

$\therefore\ -651\times10^3 = \Delta U + 6\times2\times290$

$\therefore\ \Delta U = -654480$ cal

$\therefore\ \Delta U = \mathbf{-654.48\ kcal}$

NOTE : For $C_6H_{12}O_6(s)+6O_2(g) \longrightarrow 6CO_2(g)+6H_2O(v)$

Δn = No. of products molecules – No. of reactants molecules (only in gaseous phase)

$= 6+6-6 = 6$

2. For $NH_2CN(s)+\frac{3}{2}O_2(g) \longrightarrow N_2(g)+CO_2(g)+H_2O(l)$

$\therefore\ \Delta n = 2-\frac{3}{2} = \frac{1}{2}$

Given, $\Delta U = -742.7$ kJ; $T = 298$K; $R = 8.314\times10^{-3}$ kJ

$\because\ \Delta H = \Delta U + \Delta nRT$

$= -742.7+\frac{1}{2}\times8.314\times10^{-3}\times298$

$= \mathbf{-741.46\ kJ}$

3. $C_6H_6(l)+\frac{15}{2}O_2(g) \longrightarrow 6CO_2(g)+3H_2O(l)$

$\therefore\ \Delta n = 6-\frac{15}{2} = -\frac{3}{2}$

Also, ΔU per mol $= -\frac{327\times78}{7.8} = \mathbf{-3270\ kJ}$

Now, $\Delta H = \Delta U + \Delta nRT = -3270+\left(-\frac{3}{2}\right)\times8.3\times300\times10^{-3}$

$\Delta H = \mathbf{-3273.735\ kJ}$

4. $\Delta H = \Delta U + \Delta(PV)$

$= \Delta U + P_2V_2 - P_1V_1$ ...(1)

We cannot use here $\Delta H = \Delta U + \Delta nRT$ since, gases deviate from ideal gas behaviour. Thus,

$\Delta(PV) = P_2V_2 - P_1V_1 = 40\times1-70\times1$

$= -30$ litre-atm $= -3.0$ kJ

$\therefore$ By Eq. (1) $-560 = \Delta U - 3.0\ \ \therefore\ \Delta U = \mathbf{-557\ kJ}$

5. Water $\rightleftharpoons$ Vapour

Mole before evaporation 90/18 = 5 0

The evaporation of 5 moles of water takes place reversibly and isothermally into vapours.

Thus, heat given at constant pressure

ΔH = heat of evaporation × amount evaporated

$\Delta H = 540\times90$

$\Delta H = \mathbf{48600\ cal}$

Also, $\Delta H = \Delta U + \Delta nRT$

$\Delta U = 48600 - \Delta nRT$

$= 48600-5\times1\times2\times373 = 48600-3730$

$\Delta U = \mathbf{44870\ cal}$

6. Ice $\longrightarrow$ Water ; $\Delta H = 1440$ cal/mol

(Since, at constant pressure heat is given)

$\because\ \Delta H = \Delta U + P\Delta V$

and $P\Delta V = 76\times13.6\times981\times(18-19.6)$ erg

(where, P in dyne cm^{-2} ; V in mL)

$= -1.62\times10^6$ erg $= -\frac{1.62\times10^6}{4.18\times10^7} = -0.039$ cal

$\because\ P\Delta V$ is negligible amount.

$\therefore\ \Delta H \simeq \Delta U$

7. Given, $Hg(l)+\frac{1}{2}O_2(g) \longrightarrow HgO(s)$; $\Delta H^\circ = -90.8$ kJ

$\therefore\ HgO(s) \longrightarrow Hg(l)+\frac{1}{2}O_2(g)$; $\Delta H^\circ = +90.8$ kJ

$\Delta H^\circ = \Delta U^\circ + \Delta nRT$

$90.8\times10^3 = \Delta U^\circ - \frac{1}{2}\times8.314\times298\ \ (\because \Delta n = -\frac{1}{2})$

$\therefore\ \Delta U^\circ = \mathbf{89.56\ kJ\ mol^{-1}}$

ΔU° is heat of formation of $Hg(l)$ from $HgO(s)$.

Now 41.84 kJ heat is absorbed by HgO, thus mole of Hg formed

$= \frac{41.84}{89.56} = 0.4672$

$\therefore\ w_{Hg} = 0.4672\times200 = \mathbf{93.44\ g}$

8. Ice $\longrightarrow$ Vapour

$\Delta H = \Delta H_f + \Delta H_v = 80\times18+536\times18$

$= \mathbf{11088\ cal\ /\ mol}$

Now, $\Delta H = \Delta U + P\Delta V$

ΔV = Volume of vapours – Volume of ice = Volume of vapours at 4.6 mm and 0°C ($\because V_{ice}$ = negligible)

Now, $PV = nRT$ for gas

$\therefore\ PV$ or $P\Delta V = nRT = 1\times8.314\times273$ Nm or J

$= \frac{8.314\times273}{4.18}$ cal $= 543$ cal

$\Delta U = \Delta H - P\Delta V = 11088-543.0 = \mathbf{10545\ cal}$

9. Given,

$C_D + O_2 \longrightarrow CO_2(g)$; $\Delta H = -94.3$ kcal ...(1)

$C_A + O_2 \longrightarrow CO_2(g)$; $\Delta H = -97.6$ kcal ...(2)

– – – +

Subtracting Eq. (2) from Eq. (1);

$C_D - C_A \longrightarrow 0$; $\Delta H = +3.3$

or $C_D \longrightarrow C_A$; $\Delta H = \mathbf{+3.3\ kcal}$

i.e., heat of transition for $C_D \longrightarrow C_A$ $= \mathbf{+3.3\ kcal}$

Also, 12 g C_D changes to C_A with heat change $= +3.3$ kcal

$\therefore$ 1 g C_D changes to C_A with heat change $= +\frac{3.3}{12}$ kcal

$= \mathbf{0.275\ kcal}$

10. Given,

$H_2(g)+\frac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta H = -57.0$ kcal ...(1)

$H_2(g)+\frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -68.3$ kcal ...(2)

$-\quad -\quad -\quad +$

Subtracting Eq. (2) from Eq. (1);

$H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = -11.3$ kcal

$\therefore$ Enthalpy of vaporisation for $H_2O = +11.3$ **kcal**

Also, 18 g H_2O requires enthalpy of vaporisation $= +11.3$ kcal

$\therefore$ 1 g H_2O requires enthalpy of vaporisation $= \frac{11.3}{18}$ kcal

$=$ **0.628 kcal**

11. Given, $I_2(s) \longrightarrow I_2(v)$; $\Delta H = 24$ cal/g at 200°C

$\Delta C_{p(\text{cal/g})} = C_p$ of product $- C_p$ of reactant

$= 0.031 - 0.055$

$= -0.024$ cal / g

Now, $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

$\Delta H_2 - 24 = -0.024 \times (523 - 473)$

$\therefore$ $\Delta H_2 = 24 - 1.2 =$ **22.8 cal / g**

12. Given,

$N_2 + 3H_2 \longrightarrow 2NH_3$; $\Delta H = -91.94$ kJ at 300 K

$\Delta C_{p(\text{J/mol})} = 2 \times C_p$ of $NH_3 - C_p$ of $N_2 - 3 \times C_p$ of H_2

$= 2 \times 37.07 - 28.45 - 3 \times 28.32$

$= -39.27$ joule

$\therefore$ $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

$\Delta H_2 + 91940 = -39.27 \times (323 - 300)$

$\Delta H_2 = -92843.2$ joule $=$ **−92.843 kJ**

13. $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$

Given,

$\frac{1}{2}O_2(g) + F_2(g) \longrightarrow OF_2(g)$; $\Delta H^\circ = +20$ kJ ...(1)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta H^\circ = -250$ kJ ...(2)

$\frac{1}{2}H_2(g) + \frac{1}{2}F_2 \longrightarrow HF(g)$; $\Delta H^\circ = -270$ kJ ...(3)

Adding Eqs. (1) and (2);

$H_2(g) + F_2(g) + O_2(g) \longrightarrow OF_2(g) + H_2O(g)$;

$\Delta H^\circ = -230$ kJ ...(4)

Multiply Eq. (3) by 2 and subtract from Eq. (4),

$O_2(g) + 2HF(g) \longrightarrow OF_2(g) + H_2O(g)$; $\Delta H^\circ = +310$ kJ

or $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$;

$\Delta H^\circ = -310$ kJ

Now, $\Delta H^\circ = \Delta U^\circ + \Delta n\, RT$

$\Delta n = 3 - 2 = 1, R = 8.314$ J, $T = 298$ K

$\therefore$ $-310000 = \Delta U^\circ + 1 \times 8.314 \times 298$

$\therefore$ $\Delta U^\circ = -312477.5$ joule $=$ **−312.48 kJ**

14. We have to calculate

$2C_{\text{Graphite}} + H_2(g) \longrightarrow C_2H_2(g)$; $\Delta H = ?$

Given, $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$;

$\Delta H = -310.62$ kcal ...(1)

$C_{\text{Graphite}} + O_2(g) \longrightarrow CO_2(g)$;

$\Delta H = -94.05$ kcal ...(2)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$;

$\Delta H = -68.32$ kcal ...(3)

Multiply Eq. (2) by 2 and add in Eq. (3)

$2C_{\text{Graphite}} + \frac{5}{2}O_2(g) + H_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$;

$\Delta H = -256.42$ kcal ...(4)

Subtract Eq. (1) from Eq. (4)

$2C_{\text{Graphite}} + H_2(g) \longrightarrow C_2H_2(g)$;

$\Delta H =$ **+54.2 kcal**

15. To find,

$C_2H_2 + 2H_2 \longrightarrow C_2H_6$; $\Delta H = ?$

Given, $C_2 + O_2 \longrightarrow CO_2$; $\Delta H = -394$ kJ ...(1)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -286$ kJ ...(2)

$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$;

$\Delta H = -1560$ kJ ...(3)

and $2C + H_2 \longrightarrow C_2H_2$; $\Delta H = +227$ kJ ...(4)

Multiplying Eq. (1) by 2, Eq. (2) by 3, and then add them

$2C + \frac{7}{2}O_2 + 3H_2 \longrightarrow 2CO_2 + 3H_2O$;

$\Delta H = -1646$ kJ ...(5)

Subtract Eq. (3) from Eq. (5)

$2C + 3H_2 \longrightarrow C_2H_6$; $\Delta H = -86$ kJ ...(6)

Subtract Eq. (4) from Eq. (6)

$C_2H_2 + 2H_2 \longrightarrow C_2H_6$; $\Delta H = -313$ kJ

i.e., Heat of hydrogenation of $C_2H_2 =$ **−313 kJ**

16. We have to find ΔH for

$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$; $\Delta H = ?$

$\Delta H_{\text{Reaction}} = \Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}$

$= \Delta H_{N_2O} + \Delta H_{H_2O} \times 2 - \Delta H_{NH_4NO_3}$

Given, $\Delta H_{N_2O} = +81.46$ kJ

$\Delta H_{H_2O} = -285.8$ kJ

$\Delta H_{NH_4NO_3} = -367.54$ kJ

$\therefore$ $\Delta H_{\text{Reaction}} = +81.46 + 2(-285.8) - (-367.54)$

$\Delta H =$ **−122.6 kJ**

Further $\Delta H = \Delta U + \Delta nRT$ ($\Delta n = 1 - 0$, $R = 8.314$ J, $T = 298$ K)

$\therefore$ $-122.6 \times 10^3 = \Delta U + 1 \times 8.314 \times 298$

$\therefore$ $\Delta U = -125077$ joule

$=$ **−125.077 kJ**

17. Given,

$7C(s) + 3H_2(g) + O_2(g) \longrightarrow C_6H_5COOH(s)$

$\Delta H^\circ = -408$ kJ ...(1)

$C(s) + O_2(g) \longrightarrow CO_2(g)$;

$\Delta H^\circ = -393$ kJ ...(2)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H^\circ = -286$ kJ ...(3)

$C_6H_5COOH(s)+\frac{15}{2}O_2(g)\longrightarrow 7CO_2(g)+3H_2O(l);$

$\Delta H=?$...(4)

By Eq. (2)×7+(3)×3−(1)

$C_6H_5COOH(s)+\frac{15}{2}O_2(g)\longrightarrow 7CO_2(g)+3H_2O(l);$

$\Delta H^\circ=[-393\times7-286\times3+408]$

$\therefore\quad \Delta H^\circ=\mathbf{-3201\ kJ}$

Also, $\Delta H^\circ=\Delta H+\Delta nRT$

$\therefore\quad -3201=\Delta U^\circ+(-0.5)\times8.314\times10^{-3}\times300$

$(\because \Delta n=0.5$ and $R=8.314\times10^{-3}$ kJ)

$\therefore\quad \Delta U^\circ=-3201+1.2471=\mathbf{-3199.7529}$

18. Standard heats of reaction means ΔH at 1 atm and 25°C.

Given,

$H_2+\frac{1}{2}O_2\longrightarrow H_2O;\ \Delta H=-68.3$ kcal ...(1)

$C_2H_2+\frac{5}{2}O_2\longrightarrow 2CO_2+H_2O;$

$\Delta H=-310.6$ kcal ...(2)

$C_2H_4+3O_2\longrightarrow 2CO_2+2H_2O;$

$\Delta H=-337.2$ kcal ...(3)

$C_2H_2+H_2\longrightarrow C_2H_4;\quad \Delta H=?$

Add Eqs. (1) and (2) and subtract Eq. (3)

$C_2H_2+H_2\longrightarrow C_2H_4;\quad \Delta H=-41.7$ kcal

Now, $\Delta H=\Delta U+\Delta nRT$

$\Delta n=1-2=-1,\quad R=2$ cal, $T=298$ K

$-41.7\times10^3=\Delta U+(-1)\times2\times298$

$\Delta U=-41104$ cal

$\therefore\quad \Delta U=\mathbf{-41.104\ kcal}$

19. We have to find

$2C(s)+3H_2(g)\longrightarrow C_2H_6(g);\quad \Delta H=?$...(1)

Given, $C(s)+O_2(g)\longrightarrow CO_2(g);\quad \Delta H=-395$ kJ ...(2)

$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l);\quad \Delta H=-286$ kJ ...(3)

$C_2H_6(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l);$

$\Delta H=-\frac{3129}{2}$ kJ ...(4)

$=-1564.5$ kJ

Multiplying Eq. (2) by 2 and Eq. (3) by 3, then adding

$2C(s)+3H_2(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l);$

$\Delta H=-1648$ kJ ...(5)

Subtracting Eq. (4) from Eq. (5)

$2C(s)+3H_2(g)\longrightarrow C_2H_6(g);\quad \Delta H=-83.5$ kJ

$\therefore\quad \Delta H_f$ of $C_2H_6=\mathbf{-83.5\ kJ}$

20. At 298 K, ΔH values are ΔH°, *i.e.*, standard heat of formation. For

$CCl_4(g)+2H_2O(g)\longrightarrow CO_2(g)+4HCl(g);\quad \Delta H^\circ=?$

$\Delta H^\circ_{Reaction}=\Delta H^\circ_{Products}-\Delta H^\circ_{Reactants}$

$=\Delta H^\circ_{CO_2}+4\times\Delta H^\circ_{HCl}-\Delta H^\circ_{CCl_4}-2\times\Delta H^\circ_{H_2O}$

$=-94.1+4\times(-22.1)-(-25.5)-2\times(-57.8)$

$\Delta H^\circ_{Reaction}=\mathbf{-41.4\ kcal}$

21. We have to find ΔH for

$C_6H_{10}+H_2\longrightarrow C_6H_{12};\quad \Delta H=?$

Given, $H_2+\frac{1}{2}O_2\longrightarrow H_2O;\quad \Delta H=-241$ kJ ...(1)

$C_6H_{10}+\frac{17}{2}O_2\longrightarrow 6CO_2+5H_2O;$

$\Delta H=-3800$ kJ ...(2)

$C_6H_{12}+9O_2\longrightarrow 6CO_2+6H_2O;$

$\Delta H=-3920$ kJ ...(3)

Adding Eqs. (1) and (2) and then subtracting Eq. (3) as above

$C_6H_{10}+H_2\longrightarrow C_6H_{12};\quad \Delta H=-121$ kJ

$\therefore$ Heat of hydrogenation of $C_6H_{10}=\mathbf{-121\ kJ}$

22. We have to find ΔH for

$C+2S\longrightarrow CS_2;\quad \Delta H=?$

Given, $C+O_2\longrightarrow CO_2;\quad \Delta H=-393.3$ kJ ...(1)

$S+O_2\longrightarrow SO_2;\quad \Delta H=-293.72$ kJ ...(2)

$CS_2+3O_2\longrightarrow CO_2+2SO_2;\ \Delta H=-1108.76$ kJ ...(3)

Multiply Eq. (2) by 2 and add in Eq. (1)

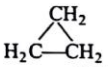
$C+2S+3O_2\longrightarrow CO_2+2SO_2;\ \Delta H=-980.74$ kJ ...(4)

Subtract Eq. (3) from Eq. (4)

$C+2S\longrightarrow CS_2;\quad \Delta H=+128.02$ kJ

ΔH_f of $CS_2=\mathbf{+128.02\ kJ}$

23. Given,



$\longrightarrow CH_3CH=CH_2;\ \Delta H=-33.0$ kJ ...(1)

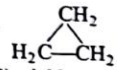
$C+O_2\longrightarrow CO_2(g);\quad \Delta H=-393.5$ kJ ...(2)

$H_2+\frac{1}{2}O_2\longrightarrow H_2O(l);\quad \Delta H=-285.8$ kJ ...(3)

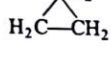
$3C+3H_2\longrightarrow CH_3\cdot CH=CH_2(g);$

$\Delta H=20.42$ kJ ...(4)

(4)−(1) yields

$3C+3H_2\longrightarrow$  ; $\Delta H=53.42$ kJ ...(5)

[3×(2)+3×(3)]−(5) yields



$+\frac{9}{2}O_2\longrightarrow 3CO_2+3H_2O;$

$\Delta H=\mathbf{-2091.32\ kJ}$

24. Given,

$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g);\quad \Delta H=-285.8$ kJ ...(1)

$CH_4(g)+2O_2(g)\longrightarrow CO_2(g)+2H_2O(g);$

$\Delta H=-890$ kJ ...(2)

$C_2H_6(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(g);$

$\Delta H=-1560.0$ kJ ...(3)

$3C(s)+4H_2(g) \longrightarrow C_3H_8(g)$; $\Delta H = -103.8$ kJ ...(4)

$C(s)+O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ kJ ...(5)

Add Eqs. (2) and (3)

$CH_4(g)+C_2H_6(g)+\frac{11}{2}O_2(g) \longrightarrow 3CO_2(g)+5H_2O(g)$;

$\Delta H = -2450$ kJ ...(6)

Add Eqs. (4) and (6)

$CH_4(g)+C_2H_6(g)+3C(s)+4H_2(g)+\frac{11}{2}O_2(g) \longrightarrow$

$3CO_2(g)+5H_2O(g)+C_3H_8(g)$; $\Delta H = -2553.8$ kJ ...(7)

Multiply Eq. (1) by 5 and Eq. (5) by 3, then add them

$5H_2(g)+3C(s)+\frac{11}{2}O_2(g) \longrightarrow 5H_2O(g)+3CO_2(g)$;

$\Delta H = -2609.5$ kJ ...(8)

Subtract Eq. (8) from Eq. (7) and on rearranging

$CH_4(g)+C_2H_6(g)+3C(s)+4H_2(g)+\frac{11}{2}O_2(g) \longrightarrow$

$3CO_2(g)+5H_2O(g)+C_3H_8(g)$; $\Delta H = -2553.8$ kJ

$5H_2(g)+3C(s)+\frac{11}{2}O_2(g) \longrightarrow 5H_2O(g)+3CO_2(g)$;

$\Delta H = -2609.5$ kJ

$H_2(g)+C_3H_8(g) \longrightarrow CH_4(g)+C_2H_6(g)$;

$\Delta H = -55.7$ kJ

25. Given,

$C+2H_2 \longrightarrow CH_4$; $\Delta H = -76.2$ kJ ...(1)

$C+O_2 \longrightarrow CO_2$; $\Delta H = -394.8$ kJ ...(2)

$H_2+\frac{1}{2}O_2 \longrightarrow H_2O(g)$; $\Delta H = -241.6$ kJ ...(3)

Multiply Eq. (3) by 2 and add in Eq. (2)

$C+2H_2+2O_2 \longrightarrow CO_2+2H_2O(g)$; $\Delta H = -878$ kJ ...(4)

Subtract Eq. (1) from Eq. (4)

$CH_4+2O_2 \longrightarrow CO_2+2H_2O(g)$; $\Delta H = -801.8$ kJ

$\because$ 22.4 litre CH_4 on burning gives energy = 801.8 kJ

or 22.4×10^{-3} m^3 CH_4 on burning gives energy = 801.8 kJ

$\therefore$ 1 m^3 CH_4 on burning gives energy

$$= \frac{801.8}{22.4\times10^{-3}} = 35.795\times10^3 \text{ kJ}$$

$\therefore$ Heat evolved by burning 1 m^3 CH_4 = **35.795×10^3 kJ**

26. To get $B_2H_6(g)+3O_2(g) \longrightarrow B_2O_3(s)+3H_2O(g)$

By Eqs. (1) $+3\times$(2)$+3\times$(3)

$2B(s)+3H_2(g)+3O_2(g) \longrightarrow B_2O_3(s)+3H_2O(g)$;

$\Delta H = -1999$ ...(A)

By Eq. (A) – (4)

$B_2H_6(g)+3O_2(g) \longrightarrow B_2O_3(s)+3H_2O(g)$;

$\Delta H = -2035$ kJ

27. We have to evaluate ΔH for

$K(s)+\frac{1}{2}O_2(g)+\frac{1}{2}H_2(g) \longrightarrow KOH(s)$; $\Delta H = ?$

Adding Eqs. (1) and (2),

$K(s)+\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g)+aq. \longrightarrow KOH(aq.)$;

$\Delta H = -116.4$ kcal ...(4)

Subtracting Eq. (3) from Eq. (4)

$K(s)+\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g) \longrightarrow KOH(s)$;

$\Delta H = -102.4$ kcal

28. Given,

$\frac{1}{2}H_2(g)+aq. \longrightarrow H^+(aq.)+e$;

$\Delta H^\circ = 0$ ...(1)

$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$;

$\Delta H^\circ = -92.4$ kJ ...(2)

$HCl(g)+nH_2O(l) \longrightarrow H^+(aq.)+Cl^-(aq.)$;

$\Delta H^\circ = -74.8$ kJ ...(3)

Add Eqs. (2) and (3)

$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)+nH_2O \longrightarrow H^+(aq.)+Cl^-(aq.)$;

$\Delta H = -167.2$ kJ ...(4)

Subtract Eq. (1) from (4)

$\therefore$ $e+\frac{1}{2}Cl_2(g)+aq. \longrightarrow Cl^-(aq.)$;

$\Delta H = -167.2$ kJ

Heat of formation for $Cl^-(aq.)$ = **-167.2 kJ**

29. Standard heat enthalpy of a compound (H°)

= Standard heat of formation of that compound (ΔH°)

$\therefore$ $6C+3H_2 \longrightarrow C_6H_6(l)$; $\Delta H^\circ = 11.7$ kcal ...(1)

$H_2+\frac{1}{2}O_2 \longrightarrow H_2O(g)$; $\Delta H^\circ = -68.3$ kcal ...(2)

$C+O_2 \longrightarrow CO_2(g)$; $\Delta H^\circ = -94.0$ kcal ...(3)

Multiplying Eq. (2) by 3 and Eq. (3) by 6, and then add

$6C+3H_2+\frac{15}{2}O_2 \longrightarrow 6CO_2+3H_2O$;

$\Delta H^\circ = -768.9$ kcal ...(4)

Subtracting Eq. (1) from Eq. (4)

$C_6H_6+\frac{15}{2}O_2 \longrightarrow 6CO_2+3H_2O$; $\Delta H^\circ = -780.6$ kcal

$\therefore$ 78 g C_6H_6 gives heat = 780.6 kcal

$\therefore$ 1000 g C_6H_6 gives heat = $\frac{780.6\times1000}{78} = 10007.7$ kcal

Thus, heat produced by burning 1 kg C_6H_6 = **10007.7 kcal**

30. Given, $H_2+\frac{1}{2}O_2 \longrightarrow H_2O(l)$; $\Delta H = -285.85$ kJ ...(1)

$C+O_2 \longrightarrow CO_2(g)$; $\Delta H = -293.7$ kJ ...(2)

$\because$ 1 g starch on combustion gives 17.49 kJ energy

$\therefore$ 162n g starch on combustion gives = $17.49\times162n$ kJ energy = $2833.38n$ kJ

Molar mass of starch $(C_6H_{10}O_5)_n = 162n$

Therefore,

$(C_6H_{10}O_5)_n+6nO_2 \longrightarrow 6nCO_2+5nH_2O$;

$\Delta H = -2833.38n$ kJ ...(3)

Multiply Eq. (2) by 6n and Eq. (1) by 5n, then add

$5nH_2+\frac{5n}{2}O_2+6nC+6nO_2 \longrightarrow 5nH_2O+6nCO_2$;

$\Delta H = -3191.45n$ kJ ...(4)

Subtract Eq. (3) from Eq. (4)

$6nC + 5nH_2 + \frac{5n}{2}O_2 \longrightarrow (C_6H_{10}O_5)_n$; $\Delta H = -358.07\,n$ kJ

$\therefore$ Heat of formation for $162n$ g starch $= -358.07\,n$ kJ

$\therefore$ Heat of formation for 1 g starch $= -\frac{358.07}{162n} = \mathbf{-2.21\ kJ}$

31. ΔH needed for change $= \Delta H_{\text{Heating}} + \Delta H_{\text{Vaporisation}}$

$= 50\times10^3 \times 1\times 90 + 540\times 50\times10^3$

$= 31500\times10^3$ cal

ΔH actually needed $= \frac{31500\times10^3\times100}{60}$

(since only 60% of heat is used to do so)

Now 368×10^3 cal heat is given on combustion by 22.4 litre C_2H_6

$\therefore$ $\frac{31500\times10^3\times100}{60}$ heat is given by

$= \frac{22.4\times31500\times10^3\times100}{60\times368\times10^3}$

$= 3.196\times10^3$ litre $= \mathbf{3.196\ m^3}$

32. A better gas welder is one which posses high **calorific value, *i.e.*, heat produced by 1 g of fuel.**

$\Delta H_{\text{Combustion}}$ for $C_2H_6 = -341.1$ kcal

$\therefore$ Calorific value $= \frac{-341.1}{30}$ kcal/g $= \mathbf{-11.37\ kcal/g}$

$\Delta H_{\text{Combustion}}$ for $C_2H_2 = -310.0$ kcal

$\therefore$ Calorific value $= \frac{-310.0}{26}$ kcal/g $= \mathbf{-11.92\ kcal/g}$

$\therefore$ **C_2H_2 is better gas welder.**

33. ΔH supplied $= 10^3\times1\times37 = 37\times10^3$ cal

Thus, fuel value $= \frac{37\times10^3}{5} = \mathbf{7400\ cal/g}$

34. I. $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$;

$\Delta H = -2658$ kJ

Heat obtained by burning 11.2 kg isobutane

$= \frac{11.2\times10^3}{58}\times2658$

$= 5.13\times10^5$ kJ

$\therefore$ Day for which cylinder can serve $= \frac{5.13\times10^5}{15\times10^3} = \mathbf{34}$

II. If 30% heat is lost due to incomplete combustion, then

Heat obtained $= \frac{5.13\times10^5\times70}{100} = 3.59\times10^5$

Day for which cylinder can serve $= \frac{3.59\times10^5}{15\times10^3} = \mathbf{24}$

35. Energy supplied to athlete by consuming 100 g glucose $= 1560$ kJ

Energy utilized in event $= \frac{50}{100}\times1560 = 780$ kJ

Energy left as excess in body $= 1560 - 780 = 780$ kJ

$\because$ 44 kJ energy used to evaporate $= 18$ g H_2O

$\therefore$ 780 kJ energy used to evaporate $= \frac{18\times780}{44}$ g H_2O

$= \mathbf{319.09\ g}$

Thus, athlete should perspire 319.09 g of H_2O in order to avoid any storage of energy in body.

36. Energy available for muscular work $= \frac{2880\times25}{100}$

$= 720$ kJ / mol

$\therefore$ Energy available for muscular work for 120 g glucose

$= \frac{720\times120}{180} = 480$ kJ

$\because$ 100 kJ is used in 1 km distance.

$\therefore$ 480 kJ is used in **4.8 km** distance.

37. Inhaled O_2 in one breath $= \frac{200\times20}{100}$ mL

Exhaled O_2 in one breath $= \frac{200\times10}{100}$ mL

$\therefore$ Used O_2 in one breath $= \frac{200\times20}{100} - \frac{200\times10}{100} = 20$ mL

Now 20 breaths are taken in one minute

$\therefore$ Breaths taken in 1 hour $= 20\times60 = 1200$ breaths

$\therefore$ Volume of O_2 used in 1 hour $= 20\times1200$

$= 24000$ mL at 27°C

$= \frac{24000}{300}\times273$ mL at 0°C

$= 21840$ mL $= 21.84$ litre

For glucose $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$;

$\Delta H = -2822.5$ kJ

$\because$ 6×22.4 litre O_2 is used for 180 g glucose

$\therefore$ 21.84 litre O_2 is used for $= \frac{180\times21.84}{6\times22.4} = \mathbf{29.25\ g}$

Also, 6×22.4 litre O_2 with glucose gives $= 2822.5$ kJ

$\therefore$ 21.84 litre O_2 with glucose gives $= \frac{2822.5\times21.84}{6\times22.4}$

$= \mathbf{458.66\ kJ}$

38. Given, $\frac{1}{2}O_2 \longrightarrow O$; $\Delta H = 249$ kJ ...(1)

$NO_2 + O_2 \longrightarrow NO + O_3$; $\Delta H = +200$ kJ ...(2)

$O_3 \longrightarrow \frac{3}{2}O_2$; $\Delta H = -\frac{285.4}{2}$ kJ ...(3)

Adding Eqs. (1), (2) and (3)

$NO_2 \longrightarrow NO + O$; $\Delta H = \mathbf{306.3\ kJ}$

39. We have to find ΔH for

$N_2O_4 \longrightarrow 2NO_2$; $\Delta H = ?$

Add Eqs. (2) and (3)

$N_2 + 2O_2 \longrightarrow N_2O_4$; $\Delta H = -1.87$ kcal

$2NO_2 \longrightarrow 2NO + O_2$; $\Delta H = +26.10$ kcal

$\therefore$ $N_2 + 2O_2 + 2NO_2 \longrightarrow N_2O_4 + 2NO + O_2$;

$\Delta H = +24.23$ kcal

or $N_2 + O_2 + 2NO_2 \longrightarrow N_2O_4 + 2NO$;

$\Delta H = 24.23$ kcal ...(4)

Subtract Eq. (1) from Eq. (4)

$$2NO_2 \longrightarrow N_2O_4 ; \quad \Delta H = -18.87 \text{ kcal}$$

or $$N_2O_4 \longrightarrow 2NO_2 ; \quad \Delta H = +18.87 \text{ kcal}$$

i.e., Heat of dissociation of N_2O_4 = **+18.87 kcal**

40. Let volume of C_2H_4 and CH_4 be a and b litre respectively at 25°C.

$$a + b = 3.67 \text{ litre} \quad ...(1)$$

Also, $$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

∴ Volume of CO_2 produced by a litre $C_2H_4 = 2a$

and volume of CO_2 produced by b litre $CH_4 = b$

∴ $$2a + b = 6.11 \text{ litre} \quad ...(2)$$

By Eqs. (1) and (2)

$$a = 2.44 \text{ litre}$$

$$b = 1.23 \text{ litre}$$

∴ Volume of C_2H_4 in 1 litre mixture at 25°C

$$= \frac{2.44}{3.67} \times 1 = 0.6648 \text{ litre}$$

and volume of CH_4 in 1 litre mixture at 25°C

$$= \frac{1.23}{3.67} \times 1 = 0.3352 \text{ litre}$$

Now, volume of 1 mole C_2H_4 at 0°C = 22.4 litre

∴ Volume of 1 mole C_2H_4 at 25°C

$$= \frac{22.4 \times 298}{273} = 24.45 \text{ litre}$$

Similarly, volume of 1 mole CH_4 at 25°C

$$= \frac{22.4 \times 298}{273} = 24.45 \text{ litre}$$

∵ 24.45 litre C_2H_4 produces = + 1423 kJ at 25°C

∴ 0.6648 litre C_2H_4 produces $= \frac{+1423 \times 0.6648}{24.45}$

$$= +38.69 \text{ kJ}$$

Similarly, 24.45 litre CH_4 produces = + 891 kJ at 25°C

∴ 0.3352 litre CH_4 produces $= \frac{+891 \times 0.3352}{24.45}$

$$= +12.22 \text{ kJ}$$

Total heat produced = 38.69 + 12.22 = **50.91 kJ**

41. $$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe; \quad \Delta H = ?$$

Given, $$2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3 ; \ \Delta H = -399.0 \text{ kcal} \quad ...(1)$$

$$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3 ; \ \Delta H = -199.0 \text{ kcal} \quad ...(2)$$

Subtracting Eq. (2) from Eq. (1)

$$\underset{\text{Fuel mixture}}{2Al + Fe_2O_3} \longrightarrow 2Fe + Al_2O_3 ; \quad \Delta H = -200 \text{ kcal}$$

Molar mass of fuel mixture

$= 2 \times 27 + 2 \times 56 + 48 = 214$ g

∵ 214 g mixture produces = 200 kcal heat

∴ 1 g mixture produces $= \frac{200}{214} =$ **0.9346 kcal/g**

Also, volume of fusion mixture = vol. of Al + vol. of Fe_2O_3

$$= \frac{54}{2.7} + \frac{160}{5.2} = 20 + 30.76 = 50.76 \text{ mL}$$

∵ 50.76 mL mixture produces = 200 kcal

∴ 1 mL mixture produces $= \frac{200}{50.76} =$ **3.94 kcal/mL**

42. Given,

$$CuSO_4 + aq. \longrightarrow CuSO_4 \cdot 5H_2O(aq.); \quad \Delta H = -15.9 \text{ kcal} \quad ...(1)$$

$$CuSO_4 \cdot 5H_2O + aq. \longrightarrow CuSO_4 \cdot 5H_2O(aq.); \quad \Delta H = +2.8 \text{ kcal} \quad ...(2)$$

Subtracting Eq. (2) from Eq. (1)

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O; \quad \Delta H = -15.9 - 2.8 = -18.7 \text{ kcal}$$

∴ Heat of hydration of $CuSO_4$ = **−18.7 kcal**

43. $$H_2SO_4 + 3H_2O \longrightarrow H_2SO_4 \cdot 3H_2O$$

$$\Delta H_1 = \frac{75.6 \times 3}{3 + 1.8} =$$ **47.25 kJ**

$$H_2SO_4 + 8H_2O \longrightarrow H_2SO_4 \cdot 8H_2O$$

$$\Delta H_2 = \frac{75.6 \times 8}{8 + 1.8} =$$ **61.72 kJ**

$$H_2SO_4 \cdot 3H_2O + 5H_2O \longrightarrow H_2SO_4 \cdot 8H_2O$$

∵ $\Delta H_3 = \Delta H_2 - \Delta H_1 = 61.72 - 47.25 =$ **14.47 kJ**

44. ΔH_1 for 1 mole NaOH in 100 mole $H_2O(l) = -42.34$ kJ

ΔH_2 for 1 mole NaOH in 1000 mole $H_2O(l) = -42.76$ kJ

Thus, if 900 mole of H_2O are added to a solution containing 1 mole NaOH in 100 mole $H_2O(l)$, then

$$\Delta H = \Delta H_2 - \Delta H_1$$

$$= -42.76 + 42.34 =$$ **−0.42 kJ**

45. **For acetic acid :**

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O; \quad \Delta H = -13.2 \text{ kcal}$$

or $$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O; \quad \Delta H = -13.2 \text{ kcal} \quad ...(1)$$

Since, NaOH and CH_3COONa are strong electrolytes and thus, completely ionise. Also, CH_3COOH is weak electrolyte and thus,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

or $$CH_3COOH \longrightarrow CH_3COO^- + H^+ ; \quad \Delta H = q \quad ...(2)$$

Add Eqs. (1) and (2)

$CH_3COO^- + H^+ ; \Delta H = q ;$

$Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O; \quad \Delta H = -13.2$

or $$H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.2 - q$$

Given, $$H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.7$$

∴ $-13.7 = -13.2 - q$

∴ $q =$ **0.5 kcal**

where, q is heat of dissociation of acetic acid.

For NH_4OH:

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O; \quad \Delta H = -12.27 \text{ kcal}$$

Since, HCl and NH_4Cl are strong electrolytes and completely ionise, therefore,

$$NH_4OH + H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + H_2O; \quad \Delta H = -12.27 \text{ kcal} \quad ...(3)$$

For NH_4OH,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

or $$NH_4OH \longrightarrow NH_4^+ + OH^-; \quad \Delta H = q \quad ...(4)$$

By Eqs. (3) and (4)

$$NH_4^+ + OH^-; \Delta H = q; \; H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + H_2O; \quad \Delta H = -12.27$$

or $$H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -12.27 - q$$

$\therefore \quad -12.27 - q = -13.7 \;\therefore\; q = \mathbf{1.43 \text{ kcal}}$

where, q is heat of dissociation of NH_4OH.

46. Given total solution = 200 + 400 = 600 mL

200 mL of 1 *M* HCl neutralize 400 mL of 0.5 *M* NaOH

$\because$ Meq. $= N \times V$

$\therefore$ mM or Meq. of acid and base = 200 (For mono valent nature)

i.e., 200 Meq. of HCl react with 200 Meq. of NaOH to produce heat = ΔH

1000 Meq. of HCl + 1000 Meq. of NaOH will give heat $= 5 \times \Delta H$

i.e., heat of neutralization. Now,

ΔH, *i.e.*, heat produced during neutralization of 200 Meq. of acid and base = Heat taken up by calorimeter + solution

$$= m_1 s_1 \Delta T + m_2 s_2 \Delta T$$
$$= 12 \times 4.4 + 600 \times 1 \times 4.4 = 2692.8 \text{ cal}$$

$\therefore$ Heat of neutralization $= -5 \times 2692.8 \text{ cal} = \mathbf{-13.464 \text{ kcal}}$

47. $\Delta H^\circ_{\text{Reaction}} = \Delta H^\circ_{\text{Products}} - \Delta H^\circ_{\text{Reactants}}$

$$= 2 \times \Delta H^\circ_{Fe} + \Delta H^\circ_{Al_2O_3} - (2 \times \Delta H^\circ_{Al}) = \Delta H^\circ_{Fe_2O_3}$$
$$= 2 \times 0 + (-399.1) - (2 \times 0) - (-196.5)$$

$\Delta H^\circ = \mathbf{-202.6 \text{ kcal}}$

NOTE : ΔH° for free elements are zero.

48. Given,

$$NH_3 + \frac{3}{2}CuO \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l) + \frac{3}{2}Cu(s)$$

ΔH for change $= \Sigma H_{\text{Products}} - \Sigma H_{\text{Reactants}}$

$\because \; H^\circ_{\text{Element}} = 0$ and $H^\circ_{\text{Compound}} = \Delta H^\circ_f$

$\therefore \; \Delta H$ for change $= \frac{3}{2}H^\circ_{H_2O} - H^\circ_{NH_3} - \frac{3}{2}H^\circ_{CuO}$

$$= \frac{3}{2} \times (-285) - (-46) - \frac{3}{2}(-155) = -149 \text{ kJ}$$

$\because$ 17 g NH_3 brings change in $\Delta H = 149$ kJ

$\therefore$ 6.8 g NH_3 brings change in $\Delta H = \frac{149 \times 6.8}{17}$ kJ

$$= 59.6 \text{ kJ}$$

$\therefore \quad \Delta H = \mathbf{-59.6 \text{ kJ}}$

49. On mixing $CaCl_2(aq.)$ and Na_2CO_3

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

Solutions are very dilute and thus, 100% dissociation occurs.

$$Ca^{2+}(aq.) + 2Cl^-(aq.) + 2Na^+(aq.) + CO_3^{2-}(aq.) \longrightarrow CaCO_3 + 2Na^+(aq.) + 2Cl^-(aq.)$$

or $$Ca^{2+}(aq.) + CO_3^{2-}(aq.) \longrightarrow CaCO_3(s)$$

$\therefore \; \Delta H = \Sigma H^\circ_{\text{Products}} - \Delta H^\circ_{\text{Reactants}}$ or

$$\Delta H = \Delta H^\circ_{f\,CaCO_3} - [\Delta H^\circ_{f\,Ca^{2+}} + \Delta H^\circ_{f\,CO_3^{2-}}]$$

$\because \; H^\circ$ of a compound $= \Delta H^\circ_{\text{Formation}}$

$$= -288.5 - (-129.80 - 161.65)$$
$$= \mathbf{2.95 \text{ kcal}}$$

50. Given,

$$H_2(g) \longrightarrow 2H(g); \quad \Delta H = 104 \text{ kcal} \quad ...(1)$$
$$Cl_2(g) \longrightarrow 2Cl(g); \quad \Delta H = 58 \text{ kcal} \quad ...(2)$$
$$HCl(g) \longrightarrow H(g) + Cl(g); \quad \Delta H = 103 \text{ kcal} \quad ...(3)$$

Heat of formation for HCl

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \quad \Delta H = ?$$

Divide Eqs. (1) and (2) by 2 and then add

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow H(g) + Cl(g); \quad \Delta H = 81 \text{kcal} \quad ...(4)$$

Subtracting Eq. (3) from Eq. (4)

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \quad \Delta H = \mathbf{-22.0 \text{ kcal}}$$

$\therefore$ Enthalpy of formation for HCl gas $= \mathbf{-22.0 \text{ kcal}}$

51. $$2C + 3H_2 \longrightarrow C_2H_6; \quad \Delta H = -20.3 \text{ kcal}$$

Also,

$$\Delta H = -[1e_{C-C} + 6e_{C-H}] + [2(C(s) \rightarrow C(g)) + 3e_{H-H}]$$

$\therefore \; -20.3 = -[e_{C-C} + 6 \times 99] + [2 \times 170.9 + 3 \times (2 \times 52.1)]$

or $e_{C-C} = -594 + 341.8 + 312.6 + 20.3$

C—C bond energy = **80.7 kcal**

52. $$\Delta_C H_{C_3H_8} = 2 \times \Delta_C H_{CH_3 \text{ unit}} + 1 \times \Delta_C H_{CH_2 \text{ unit}} = -a$$

$$\Delta_C H_{C_4H_{10}} = 2 \times \Delta_C H_{CH_3 \text{ unit}} + 2 \times \Delta_C H_{CH_2 \text{ unit}} = -b$$

$\therefore \quad \Delta_C H_{CH_2} = a - b$ kcal

Also, $\Delta_C H_{CH_3} = \frac{b - 2a}{2}$ kcal

Now,

$$\Delta_C H_{C_{10}H_{22}} = \Delta_C H_{CH_3(CH_2)_8 \cdot CH_3}$$
$$= 2 \times \Delta_C H_{CH_3 \text{ unit}} + 8 \times \Delta_C H_{CH_2 \text{ unit}}$$
$$= 2 \times \frac{(b - 2a)}{2} + [8 \times (a - b)]$$
$$= \mathbf{6a - 7b \text{ kcal/mol}}$$

53. We have to find

$$O—H(g) = O(g) + H(g); \quad \Delta H = ?$$

Divide Eq. (2) by 2 and Eq. (3) by 2, then add

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H(g) + O(g); \quad \Delta H = 111.25 \text{ kcal} \quad ...(4)$$

Subtract Eq. (1) from Eq. (4)

$\therefore$ $OH(g) \longrightarrow H(g) + O(g)$; $\Delta H = 121.31$ kcal

$\therefore$ Bond energy of OH radical is **121.31 kcal**

54. $\Delta H_{Reaction}$ = Bond energy data used for formation of bond + Bond energy data used for dissociation of bond

$\Delta H_{Reaction} = -[2(C-C) + 2(C=C) + 8(C-H) + [5C_{S\to g} + 4(H-H)]$

$= -[2\times 83 + 2\times 147 + 8\times 98.8] + [5\times 171 + 4\times 104]$

$= +$**20.6 kcal**

55. Given, $CH_4 \longrightarrow C + 4H$; $\Delta H = 360$kcal

$\therefore$ Bond energy of 4(C—H) bond = 360 kcal

$\therefore$ Bond energy of C—H bond $= \frac{360}{4} = 90$ kcal

In $C_2H_6 \longrightarrow 2C + 6H$

Bond energy of $C_2H_6 = 1(C-C) + 6(C-H)$

$620 = 1(C-C) + 6\times 90$

$\therefore$ $C-C = 620 - 540 = 80$ kcal

$\therefore$ Bond energy of C—C = **80 kcal**

56. Given,

$C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$; $\Delta H = -312$ kcal ...(1)

($\because$ Heat of combustion are exothermic)

$C + O_2 \longrightarrow CO_2$; $\Delta H = -94.38$ kcal ...(2)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -68.38$ kcal ...(3)

Multiply Eq. (2) by 2 and add in Eq. (3)

$2C + H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$;

$\Delta H = -257.14$ kcal ...(4)

Subtracting Eq. (1) from Eq. (4)

$2C + H_2 \longrightarrow C_2H_2$; $\Delta H = +54.86$ kcal ...(5)

Also, ΔH for

$2C + H_2 \longrightarrow C_2H_2$

ΔH = Bond energy data of formation of bond + Bond energy data of dissociation of bond

$\Delta H = -[1(C\equiv C) + 2(C-H) + [2(C_{s\to g}) + 1(H-H)]$

Also given, $C_{s\to g} = 150$ kcal

$\frac{1}{2}H_2(g) \longrightarrow H(g) = 51.5$ kcal

$\therefore$ $e_{H-H} = 51.5\times 2$ kcal $= 103.0$ kcal

$e_{C-H} = 93.64$ kcal

$\therefore$ $54.86 = -[1(C\equiv C) + 2\times 93.64] + [2\times 150 + 1\times 103.0]$

$\therefore$ $e_{C\equiv C} =$ **160.86 kcal**

57. $\Delta H_{Reaction}$ = Bond energy data for formation of bond + Bond energy data for the dissociation of bond

$= -[1(C-C) + 6(C-H)] + [1(C=C) + 4(C-H) + 1(H-H)]$

$= -1(C-C) - 2(C-H) + 1(C=C) + 1(H-H)$

$= -347 - 2\times 414 + 615 + 435 = -125$ kJ

$\therefore$ Enthalpy change for the reaction = **-125 kJ**

58. $NH_3 \longrightarrow N(g) + 3H(g)$; $\Delta H_1 = x$ kcal mol^{-1}

$N_2H_4 \longrightarrow 2N(g) + 4H(g)$; $\Delta H_2 = y$ kcal mol^{-1}

$\Delta H_1 = 3\times e_{N-H} = x$ ...(1)

$\Delta H_2 = 4\times e_{N-H} + e_{N-N} = y$ ...(2)

From Eqs. (1) and (2)

$\therefore$ $y = 4\cdot\frac{x}{3} + e_{N-N}$

$\therefore$ $e_{N-N} = y - \frac{4x}{3} = \frac{3y-4x}{3}$ **kcal mol^{-1}**

59. For C_2H_6: $2C + 3H_2 \longrightarrow C_2H_6$; ΔH_1

For C_3H_8: $3C + 4H_2 \longrightarrow C_3H_8$; ΔH_2

$\therefore$ $\Delta H_1 = -[1(C-C) + 6(C-H)] + [2(C_{s\to g}) + 3(H-H)]$ ...(1)

and $\Delta H_2 = -[2(C-C) + 8(C-H)] + [3(C_{s\to g}) + 4(H-H)]$ ...(2)

Let C—C bond energy be a kcal

and C—H bond energy be b kcal

$\therefore$ $\Delta H_1 = -[a + 6b] + [2\times 172 + 3\times 104]$ ...(3)

and $\Delta H_2 = -[2a + 8b] + [3\times 172 + 4\times 104]$ ...(4)

Also from $C + O_2 \longrightarrow CO_2$; $\Delta H = -94.0$ kcal ...(5)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -68.0$ kcal ...(6)

$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$;

$\Delta H = -372$ kcal ...(7)

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$;

$\Delta H = -530$ kcal ...(8)

Multiply Eq. (5) by 2 and Eq. (6) by 3, then add

$2C + 3H_2 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$;

$\Delta H = -392$ kcal ...(9)

Subtracting Eq. (7) from Eq. (9)

$2C + 3H_2 \longrightarrow C_2H_6$; $\Delta H = -20$ kcal ...(10)

Similarly also from Eq. (5) multiplying by 3, Eq. (6) multiplying by 4 and adding both of them, then subtracting Eq. (8), we get

$3C + 4H_2 \longrightarrow C_3H_8$; $\Delta H_2 = -24$ kcal ...(11)

By Eqs. (3), (4), (10) and (11)

$a + 6b = 676$

$2a + 8b = 956$

$\therefore$ $a = 82$ kcal and $b = 99$ kcal

$\therefore$ Bond energy of C—C bond = **82 kcal**

Bond energy of C—H bond = **99 kcal**

60. Given, $C_6H_{10} + H_2 \longrightarrow C_6H_{12}$; $\Delta H = -119$ kJ

(involves breaking up of one double bond and addition of one H_2 molecule)

$\therefore$ $C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$; $\Delta H = 3\times(-119) = -357$kJ

(involves breaking up of three double bond and addition of three H_2 molecules)

Also given $6C + 6H_2 \longrightarrow C_6H_{12}(l)$; $\Delta H = -156$

we have $C_6H_6 + 3H_2 \longrightarrow C_6H_{12}(l)$; $\Delta H = -357$

$-\quad -\quad -\quad +$

$6C + 3H_2 \longrightarrow C_6H_6$; $\Delta H = +201$kJ

Therefore, resonance energy = $49 - 201 = -152$ **kJ**

(Exp.) (Theoretical)

61. Given, for N_2O

$$N_2 + \frac{1}{2}O_2 \longrightarrow N_2O; \qquad \Delta H_{exp} = 82\text{kJ}$$

Also, from bond energy data, using N≡N=O structure for N_2O

$$\Delta H_{f\,cal.} = -[1(N{=}N) + 1[(N{=}O)] + [(N{\equiv}N) + \frac{1}{2}(O{=}O)]$$

$$= -[418 + 607] + [946 + \frac{1}{2}(498)] = +170\text{ kJ}$$

Now, resonance energy

= Exp. $\Delta H_{f\,N_2O}$ – Calculated $\Delta H_{f\,N_2O}$

= 82 – 170 = **–88 kJ mol^{-1}**

62. $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l); \qquad \Delta H = ?$

ΔH = Bond energy data for formation + Bond energy data for dissociation + Energy released during liquefaction

$$= -[3C{-}H + 1C{-}O + 1O{-}H] + [C_{s\to g} + 2H{-}H + \frac{1}{2}O{-}O] - [CH_3OH(g) \longrightarrow CH_3OH(l)]$$

$$= -[3\times415 + 356 + 463] + [715 + 2\times436 + \frac{1}{2}\times249] - 38$$

= **–266 kJ mol^{-1}**

63. For $2C_4H_{10} \longrightarrow C_8H_{18} + H_2; \qquad \Delta H = ?$

Using bond energy data

ΔH = [Bond energy data for formation of bond + Bond energy data for dissociation of bond]

$$= -[7(C{-}C) + 18(C{-}H) + 1(H{-}H)] + 2[3(C{-}C) + 10(C{-}H)]$$

$$\Delta H = -(C{-}C) + 2(C{-}H) - 1(H{-}H)$$

Given, $\frac{1}{2}H_2 \longrightarrow H; \qquad \Delta H = 217.55$

$\therefore$ $H_2 \longrightarrow 2H; \qquad \Delta H = 2\times217.55 = 435.1\text{kJ}$

$\therefore$ BE(H—H) = 435.1 kJ;

Also, BE(C—C) = 347.3 kJ; BE(C—H) = 414.1 kJ

$\therefore$ $\Delta H = -347.3 + 2\times(414.2) - 1\times(435.1)$

ΔH = **46.0 kJ mol^{-1}**

64. **For C_6H_6 :** $6C(s) + 3H_2(g) \longrightarrow C_6H_6;$

$\Delta H_{exp.} = -358.5$ kJ

$\therefore$ $\Delta H_{cal.}$ = [BE data for formation of bonds + BE data for dissociation of bonds]

$$= -[3(C{-}C) + 3(C{=}C) + 6(C{-}H)] + [6C_{s\to g} + 3(H{-}H)]$$

$$= -[3\times340 + 3\times620 + 6\times490] + [6\times716.8 + 3\times436.9]$$

$$= \Delta H_f = -208.5\text{ kJ mol}^{-1}$$

$\therefore$ Resonance energy = Exp. ΔH_f – Calculated ΔH_f

= –358.5 – (208.5) = **–150.0 kJ mol^{-1}**

65. Temp. rise for water = 55°C

Mass of water to be heated = 150×10^3 g

$\therefore$ Heat used for water

$$= m\cdot s\times\Delta T = 150\times10^3\times4.184\times10^{-3}\times55$$

= 34518 kJ

For propane : $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O;$

$\Delta H = 2050$ kJ

$\because$ 2050 kJ heat is provided by 1 mole C_3H_8

$\therefore$ 34518 kJ heat is produced by = $\frac{34518}{2050}$

= **16.838 mol C_3H_8**

$\therefore$ Volume of C_3H_8 at NTP = 16.838 × 22.4 litre

= **3.77×10^2 litre**

66. **I Case :** Energy produced during passage of current is used to raise the temperature of calorimeter.

$\therefore$ $Q\cdot V = mS\Delta T$

$3.20\times3\times12.0 = mS\times1.617$

$\therefore$ mS calorimeter = 71.24 JK^{-1}

II Case : $Q_1V_1 = [mS$ calorimeter $+ mS$ liquid$]\times\Delta T$

$0.5\times1.50\times3\times60 = [71.24 + 100\times S]\times0.8$

$\therefore$ $S = 0.975$ J/g

$\therefore$ Molar heat = 0.975×40 = **39.04 J**

67. $q = ms\cdot\Delta T$ for combustion of benzoic acid

(**NOTE** : In bomb calorimeter reaction is made at constant volume.)

$$\frac{0.316\times3227}{122} = ms\times3.24$$

$\therefore$ Water equivalent of bomb calorimeter (ms)

$$= \frac{0.316\times3227}{122\times3.24} = 2.58\text{ kJ/°C}$$

For banana slice;

$q = ms\times\Delta T$

$q = 2.58\times3.05 = 7.87$kJ per 2.502 g banana

$\therefore$ Heat produced by 125 g banana = $\frac{7.87\times125}{2.502} = 393.18$ kJ

$$= \frac{393.18}{4.184}\text{ kcal}$$

= **93.97 kcal**

68. $C + H_2O(g) \longrightarrow H_2 + CO; \qquad \Delta H^\circ = ?$

($\because$ H° for C and H_2 are zero)

$\therefore$ $\Delta H^\circ = H^\circ_{CO} - H^\circ_{H_2O} = -110.53 - (-241.81)$

= 131.28 kJ/mol

Thus, ΔH° needed for 100 g carbon = $\frac{131.28\times100}{12}$ kJ

Now 393.51 kJ energy is provided by 12 g C

$\therefore$ $\frac{131.28\times100}{12}$ kJ energy is provided by

$$= \frac{12\times131.28\times100}{12\times393.51}$$

= **33.36 g carbon**

69. Given,

Specific heat at constt. P, c_p = 0.125 cal/g

Specific heat at constt. V, c_v = 0.075 cal/g

(i) We have $c_p - c_v = \frac{R}{M}$ $\therefore$ $0.125 - 0.075 = \frac{2}{M}$

$\therefore$ $M = 40$

(ii) For atomicity $\gamma = \frac{c_p}{c_v} = \frac{0.125}{0.075} = 1.66$

$\therefore$ **Gas is monoatomic.**

(iii) Being monoatomic nature 1 molecule of gas has 1 atom.

$\therefore$ No. of atoms of gas in 1 mole = $\mathbf{6.023 \times 10^{23}}$ **atoms**

70. Given,

$$\underset{X}{CH_4} + \underset{6X}{2O_2} \longrightarrow CO_2 + 2H_2O; \Delta H = -809 \text{ kJ mol}^{-1}$$

Initial volume/hr (in litre)

Let the temperature be T and assume volume of 1 mole of a gas is V litre at this condition.

$\therefore$ V litre or 1 mole CH_4 gives energy on combustion = 809 kJ

$\therefore$ X litre of CH_4 gives energy on combustion $= \frac{809(X)}{V}$ kJ

$\because$ 2878 kJ energy is obtained by 1 mole or V litre C_4H_{10}

$\therefore$ $\frac{809(X)}{V}$ kJ energy is obtained by $= \frac{809(X) \times V}{V \times 2878}$ litre C_4H_{10}

$= 0.281(X)$ litre C_4H_{10}

Thus, butane supplied for same calorific output $= \mathbf{0.281(X)\ litre}$

$\because C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O; \Delta H = -2878$ kJ/mol

Vol. of O_2 required = 3× vol. of O_2 for combustion of C_4H_{10}

$= 3 \times \frac{13}{2} \times$ vol. of C_4H_{10}

$= 3 \times \frac{13}{2} \times 0.281\ (X) = \mathbf{5.48\ (X)\ litre\ O_2}$

71. The first reaction is exothermic and the second one is endothermic. If a mixture of steam and O_2 is passed over coke and temperature is kept constant, the conversion of each to CO should not show any heat change, *i.e.*, total heat evolved in I = total heat absorbed in II.

$$n_1 \times 2 \times 110 = n_2 \times 132$$

$\therefore$ $\frac{n_1}{n_2} = \frac{132}{110 \times 2} = \mathbf{\frac{0.6}{1}}$

where, n_1 and n_2 are mole of O_2 and H_2O used during reaction.

72. $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O; \Delta H = -5645$ kJ

Mole of O_2 used per day $= \frac{640}{32} = 20$

$\therefore$ Mole of sucrose used per day $= \frac{20}{12}$ mole

$= \frac{20}{12} \times 342\text{ g} = \mathbf{570\ g}$

Also, $\Delta H = \frac{5645 \times 20}{12} = \mathbf{9408.33\ kJ}$

73. Given, $C + O_2 \longrightarrow CO_2$; $\Delta H = -94.05$ kcal

$C + \frac{1}{2}O_2 \longrightarrow CO$; $\Delta H = -26.41$ kcal

Let a mole of carbon reacts to form CO_2 and b mole of carbon reacts to form CO. Since, only 12 g carbon, *i.e.*, 1 mole is used up, thus,

$$a + b = \frac{12}{12} = 1 \quad \ldots(1)$$

Also, $a \times 94.05 + b \times 26.41 = 75$

$\therefore$ $a = 0.718$, *i.e.*, mole of CO_2 formed

$b = 0.282$, *i.e.*, mole of CO formed

Also, mole of O_2 used for this change $= 0.718 + \frac{0.282}{2}$

$= 0.859$

Thus, mass of O_2 used $= 0.859 \times 32 = \mathbf{27.49\ g}$

74. Total mole of Mg $= \frac{1}{24}$

Let a mole of Mg^+ and b mole of Mg^{2+} are present, then

$$a + b = \frac{1}{24} \quad \ldots(1)$$

Also, $50 = a \times 740 + b \times 2190$ ...(2)

$\therefore$ From Eqs. (1) and (2),

$a = 2.845 \times 10^{-2}$

$b = 1.322 \times 10^{-2}$

$\therefore$ % of $Mg^+ = \mathbf{68.28\%}$

% of $Mg^{2+} = \mathbf{31.72\%}$

75. Given, $S(s) + 3F_2(g) \longrightarrow SF_6$; $\Delta H = -1100$ kJ ...(1)

$S(s) \longrightarrow S(g)$; $\Delta H = 275$ kJ ...(2)

$\frac{1}{2}F_2(g) \longrightarrow F(g)$; $\Delta H = 80$ kJ ...(3)

To get $SF_6(g) \longrightarrow S(g) + 6F(g)$, we can proceed as (2) + 6×(3) − (1)

$SF_6(g) \longrightarrow S(g) + 6F(g)$; $\Delta H = 1855$ kJ

Thus, average bond energy $= \frac{1855}{6} = \mathbf{309.17}$

76. $Au(OH)_3 + 4HCl \longrightarrow HAuCl_4 + 3H_2O$; $\Delta H = -28$ kcal

$HAuBr_4 + 3H_2O \longrightarrow Au(OH)_3 + 4HBr$; $\Delta H = +36.8$ kcal

$\therefore$ $HAuBr_4 + 4HCl \longrightarrow HAuCl_4 + 4HBr$; $\Delta H = 8.8$ kcal

$\therefore$ Fraction of $HAuBr_4$ converted to $HAuCl_4 = \frac{0.44}{8.8} = 0.05$

$\therefore$ % of $HAuBr_4$ converted $= 0.05 \times 100 = \mathbf{5\%}$

77. Let a eq. of NaOH be used by HA, and b eq. of NaOH be used by HB. Also, heat of dissociation of $HB = +13.68 - 2.9 = 10.78$ kcal/eq.

$\therefore$ $a \times (-13.68) + b \times (-2.9) + b \times (10.78) = -6.9$

$\therefore$ $-13.68a + 7.88b = -6.9$

or $-13.68a + 7.88(1 - a) = -6.9$ $(a + b = 1)$

$\therefore$ $-21.56a = -14.78$ $\therefore$ $a = \mathbf{0.685}$

78. $Fe + \frac{1}{2}O_2 \longrightarrow FeO$; $\Delta H = -65$ kcal mol^{-1} ...(i)

$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3$; $\Delta H = -197$ kcal mol^{-1} ...(ii)

By Eq. (ii) $-2\times$(i)

Also,

$$2FeO+\frac{1}{2}O_2 \longrightarrow Fe_2O_3\ ;\ \Delta H=-67\ \text{kcal mol}^{-1} \quad ...(iii)$$

Let a mole of FeO and b mole of Fe_2O_3 are present such that

$$a+b=1 \text{ and } \frac{a}{b}=2$$

$$\therefore \quad a=\frac{2}{3} \text{ and } b=\frac{1}{3}$$

$$2FeO+\frac{1}{2}O_2 \longrightarrow Fe_2O_3$$

Initial $\quad a \qquad\qquad b$

After oxidation $\quad (a-2a') \qquad b+a'$

Given, $\frac{a}{b}=2$ and $\frac{a-2a'}{b+a'}=\frac{1}{2}$

$$\therefore \quad \frac{a-2a'}{\frac{a}{2}+a'}=\frac{1}{2} \qquad \therefore \quad 2a-4a'=\frac{a}{2}+a'$$

$$\therefore \quad a'=\frac{3a}{10}=\frac{3\times 2}{10\times 3}=\frac{1}{5} \qquad \therefore \quad \text{FeO used}=\frac{2}{5}$$

$\because$ 2 mole FeO gives heat = 67 kcal

$\therefore \frac{2}{5}$ mole FeO gives heat $=\frac{67\times 2}{2\times 5}=$ **13.4 kcal heat**

79. $C_2H_5OH(g) \longrightarrow C_2H_4(g)+H_2O(g)$;

$\Delta H^\circ = -45.54$ kJ ...(i)

$C_2H_5OH(g) \longrightarrow CH_3CHO(g)+H_2(g)$;

$\Delta H^\circ = -68.91$ kJ ...(ii)

Let a mole of ethanol be decomposed by Eq. (i) and b mole be decomposed by Eq. (ii)

$\therefore \quad a+b=1$ ...(iii)

Also, the ratio of C_2H_4 and CH_3CHO formed is a/b

$\therefore \quad \frac{a}{b}=8$ ...(iv)

By Eqs. (iii) and (iv)

$\therefore \quad 8b+b=1$

$$b=\frac{1}{9} \text{ and } a=\frac{8}{9}$$

$$\therefore \quad \Delta H^\circ_{\text{Total}}=-\left[45.54\times\frac{8}{9}+68.91\times\frac{1}{9}\right]=\mathbf{-48.13\ kJ}$$

80. $\Delta H=+4\times e_{Xe-F}+IE_{1\,Xe}-EA_{1\,F}-e_{F-F}$

$=4\times 34+279-85-38=$ **+292 kcal/mol**

81. Heat released during combustion of 3.5 g gas

$=(mS)\times\Delta T=2.5\times 0.45=1.125$ kJ

$\therefore$ Heat released for combustion of 1 mole (or 28 g) gas

$=\frac{28}{3.5}\times 1.125=$ **9 kJ mol**

● SINGLE INTEGER ANSWER PROBLEMS ●

1. The ΔH_f° of $BaSO_{4(s)}$, $Ba^{2+}_{(aq)}$ and $SO^{2-}_{4(aq.)}$ are –350.6, –128.3 and –216.3 kcal. The heat of reaction (in kcal) is minus :
$BaCl_{2(aq.)} + H_2SO_{4(aq.)} \longrightarrow BaSO_{4(s)} + 2HCl_{(aq.)}$ is .....
2. The heat evolved in kcal for the process at 25°C of dissolving 1.0 mole of KCl in excess of water as
$$KCl_{(s)} \longrightarrow K^+ + Cl^-$$
(Given : ΔH_f° of $K^+_{(aq)}$, $Cl^-_{(aq)}$ and $KCl_{(s)}$ are –60, –40 and –104 kcal/mole).
3. If ΔH_f° of $H_2S_{(g)}$ and $H_2S_{(aq.)}$ are –4.5 and –9.5 kcal. How much heat is required for the change ?
$$H_2S_{(aq.)} \longrightarrow H_2S_{(g)}$$
4. If heat of reaction for the given acid base reaction :
$$HA + NaOH \longrightarrow NaA + H_2O; \quad \Delta H = -4.7 \text{ kcal}$$
The heat of dissociation of HA is .....
5. For a gas the numerical value (in cal) of $\left[\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V\right]$ is equal to .....
6. The enthalpy changes of some processes are given below
α-D-glucose$_{(s)} + H_2O \longrightarrow \alpha$-$D$-glucose$_{(aq.)}$; Heat of dissolution = 10.84 kJ
β-D-glucose$_{(s)} + H_2O \longrightarrow \beta$-$D$-glucose$_{(aq.)}$; Heat of dissolution = 4.68 kJ
α-D-glucose$_{(aq.)} \longrightarrow \beta$-$D$-glucose$_{(aq.)}$; Heat of mutarotation = – 1.16 kJ
The ΔH° for α-D-glucose $\longrightarrow \beta$-D-glucose is .....
7. 10 mL of dissolution of a strong acid (HA) on mixing with 10 mL of strong alkali (BOH) at the same temperature shows a temperature rise of 4°C. If 50 mL of same acid are mixed with 50 mL of same alkali; the temperature rise will be ..... °C. Assume all the heat produced is used up in increasing temperature of mixture only.
8. Standard molar heat enthalpy for converting carbon from graphite and diamond form into vapour state directly are 725 and 713 kJ respectively. The standard enthalpy change for polymorphism of 1 g carbon $C_{G \rightarrow D}$ is .....
9. If heat of formation of $CaCl_2$ and NaCl are 191 and 97.5 kcal, the heat of reaction for $CaCl_2 + 2Na \longrightarrow 2NaCl + Ca$ is .....
10. The difference of $\Delta H - \Delta U$ for the given reaction is nRT. The value of n is .....
$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_v$$
11. Heat of combustion of a fuel molar mass 86 is 688 kJ/mole. The calorific value of fuel is .....
12. The combustion of 5.0 g of coke raised the temperature of 1.0 g of water from 10°C to 55°C. If specific heat of water of 1 cal/g, the calorific value of coke is .....
13. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. 25% of this energy is available for muscular work. If 80 kJ of muscular work is needed to walk one km, what is the maximum distance that a person will walk after eating 120g glucose.
14. Heat of solution of anhydrous $CuSO_4$ is –15.9 kcal and heat of hydration of anhydrous $CuSO_4$ is –18.9 kcal. The heat of solution of $CuSO_4 \cdot 5H_2O$ is .....
15. ΔH_f° of Fe_2O_3 and Al_2O_3 are –189 kJ mol^{-1} and –405 kJ mol^{-1} respectively. How much heat (in kJ) is given out during reaction of 1 g Al according to
$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe \text{ ?}$$
16. How much of the following have their standard heat of formation zero at 298K. $O_2(l)$, $C_{graphite}$, P_{Black}, $S_{monoclinic}$, $I_{2\,(solid)}$
17. How much of the following possess heat of neutralization less than –13.7 kcal.
$HCl(aq.) + NaOH(aq.)$, $HF(aq.) + NaOH(aq.)$,
$CH_3COOH(aq.) + NH_4OH(aq.)$,
$CCl_3COOH(aq.) + KOH(aq.)$,
$C_6H_5COOH(aq.) + KOH(aq.)$
18. For $Au(OH)_3 + 4HCl \longrightarrow HAuCl_4 + 3H_2O$; $\Delta H = -28$ kcal
and $Au(OH)_3 + 4HBr \longrightarrow HAuBr_4 + 3H_2O$; $\Delta H = -36.8$ kcal
If 1 mole of $HAuBr_4$ was mixed with 4 mole of HCl, 0.44 kcal heat was absorbed. The percentage conversion of $HAuBr_4$ to $HAuCl_4$ is .....

ANSWERS

1. Six **2.** Four **3.** Five **4.** Nine **5.** Two **6.** Five **7.** Four **8.** One **9.** Four **10.** Six **11.** Eight **12.** Nine
13. Six **14.** Three **15.** Four **16.** Three **17.** Two **18.** Five

OBJECTIVE PROBLEMS (One Answer Correct)

1. The e_{P-H} and e_{P-P} are 76 and 51 kcal mol^{-1}. The difference in the heat of atomisation for PH_3 and P_2H_4 in kcal mol^{-1} is:
   (a) 127 (b) 178
   (c) 203 (d) 25
2. Which of the following on mixing will give rise to maximum heat of reaction ?
   (a) 100 mL of 0.1 *M* HCl + 40 mL of 0.1 *M* NaOH
   (b) 60 mL of 0.1 *M* HCl + 60 mL of 0.1 *M* NaOH
   (c) 40 mL of 0.1 *M* HCl + 30 mL of 0.1 *M* NaOH
   (d) 40 mL of 0.1 *M* HCl + 100 mL of 0.1 *M* NaOH
3. The amount of heat released during the reaction of 300 mL of 1 *M* HCl with 100 mL of 1 *M* NaOH is :
   (a) 57.3 kJ (b) 5.73 kJ
   (c) 573 kJ (d) 573×10^3 kJ
4. Equal volumes of 1 *M* HCl and 1 *M* H_2SO_4 are neutralised by dilute NaOH solution producing *X* and *Y* kcal of heat respectively, then $(Y - X)$ is :
   (a) 1 *Y* (b) 0.5 *Y*
   (c) 0.1 *Y* (d) 5 *Y*
5. A solution of 200 mL of 1 *M* KOH is added to 200 mL of 1 *M* HCl and the mixture after attaining reaction equilibrium shows a rise in temperature by ΔT_1. The experiment is repeated by using 50 mL of 1 *M* KOH and 50 mL 1 *M* HCl which at equilibrium shows a rise in temperature by ΔT_2. Thus :
   (a) $\Delta T_1 = \Delta T_2$ (b) $\Delta T_1 = 4 \times \Delta T_2$
   (c) $\Delta T_1 = 2 \times \Delta T_2$ (d) $\Delta T_1 > \Delta T_2$
6. Given :
   $HCl_{(g)} + 40H_2O \longrightarrow HCl(40H_2O)$; $\Delta H = -73.0$ kJ
   $HCl_{(g)} + 10H_2O \longrightarrow HCl(10H_2O)$; $\Delta H = -69.0$ kJ
   then integral heat of dilution for two moles of $HCl(10H_2O)$ to $HCl(40H_2O)$ is :
   (a) – 4.5 kJ (b) – 3.5 kJ
   (c) – 8.0 kJ (d) – 2.0 kJ
7. Heat of neutralisation for weak acid HF is :
   (a) 13.7 kcal (b) > 13.7 kcal
   (c) < 13.7 kcal (d) either of these
8. Molar heat capacity of water in equilibrium water $\rightleftharpoons$ vapours at constant pressure is :
   (a) zero (b) infinity
   (c) $\frac{80}{18}$ cal/mol (d) $\frac{540}{18}$ cal/mol
9. Which of the following is not endothermic ?
   (a) $C + 2S \longrightarrow CS_2$ (b) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O$
   (c) $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O$ (d) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$
10. Two moles of CO and 1 mole of O_2 were allowed to react completely to form CO_2 at 300 K. If the heat liberated during the course of reaction : $2CO + O_2 \longrightarrow 2CO_2$ at constant pressure is 560 kJ, the amount of heat liberated by carrying the reaction in 1 litre vessel will be:
    (1 litre-atm = 0.1 kJ)
    (a) + 58 kJ (b) + 535.37 kJ
    (c) + 557.54 kJ (d) + 55.75 kJ
11. One mole of ice melts at 0°C and 1 atm absorbing 1440cal of heat. The molar volume of ice and water are 0.0196 and 0.0180 litre respectively. The ΔU for the change is :
    (a) $\simeq$ 1440 cal (b) >> 1400 cal
    (c) << 1440 cal (d) = 1440 cal
12. The combustion of 10.0 g coke raised the temperature of 1.0 kg water from 10°C to 50°C. If specific heat of H_2O is 1 cal/g then the fuel value of coke is :
    (a) 1000 cal (b) 2000 cal
    (c) 3000 cal (d) 4000 cal
13. Molar heat capacity of water in equilibrium with the ice at constant pressure is :
    (a) zero (b) infinity (∞)
    (c) 40.45 kJ K^{-1} mol^{-1} (d) 75.48 JK^{-1} mol^{-1}
14. Standard molar enthalpy of formation of CO_2 is equal to :
    (a) zero
    (b) the standard molar enthalpy of combustion
    (c) the sum of standard molar enthalpies of formation of CO and O_2
    (d) the standard molar enthalpy of combustion of carbon (graphite)
15. For the reaction, $2O_3 \rightarrow 3O_2$, $\Delta H, \Delta S$ and ΔG are respectively:
    (a) +ve, +ve, +ve (b) –ve, +ve, –ve
    (c) –ve, –ve, +ve (d) +ve, –ve, –ve
16. For the reaction, $2Br_{(g)} \rightarrow Br_{2(l)}$, ΔH and ΔS are :
    (a) –ve, –ve (b) +ve, –ve
    (c) –ve, +ve (d) +ve, +ve
17. A reaction $X \rightarrow Y$ involves three steps. If
    $X \rightarrow A; \Delta H = -a$ kcal ...(i)
    $B \rightarrow A; \Delta H = -b$ kcal ...(ii)
    $B \rightarrow Y; \Delta H = -c$ kcal ...(iii)
    then ΔH for $X \rightarrow Y$ is:
    (a) $a + b + c$ (b) $b - a - c$
    (c) $a + b - c$ (d) $c + b - a$
18. Which of the following reaction shows standard enthalpy of formation of $CH_3Cl_{(g)}$, if reactions are made at 1 atm and 25°C:
    (a) $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$

(b) $C_{(G)} + \frac{3}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CH_3Cl_{(g)}$

(c) $C_{(D)} + \frac{3}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CH_3Cl_{(g)}$

(d) $C_{(S)} + \frac{3}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CH_3Cl_{(g)}$

19. If $\Delta_f H°$ of $C_2H_{4(g)}$ and $\Delta_f H°$ of $C_2H_{6(g)}$ are q_1 and q_2 kcal mol^{-1}, then heat of hydrogenation of $C_2H_{4(g)}$ is:

(a) $q_2 - q_1$ (b) $q_2 + q_1$
(c) $q_1 + 2q_2$ (d) $q_1 - q_2$

20. If heat of formation of $NH_{3(g)}$ is -46 kJ mol^{-1}, then ΔH for the reaction : $2NH_3 \rightleftharpoons N_2 + 3H_2$ is :

(a) +46 kJ (b) +92 kJ
(c) –92 kJ (d) None of these

21. e_{H-H} is 436.4 kJ, then heat of formation of H atom is:

(a) 872.8 kJ mol^{-1} (b) – 218.2 kJ mol^{-1}
(c) +218.2 kJ mol^{-1} (d) – 436.4 kJ mol^{-1}

22. The amount of heat released when 20 mL of 0.5 *M* NaOH is mixed with 100 mL of 0.1 *M* HCl is *x* kJ. The heat of neutralisation (in kJ) is:

(a) $-100x$ (b) $-50x$
(c) $100x$ (d) $50x$

23. For the reactions:

$A \rightarrow B$; $\Delta H = +24$ kJ mol^{-1}

$B \rightarrow C$; $\Delta H = -18$ kJ mol^{-1}

The decreasing order of enthalpy of *A*, *B*, *C* is:

(a) $A > B > C$ (b) $B > C > A$
(c) $C > B > A$ (d) $C > A > B$

24. One g sample of NH_4NO_3 is decomposed

$(NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)})$

in bomb calorimeter. The temperature of calorimeter increases by 6.12 K. The heat capacity of system is 1.23 kJ|g|°. The molar heat of decomposition is:

(a) –7.5 kJ (b) +7.5 kJ
(c) –16.1 kJ (d) +16.1 kJ

25. The enthalpy change for the process $C_{(s)} \rightarrow C_{(g)}$ is called:

(a) heat of vaporisation
(b) heat of atomisation
(c) heat of allotropic change
(d) heat of sublimation

26. The difference between heats of reaction at constant pressure and constant volume for the reaction:

$2C_6H_{6(l)} + 15O_{2(g)} \rightarrow 12CO_{2\,g)} + 6H_2O_{(l)}$ at 25°C in kJ is:

(a) –7.43 (b) +3.72
(c) –3.72 (d) +7.43

27. The products of combustion of an aliphatic thiol at 298 K are:

(a) $CO_{2(g)}$, $H_2O_{(g)}$ and $SO_{2(g)}$
(b) $CO_{2(g)}$, $H_2O_{(l)}$ and $SO_{2(g)}$
(c) $CO_{2(l)}$, $H_2O_{(l)}$ and $SO_{2(g)}$
(d) $CO_{2(g)}$, $H_2O_{(l)}$ and $SO_{2(l)}$

28. For which change, $\Delta H \neq \Delta E$

(a) $H_2 + I_2 \rightarrow 2HI$
(b) $HCl + NaOH \rightarrow NaCl + H_2O$
(c) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
(d) $N_2 + 3H_2 \rightarrow 2NH_3$

29. Under the same conditions how many mL of 1*M* KOH and 0.5 *M* H_2SO_4 solution respectively when mixed for a total volume of 100 mL produce the highest rise in temperature :

(a) 67 : 33 (b) 33 : 67
(c) 40 : 60 (d) 50 : 50

30. One mole of ideal gas is kept in a cubical vessel of length *a* cm at 330 K. The gas is then transferred completely to a large cubical vessel of length 2*a* cm at 330 K. The change in entropy in cal/° for the ideal gas assuming reversible process.

(a) 2.07 (b) 4.15
(c) 6.21 (d) 1.03

31. The standard enthalpy of combustion of propane gas at 27°C –2220 kJ mol^{-1} and standard enthalpy of vaporisation of C_3H_8 is 15 kJ mol^{-1} at 27°C. What is the standard internal energy change for combustion of liquid propane. Water is formed during combustion.

(a) – 2205 kJ (b) – 2200 kJ
(c) – 1100 kJ (d) – 6600 kJ

32. $\Delta G°$ for the reaction : $Br_2(g) \rightleftharpoons 2Br(g)$ at 2400 K is -72.8 kJ mol^{-1}. If $\Delta H°$ being independent of temperature and equal to 205 kJ mol^{-1}, what will be the value of K at 2600 K.

(a) 38.39 (b) 84.46
(c) 19.19 (d) 42.32

SOLUTIONS (One Answer Correct)

1. (a) $PH_3 \longrightarrow P + 3H$; $\Delta H_1 = e_{P-H} \times 3 = 76 \times 3 = 228$ kcal

$P_2H_4 \longrightarrow 2P + 4H$; $\Delta H_2 = e_{P-P} + 4\,e_{P-H}$

$= 51 + (76 \times 4) = 355$ kcal

$\Delta H_2 - \Delta H_1 = 355 - 228 = 127$ kcal mol^{-1}

2. (b) 6 Meq. of HCl will react with 6 Meq. of NaOH to give maximum heat of reaction.

3. (b) Meq. of NaOH = $100 \times 1 = 100$

Meq. of HCl = $300 \times 1 = 300$

$\therefore$ 100 Meq. of HCl will react with 100 Meq. of NaOH

1000 Meq. of each react to give 57.27 kJ

$\therefore$ 100 Meq. of each react to give 5.727 kJ

4. (b) 1 *M* HCl = 1*N* HCl, *i.e.*, $1 \times V$ Meq. gives heat = *X* kcal

$1\,M\,H_2SO_4 = 2\,N\,H_2SO_4$, *i.e.*, $2\times V$ Meq. gives heat $= Y$ kcal

Thus, $Y = 2X$ or $X = 0.5\,Y$

$Y - X = Y - 0.5\,Y = 0.5\,Y$

5. (a) No doubt more heat will be liberated in I reaction which will be used to heat mixture (400 mL). In II heat liberated will be 1/4 of I which will be used to heat mixture (1/4 of I, *i.e.*, 100 mL).

6. (c) Integral heat of dilution is the change in enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to other.

7. (b) Due to extensive hydration of F^- ion because of smallest size.

8. (b) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$; At equilibrium T is constant, *i.e.*, molar heat capacity at equilibrium is infinity.

9. (d) Rest all are endothermic.

10. (c) $\Delta H = \Delta U + \Delta nRT$

$\Delta n = -1$

Now, $\Delta H = \Delta U - 1\times 0.0821\times 300 = \Delta U - 24.62$

$-560 = \Delta U - 2.463$ ($\because$ 1 litre-atm = 1 kJ)

$\therefore \quad \Delta U = -557.54$ kJ

$\therefore$ Heat liberated at constant volume = 557.54 kJ

11. (a) $\Delta H = \Delta U + P\Delta V$

$P\Delta V = 76\times 13.6\times 981\times (18-19.6)$ erg

$= -1.62\times 10^6$ erg

$= \frac{-1.62\times 10^6}{4.18\times 10^7} = -0.039$ cal

$\therefore \quad \Delta U = 1440 + 0.039$ cal $\simeq \Delta H$

12. (d) Heat supplied to heat water $= ms\Delta T = 10^3\times 1\times 40$

$= 40\times 10^3$

$$\text{Calorific value} = \frac{\Delta H}{\text{Mass of fuel}} = \frac{40\times 10^3}{10} = 4000\,\text{cal}$$

13. (b) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$; At equilibrium T is constant, *i.e.*, $\partial T = 0$; thus, $C_p = \infty$.

14. (d) Standard molar heat enthalpy (H°) of a compound is equal to its standard heat of formation from most stable states of initial components.

15. (b) $2O_3 \xrightarrow{300\,K} 3O_2$; $\Delta H = -68$ kcal; $\Delta S = +$ve.

16. (a) Bond formation shows $\Delta H = -$ve also entropy in liquid state is lesser than gaseous state.

17. (b) By (i) – (ii) + (iii)

18. (b) Carbon in graphite form has $H^\circ = 0$.

19. (a) $2C + 3H_2 \rightarrow C_2H_6$; $\Delta H = q_2$

$2C + 2H_2 \rightarrow C_2H_4$; $\Delta H = q_1$

$C_2H_4 + H_2 \rightarrow C_2H_6$; $\Delta H = q_2 - q_1$

20. (b) $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$; $\Delta H = -46$ kJ

21. (c) e_{H-H} = heat of formation of H atom $\times 2$

$H_{2(g)} \rightarrow 2H$; e_{H-H}

$\frac{1}{2}H_2 \rightarrow H$; $\Delta_f H^\circ$ of H

22. (a) Meq. of NaOH = $20\times 0.5 = 10$

Meq. of HCl = $100\times 0.1 = 10$

$\therefore$ 10 Meq. (of HCl + NaOH) each reacts to give x kJ

$\therefore$ 1000 Meq. (of HCl + NaOH) each reacts to give $100\cdot x$ kJ

Heat of neutralisation = $-100x$

23. (b) $H_B > H_A$ Also $H_B - H_A = 24$

$H_C < H_B$ $H_B - H_C = 18$

$\therefore \quad H_B > H_C > H_A$

24. (a) $\Delta U = 1.23\times 10^3\times 6.12 = 7.5\times 10^3$ J $= -7.5$ kJ

Heat is given out and thus – 7.5 kJ.

25. (d) C is converted directly from solid to gas.

26. (a) $\Delta H = \Delta U + \Delta nRT$

$\Delta H - \Delta U = \Delta nRT$

$= -3\times 8.314\times 298 = -7432.7$ J $= -7.43$ kJ

27. (b) Thiol is RSH

28. (d) $\Delta H = \Delta U + \Delta nRT$; $\Delta n = -2$ in (d)

29. (d) 50 Meq. of KOH and 50 Meq. of H_2SO_4 will neutralise completely.

30. (b) Initial volume = a^3 cm^3

Final volume = $8a^3$ cm^3

$$\therefore \quad \Delta S = 2.303R\log\frac{V_2}{V_1}$$

$= 2.303\times 2\log 8$

$= 4.15$ cal/°

31. (b) $C_3H_8(l) \longrightarrow C_3H_8(g)$; $\Delta H_1 = +15$ kJ

$C_3H_8(g) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta H_2 = -2220$ kJ

$C_3H_8(l) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta H_3 = ?$

$\therefore \quad \Delta H_3 = \Delta H_1 + \Delta H_2 = 15 - 2220 = -2205$ kJ

Now, $\Delta H = \Delta U + \Delta nRT$

$-2205 = \Delta U + (-2)\times 8.314\times 300\times 10^{-3}$ ($\Delta n = 3 - 5 = -2$)

$\therefore \quad \Delta U = -2200$ kJ

32. (b) $-\Delta G^\circ = 2.303RT\log K$

$72800 = 2.303\times 8.314\times 2400\log K$

$K = 38.39$ at 2400 K

Also at $2.303\log\frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$2.303\log\frac{K_2}{38.39} = \frac{205000}{8.314}\times\left[\frac{2600-2400}{2600\times 2400}\right]$$

$$\frac{K_2}{38.39} = 2.20$$

$\therefore \quad K_2 = 84.46$

PREVIOUS YEARS PROBLEMS

1. ΔH_f° for $CO_{2(g)}$, $CO_{(g)}$ and $H_2O_{(g)}$ are –393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for given reaction is : **(IIT 2000)**

$CO_{2(g)} + H_{2(g)} \longrightarrow CO_{(g)} + H_2O_{(g)}$

(a) +524.1 (b) +41.2
(c) –262.5 (d) – 41.2

2. Which of the reaction defines $\Delta_f H^\circ$: **(IIT 2003)**

(a) $C_{(Diamond)} + O_2 \longrightarrow CO_{2(g)}$
(b) $1/2H_{2(g)} + 1/2F_{2(g)} \longrightarrow HF_{(g)}$
(c) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$
(d) $CO_{(g)} + 1/2O_{2(g)} \longrightarrow CO_{2(g)}$

3. For which reaction ΔH_r° is equal to ΔH_f°: **(IIT 2002)**

(a) $CH_{4(g)} + 2Cl_{2(g)} \longrightarrow CH_2Cl_{2(l)} + 2HCl_{(g)}$
(b) $Xe_{(g)} + 2F_{2(g)} \longrightarrow XeF_{4(g)}$
(c) $2CO + O_{2(g)} \longrightarrow 2CO_{2(g)}$
(d) $N_{2(g)} + O_{3(g)} \longrightarrow N_2O_{3(g)}$

4. $\Delta H_{vap} = 30$ kJ/mol and $\Delta S_{vap} = 75$ J $mol^{-1}K^{-1}$. Find temperature of vapour at one atmosphere: **(IIT 2004)**

(a) 400 K (b) 350 K
(c) 298 K (d) 250 K

5. The bond energy (in kcal mol^{-1}) of a C—C single bond is approximately : **(IIT 2010)**

(a) 1 (b) 10
(c) 100 (d) 1000

6. The species which by definition has zero standard molar enthalpy of formation at 298 K : **(IIT 2010)**

(a) $Br_2(g)$ (b) $Cl_2(g)$
(c) $H_2O(g)$ (d) $CH_4(g)$

7. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C≡C bond in C_2H_2. Given that the heat of formation of $C_2H_2 = 225$ kJ mol^{-1}. (take the bond energy of a C–H bond as 350 kJ mol^{-1}):

$2C(s) \longrightarrow 2C(g)$ $\Delta H = 1410$ kJ mol^{-1}
$H_2(g) \longrightarrow 2H(g)$ $\Delta H = 330$ kJ mol^{-1}

(IIT 2012)

(a) 1165 (b) 837
(c) 865 (d) 815

8. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are – 400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is : **[JEE (Advanced-I) 2013]**

(a) +2900 kJ (b) –2900 kJ
(c) –16.11 kJ (d) +16.11 kJ

9. For complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, $\Delta_C H$, for the reaction will be : **[JEE (Main) 2014]**

($R = 8.314$ kJ mol^{-1})

(a) –1366.95 kJ mol^{-1} (b) –1361.95 kJ mol^{-1}
(c) –1460.50 kJ mol^{-1} (d) –1350.50 kJ mol^{-1}

10. The heats of combustion of carbon and carbon monoxide are – 393.5 and – 283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[JEE (Main) 2016]**

(a) 676.5 (b) – 676.5
(c) – 110.5 (d) 110.5

11. Given :

$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$;
$\Delta_r H^\circ = -393.5$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$;

$\Delta_r H^\circ = -285.8$ kJ mol^{-1}

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$;
$\Delta_r H^\circ = +890.3$ kJ mol^{-1}

Based on the above thermochemical equations, the value of $\Delta_r H^\circ$ at 298 K for the reaction :

$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g)$ will be : **[JEE (Main) 2017]**

(a) + 74.8 kJ mol^{-1} (b) + 144.0 kJ mol^{-1}
(c) – 74.8 kJ mol^{-1} (d) – 144.0 kJ mol^{-1}

SOLUTIONS (Previous Year Problems)

1. (b) Given,

$C + O_2 \longrightarrow CO_2$; $\Delta H^\circ = -393.5$ kJ ...(1)

$C + 1/2O_2 \longrightarrow CO$; $\Delta H^\circ = -110.5$ kJ ...(2)

$H_2 + 1/2O_2 \longrightarrow H_2O$; $\Delta H^\circ = -241.8$ kJ ...(3)

By Eqs. (2) + (3) − (1) $CO_2 + H_2 \longrightarrow CO + H_2O$;

$\Delta H^\circ = +41.2$

2. (b) No doubt (a) and (b) both represents heat of formations but standard heat of formation $\Delta_f H^\circ$ for CO_2 will be formed from carbon graphite.

$C_{Graphite} + O_2 \longrightarrow CO_2$ as graphite is most stable form of carbon.

3. (b) It is based on definitions of heat of formation of $XeF_{4(g)}$.

4. (a) $\Delta H = \Delta S \cdot T$

$\therefore \quad T = \dfrac{\Delta H}{\Delta S} = \dfrac{30 \times 10^3}{75} = 400$ K

5. (c) e_{C-C} ranges between 85 to 150 kcal mol^{-1}.

6. (b) Standard molar enthalpy of elements in their most stable state is zero.

$H^\circ_{Br_2(l)} = 0$; $H^\circ_{Cl_2(g)} = 0$; $H^\circ_{I_2(s)} = 0$

7. (d) (i) $2C(s) + H_2(g) \longrightarrow H-C \equiv C-H(g)$, $\Delta H = 225$ kJ mol^{-1}

(ii) $2C(s) \longrightarrow 2C(g)$ $\Delta H = 1410$ kJ mol^{-1}

(iii) $H_2(g) \longrightarrow 2H(g)$ $\Delta H = 330$ kJ mol^{-1}

From equation (i) :

$225 = [2 \times \Delta H_{C(s) \to C(g)} + 1 \times e_{H-H}] - [2 \times e_{C-H} + 1 \times e_{C \equiv C}]$

$225 = [1410 + 1 \times 330] - [2 \times 350 + 1 \times e_{C \equiv C}]$

$225 = [1410 + 330] - [700 + e_{C \equiv C}]$

$225 = 1740 - 700 - e_{C \equiv C}$

$e_{C \equiv C} = 1040 - 225 = 815$ kJ mol^{-1}

$BE_{C \equiv C} = 815$ kJ mol^{-1}

8. (c) $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta_{f\,comb.C_6H_{12}O_6} H^\circ = 6\Delta_f H^\circ_{CO_2} + 6\Delta_f H^\circ_{H_2O(l)} - \Delta_f H^\circ_{C_6H_{12}O_{6(S)}}$

$= 6 \times (-400) + 6 \times (-300) - (-1300) = -2900$ kJ/mol

$\therefore$ Standard enthalpy of combustion per gram of glucose

$= \dfrac{-2900}{180} = -16.11$ kJ

9. (a) $\Delta_C H = \Delta_C U + \Delta n_{(g)} RT$

$\Delta_C U = -1364.47$ kJ mol^{-1}, $\Delta n_{(g)} = 2 - 3 - 1$

$\therefore \quad \Delta_C H = -1364.47 \times 10^3 + (-1) \times 8.314 \times 298$

$= -1364470 - 2477.57 = -1366.95$ J

$= -1366.95$ kJ mol^{-1}

The value of *R* given in question is wrong, it is 8.314 J mol^{-1}.

10. (c) Given,

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ kJ/mol ...(1)

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -283.5$ kJ/mol ...(2)

By eq. (1) − eq. (2)

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$;

$\Delta H = -393.5 + 283.5$ kJ/mol $= -110$ kJ/mol

Note : However choice (c) shows − 110.5 kJ/mol

11. (c)

$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\circ = -393.5$ kJ mol^{-1} ...(i)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta_r H^\circ = -285.8$ kJ mol^{-1} ...(ii)

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$; $\Delta_r H^\circ = 890.3$ kJ mol^{-1} ...(iii)

By (i) + 2 × (ii) + (iii), we get

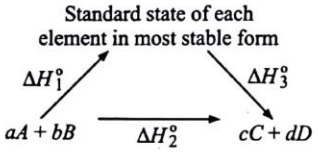
$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g)$; $\Delta_r H^\circ$

$\Delta_r H^\circ = -393.5 - 285.8 \times 2 + 890.3$

$= -74.8$ kJ mol^{-1}

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which of the following mixtures on neutralisation will show a same rise in temperature ?
   (a) 60 mL of 0.1 *M* HCl + 60 mL of 0.1 *M* NaOH
   (b) 30 mL of 0.1 *M* HCl + 30 mL of 0.1 *M* NaOH
   (c) 40 mL of 0.1 *M* HCl + 30 mL of 0.1 *M* NaOH
   (d) 60 mL of 0.1 *M* HCl + 100 mL of 0.1 *M* NaOH
2. If $\Delta_f H^\circ_{(C_2H_6)g} = -85$ kJ mol^{-1}, $\Delta H^\circ_{f(C_3H_8)g} = -104$ kJ mol^{-1}, ΔH° for $C_{(s)} \longrightarrow C_{(g)}$ is 718 kJ mol^{-1} and heat of formation of H-atom is 218 kJ mol^{-1}, then :
   (a) $e_{C-C} = 345$ kJ (b) $e_{C-H} = 414$ kJ
   (c) $e_{H-H} = 436$ kJ (d) $e_{H-H} = 218$ kJ
3. For which reaction $\Delta H < \Delta U$:
   (a) $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$
   (b) $NH_4Cl_{(s)} \rightleftharpoons NH_{3(v)} + HCl_{(v)}$
   (c) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
   (d) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
4. Melting of ice at –1°C shows :
   (a) $\Delta S = +$ ve (b) $\Delta H = +$ ve
   (c) $\Delta G = +$ ve (d) process is spontaneous
5. Select the correct statements :
   (a) All combustion reactions are exothermic
   (b) Heat of combustion are always exothermic
   (c) $N_2 + O_2 \longrightarrow 2NO$; $\Delta H = +$ ve
   (d) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O$; $\Delta H = +$ ve
6. Which of the following are incorrect ?



   (a) $\Delta H^\circ_1 = -aH^\circ_A - bH^\circ_B$
   (b) $\Delta H^\circ_2 = cH^\circ_C + dH^\circ_D$
   (c) $\Delta H^\circ_3 = cH^\circ_C + dH^\circ_D - aH^\circ_A - bH^\circ_B$
   (d) $\Delta H^\circ_3 = \Delta H^\circ_2 - \Delta H^\circ_1$
7. Which of the following reactions are exothermic ?
   (a) Rusting of iron (b) Burning of wax
   (c) Synthesis of NH_3 (d) Condensation of steam
8. Select the correct statements :
   (a) A good fuel has higher calorific value
   (b) Endothermic reactions always becomes faster as we approach absolute zero
   (c) Enthalpy of vaporisation increases from F_2 to I_2
   (d) Bond enthalpy of *X*—*X* bond has the order :
   F—F > Cl—Cl > Br—Br > I—I
9. Select the correct statements :
   (a) Bond energy of $e_{H-H} = 2 \times \Delta_f H$ of H-atom
   (b) The ratio of heat of vaporisation and the normal boiling point of a liquid is $\simeq 88$ J mol^{-1}
   (c) Heat of neutralisation for HF is – 16.4 kcal eq.$^{-1}$
   (d) Hess's law can be proved experimentally
10. Which of the following are endothermic reactions ?
   (a) Combustion of CH_4
   (b) Decomposition of H_2O
   (c) Dehydrogenation of ethane
   (d) Conversion of graphite to diamond

SOLUTIONS (More Than One Answer Correct)

1. (a,b)(a) Generates $\frac{60 \times 0.1 \times 13.7}{1000}$ kcal heat which is used by 120 mL solution.
   (b) Generates $\frac{30 \times 0.1 \times 13.7}{1000}$ kcal heat which is used by 60 mL solution.
2. (a,b,c) $\frac{1}{2}H_2 \longrightarrow H$; $\Delta H^\circ = 218$ kJ; Let e_{C-C} be *a* and e_{C-H} be *b* kJ.
   $\therefore$ $e_{H-H} = 436$ kJ
   $2C + 3H_2 \longrightarrow C_2H_6$; $\Delta_f H^\circ$
   Also, $\Delta_f H^\circ C_2H_6 = -[e_{C-C} + 6e_{C-H}] + [2C_{s\to g} + 3e_{H-H}]$
   $-85 = -[e_{C-C} + 6b] + [2 \times 718 + 3 \times 436]$ or $a + 6b = 2829$
   $3C + 4H_2 \longrightarrow C_3H_8$; ΔH°
   $\Delta_f H^\circ C_3H_8 = -[2e_{C-C} + 8e_{C-H}] + [3C_{s\to g} + 4e_{H-H}]$
   $-104 = -[2a + 8b] + [3 \times 718 + 4 \times 436]$ or $2a + 8b = 4002$
   $\therefore$ $a = 345$ kJ, $b = 414$ kJ
3. (c,d) $\Delta H = \Delta U + \Delta nRT$ if Δn is – ve, then $\Delta H < \Delta U$.
4. (a,b,c) ΔH and ΔS both increase on melting of ice.
5. (b,c,d) Only three combustions are endothermic. The third one is $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O$; $\Delta H = +$ ve.
6. (b,c) $\Delta H^\circ_1 = \Sigma H^\circ_{s.s} - \Sigma H^\circ_R$ and so on.
7. (a,b,c,d) All are exothermic.
8. (a,c) $e_{Cl-Cl} > e_{F-F}$
9. (a,b,c) $\frac{1}{2}H_2 \longrightarrow H$; $\Delta_f H$ $\therefore$ $e_{H-H} = 2 \times \Delta_f H$; Also, HF has higher ΔH neutralisation due to extensive hydration of F^- ions. Also, Hess's law has been proved theoretically. Trouton's rule $\frac{\Delta H_V}{T_b} \simeq 88$ J mol^{-1}
10. (b,c,d) Heat of combustion is always – ve.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Chemical reactions are usually exothermic or endothermic. A balanced thermochemical equation involving physical states of reactants and products expresses the chemical changes as well as heat of reaction. Heat changes are usually expressed in terms of ΔH (at constant P) or ΔU (at constant V). The heats of reactions varies with physical state of reactants and products, conditions of constant pressure or volume and temperature. Heats of combustion and heat of neutralization, heat of condensation are always exothermic. Standard heat enthalpy of a compound is its heat of formation at 1 atm P and 25°C.

[1] The heat energy released during neutralization of 1eq. of HF with 1 eq. of NaOH and with 1 eq. of CH_3COOH and 1 eq. of NaOH are respectively :
(a) −16.4 kcal, −12.0 kcal (b) −12.0 kcal, −10 kcal
(c) −13.7 kcal in both (d) −12.0 kcal, −16.4 kcal

[2] Heat of dissociation for H_2O in H^+ and OH^- ions is :
(a) −57.27 kJ/mol (b) +57.27 kJ/mol
(c) −50 kJ/mol (d) +50 kJ/mol

[3] In which case of mixing a strong acid and a base each of 1 N concentration, temperature rise is highest :
(a) 20 mL acid + 30 mL alkali
(b) 10 mL acid + 40 mL alkali
(c) 25 mL acid + 25 mL alkali
(d) 30 mL acid + 20 mL alkali

[4] Heat of combustion of CH_4, C_2H_4, C_2H_2 and C_2H_6 are $-890, -1411, -1300$ and -1560 kJ mol^{-1}. The best fuel is :
(a) CH_4 (b) C_2H_4
(c) C_2H_6 (d) C_2H_2

[5] The enthalpy of which form of carbon has been supposed to be zero at 25°C and 1 atm :
(a) Graphite (b) Diamond
(c) Coke (d) Charcoal

[6] Molar heat capacity of diamond carbon in equilibrium with graphite carbon at constant pressure is :
(a) zero (b) infinity
(c) 3.4 kJ/mol (d) −3.4 kJ/mol

Comprehension 2 : When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents. **(Expt-1).** Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (– 57.0 kJmol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment **(Expt-2),** 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0M NaOH (under identical conditions to **(Expt-1)**) where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 Jg^{-1}K^{-1} and density of all solutions as 1.0 g mL^{-1}) **[JEE (Advanced II) 2015]**

[1] Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt-2** is :
(a) 1.0 (b) 10.0
(c) 24.5 (d) 51.4

[2] The pH of the solution after **Expt-2 :**
(a) 2.8 (b) 4.7
(c) 5.0 (d) 7.0

SOLUTIONS

Comprehension 1

[1] (a) Heat released during neutralization of weak acid < -13.7. In HF, hydration of F^- ion is responsible for higher value.

[2] (b) $H^+ + OH^- \longrightarrow H_2O$; $\Delta H = -13.7 \times 4.18$ kJ

[3] (c) 25 Meq. of acid and 25 Meq. of alkali reacts to give $\frac{13.7 \times 25}{1000}$ kcal heat

[4] (a) Best fuel is CH_4 as its calorific value $= \frac{890}{16} = 55.63$ kJ

[5] (a) Graphite is the most stable form of carbon.

[6] (b) $C_p = \left[\frac{\Delta H}{\Delta T}\right]_p$. At equilibrium during phase transition $\Delta T = 0$

Comprehension 2

[1] (a)

	HCl	+ NaOH	⟶ NaCl	+ H_2O
m.mol before reaction	100	100	–	–
m.mol after reaction	–	–	100	100

Heat released by the reaction of 100 m.mol of HCl and NaOH each $= [200 \times 4.2 + C] \times 5.7$ ...(1)

Heat of neutralisation for 100 m. mol of NaOH and HCl each $= 57 \times 1000 \times \frac{100}{1000}$ ...(2)

By (1) and (2)

$\therefore \quad 57 \times 1000 \times \frac{100}{1000} = [200 \times 4.2 + C] \times 5.7$ ...(3)

Similarly for the neutralisation of 100 m.mol of NaOH and CH_3COOH each is given by

CH_3COOH	+ NaOH	⟶ CH_3COONa	+ H_2O
200	100	–	–
100	–	100	–

$\Rightarrow |\Delta H| \times 1000 \times \frac{100}{1000} = [200 \times 4.2 + C] \times 5.6$ ...(4)

By eq. (3) eq. (4)

$|\Delta H| = 56$ kJ/mol

$\Delta H_{\text{neutralisation}} = -56$ kJ/mol

$-56 = -57 + \Delta H_{IE}$

$\Delta H_{IE} = 1$ kJ/mol

[2] (b) Solution is buffer which cantains 100 m.mol of CH_3COOH and 100 m.mol of CH_3COONa

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= -\log(2 \times 10^{-5}) + \log \frac{100/1000}{100/1000}$$

$$= 5 - \log 2$$

$$= 4.7$$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E) is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. **S :** Heat of neutralization for HF is – 68.552 kJ/eq. where as for HCl it is –57.26 kJ/eq.
   E : The acid HF is weak acid.
2. **S :** In a diatomic molecule involving two like atoms covalently bonded with each other, bond energy = 2 × heat of formation of atom.
   E : $H_2 \longrightarrow 2H; e_{H-H} = \Delta H$.
3. **S :** Bond energy for breaking up a bond is endothermic.
   E : Heat is required to overpower the attractions between two atoms.
4. **S :** $C + \frac{1}{2}O_2 \longrightarrow CO;$ $\Delta H = -26.0$ kcal

   $CO + \frac{1}{2}O_2 \longrightarrow CO_2;$ $\Delta H = -68.3$ kcal

   $\therefore \quad C + O_2 \longrightarrow CO_2;$ $\Delta H = -94.3$ kcal

   E : This is an experimental proof of Hess's law.
5. **S :** Heat of combustion are always exothermic.
   E : Combustion of N_2 to give NO is exothermic.
6. **S :** Combustion of N_2 to give NO is endothermic.
   E : Bond energy of N_2 is very high.
7. **S :** The ratio of heat of vaporisation and the normal boiling point of a liquid is approximately 88 J/mol.
   E : This is Trouton's rule derived by experimental data.
8. **S :** Standard heat enthalpy of a compound is its heat of formation at 25°C and 1 atm.
   E : Standard heat enthalpy of pure elements have arbitrarily assumed to be zero.
9. **S :** The variation of heat of reaction with temperature are given in terms of Kirchhoff's equation.
   E : The Kirchhoff's equation is : $\Delta H = \Delta U + \Delta nRT$.
10. **S :** Heat of neutralization can be given as :
    $H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.6$ kcal
    E : Heat of neutralization can be alternatively defined as heat of formation of water.
11. **S :** The dissolution of NaCl in water is endothermic, though it is spontaneous process.
    E : ΔG for the process is –ve because ΔH_{sol} is very low and thus $T\Delta S > \Delta H$.
12. **S :** Heat of combustion of C_2H_6 is –341.1 kcal mol^{-1} and heat of combustion of C_2H_2 is –310 kcal mol^{-1} but C_2H_2 is better fuel.
    E : The better fuel has high calorific value.

ANSWERS (Statement Explanation Problems)

1. (d) No doubt HF is weak acid but the higher values are due to extensive hydration of F^- ion being smallest anion (only H^- is smaller than F^-)
2. (c) Heat of formation of H atom = $\Delta H = \frac{e_{H-H}}{2}$.
3. (c) Explanation is correct reason for statement.
4. (a) This is an application of Hess's law and not an experimental proof. Hess's law has been verified theoretically.
5. (a) $\frac{1}{2}N_2 + \frac{1}{2}O_2 \longrightarrow NO$; ΔH = + ve. It is due to high bond energy of N_2. Note this equation does not represent heat of combustion of N_2 (Partial combustion).
6. (c) Explanation is correct reason for statement.
7. (c) This is Trouton's rules derived from exp. data.
8. (c) Explanation is correct reason for statement.
9. (a) Kirchhoff's equation is $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$.
10. (a) Heat of formation of water is $H_2 + 1/2O_2 \longrightarrow H_2O$; ΔH_{for}.
11. (c) Explanation is correct reason for statement.
12. (c) Calorific value is defined as the heat given out by burning 1 g fuel.

    Calorific value for $C_2H_6 = \frac{-341.1}{30} = -11.37$ kcal/g

    Calorific value for $C_2H_2 = \frac{-310}{26} = -11.92$ kcal/g

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

	List A	List B
A.	$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$	(a) $\Delta H = -13.7$ kcal
B.	$H^+ + OH^- \rightarrow H_2O$	(b) $\Delta H > -13.7$ kcal
C.	$HF + NaOH \rightarrow NaF + H_2O$	(c) $\Delta H < -13.7$ kcal

2.

	List A	List B
A.	$2P_W + 5O_2 \rightarrow P_2O_5$	(a) $\Delta_f H$ of P_2O_5
B.	$2P_G + 5O_2 \rightarrow P_2O_5$	(b) $\Delta_f H^\circ$ of P_2O_5
C.	$C_A + O_{2(g)} \rightarrow CO_{2(g)}$	(c) $\Delta_f H^\circ$ of CO_2
D.	$C_G + O_{2(g)} \rightarrow CO_{2(g)}$	(d) $\Delta_f H$ of CO_2

3.

	List A	List B
A.	$O_{2(g)} \rightarrow O_{2(l)}$	(a) $\Delta_r H^\circ = \Delta_{cond} H^\circ$
B.	$Br_{2(l)} \rightarrow Br_{2(g)}$	(b) $\Delta_r H^\circ = \Delta_v H^\circ$
C.	$I_{2(s)} \rightarrow I_{2(l)}$	(c) $\Delta_r H^\circ = \Delta_s H^\circ$
D.	$H_2O_{(s)} \rightarrow H_2O_{(v)}$	(d) $\Delta_r H = \Delta_s H$

4.

	List A	List B
A.	$H_2 \rightarrow 2H$	(a) $\Delta H = \Delta_f$H of H×2
B.	$CH_4 \rightarrow C + 4H$	(b) ΔH = Average bond energy ×4
C.	$C_2H_2 + 2H_2 \rightarrow C_2H_6$	(c) $\Delta H = -e_{C\equiv C} - 4e_{C-H} + 2e_{H-H} + e_{C-C}$
D.	$C_2H_4 + H_2 \rightarrow C_2H_6$	(d) $\Delta H = -e_{C=C} - e_{H-H} + e_{C-H} + e_{C-C}$

Type II : More Than One Match Are Possible

5.

	List A	List B
(A)	$C_6H_{12}O_6 + (aq) \rightleftharpoons C_6H_{12}O_6(aq)$	(i) Exothermic
(B)	$CaO + (aq) \rightleftharpoons Ca(OH)(aq)$	(ii) Endothermic
(C)	$C + O_2 \rightarrow CO_2$; at 298 K	(iii) ΔH is heat of reaction
(D)	$C_{graphite} + O_2 \rightarrow CO_2$; $\Delta H_{298\,K}$ at 298 K	(iv) ΔH is heat of formation of CO_2
		(v) ΔH is standard heat of formation of CO_2
		(vi) ΔH is standard heat enthalpy of CO_2

6.

	List A	List B
(A)	$\Delta_f H^\circ(O_2, g)$	(i) Zero
(B)	$\Delta_f H^\circ(S_R)$	(ii) Not equal to zero
(C)	$\Delta_f H^\circ(S_M)$	(iii) Most stable form
(D)	$\Delta_f H^\circ(P_{white})$	(iv) Less stable form
(E)	$\Delta_f H^\circ(P_{black})$	

7.

	List A	List B
(A)	$CO_2(s) \longrightarrow CO_2(g)$	(p) Phase transition
(B)	$CaCO_3(s) \longrightarrow CaO(s) + CO(g)$	(q) Allotropic change
(C)	$2H \longrightarrow H_2(g)$	(r) $\Delta H = +ve$
(D)	$P_{(White, solid)} \longrightarrow P_{(red, solid)}$	(s) $\Delta S = +ve$
		(t) $\Delta S = -ve$

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8.

	List A	List B
(A)	$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	(p) Standard enthalpy of $CO_2(g)$
(B)	$C_{graphite} + O_2(g) \rightarrow CO_2(g)$	(q) Enthalpy of reaction
(C)	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	(r) Enthalpy of combustion of CO(g)
(D)	$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	(s) Standard enthalpy of $H_2O(l)$

ANSWERS

1. A – c; B – a; C – b
2. A – b; B – a; C – d; D – c
3. A – a; B – b; C – c; D – d
4. A – a; B – b; C – c; D – d
5. A – ii, iii; B – i, iii; C – i, iii, iv; D – i, iii, v, vi
6. A – i, iii; B – i, iii; C – ii, iv; D – i, iv; e – ii, iii
7. A –p,r,s; B –r,s; C – t; D – p,q,r
8. A – q,r; B – p,q; C – q,s; D – q

17 Crystallography

The solid state : The physical state of matter in which the constituent molecules, atoms or ions have no translatory motion although they vibrate about the fixed position, that they occupy in a crystal lattice.

A solid is said to possess cohesion forces, remaining in the same shape unless changed by certain forces. Solids are of two types:

1. Crystalline solids : A crystalline solid has a definite melting point at which it becomes liquid, bounded by well defined plane faces, having same geometry irrespective of the source from which they have been obtained.

2. Amorphous solids : Amorphous solids have no precise melting point but when heated, become increasingly pliable until they assume the properties usually associated with liquids; they are super-cooled liquids in which the force of attraction holding the molecules together is so great that the material is rigid but there is **no regularity of structure.**

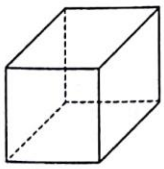
Crystal : A crystalline solid consists of a large number of unit cells, called crystal, each of which possess a definite geometric shape bounded by plane faces. The crystals of a given substance produced under a definite set of conditions are always of the same shape. On the change of condition, one crystalline form of a given substance may change into another altogether different crystalline form.

External features of crystals : The salient external features of crystals are given below :

1. Faces : Crystals are bounded by a number of surfaces which are generally perfect, flat. These are known as faces. Faces are of two types:

Like : All faces are alike, *e.g.*, Fluorspar.

Unlike : All faces are not alike, *e.g.*, Galena.



Fluorspar
Fig.1



Galena
Fig.2

2. Form : All the faces corresponding to a crystal are said to constitute a form.

3. Edges and interfacial angle : An edge is formed by the intersection of two adjacent faces where the angle between any two faces of crystal is known as interfacial angle.

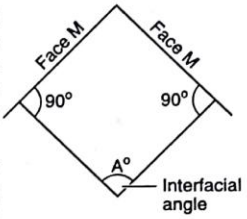


Fig. 3

The crystals are bounded by plane faces (F), straight edges (e) and interfacial angle (c). The relationship between these can be given as,

$$F + c = e + 2$$

4. Zone and zone axis : The faces of a crystal occur in sets called zones, which meet in parallel edges or would do so if the planes of the faces were extended. Each zone forms a complete belt around the crystal.

A line drawn through the centre of a crystal in a direction parallel to the edge of a zone is called the zone axis.

Elements of symmetry in crystals

(a) Plane of symmetry : A crystal is said to have a plane of symmetry when an imaginary plane passing through the centre of crystal can divide it into two parts such that one is the exact mirror image of the other.

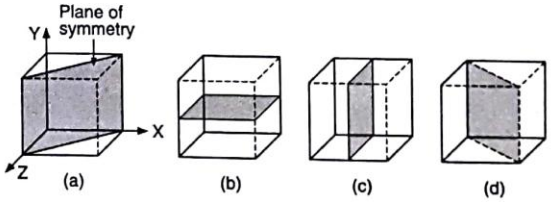
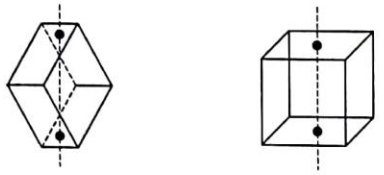


Fig. 4 Plane of symmetry

(b) Axis of symmetry : It is a line about which the crystal may be rotated so that it represents the same appearance more than once during a complete revolution. If the equivalent configuration occurs twice, thrice, four and six times, *i.e.*, after rotation of 180°, 120°, 90° and 60°, the axis of rotation are

known as two-fold (diad), three-fold (triad), four-fold (tetrad) and six-fold (hexad), axes of symmetry respectively.



(a) (b)

Fig. 5 Axes of symmetry

(c) Centre of symmetry : It is a point when any line drawn through it meets the surface of the crystal at equal distances on either side. A crystal may possess a number of planes or axes of symmetry but it can have only one centre of symmetry.



(a) (b)

Fig. 6 Centre of symmetry

The total number of planes, axes and centres of symmetry possessed by a crystal is termed as elements of symmetry. A **cubic crystal possess a total of 23 elements of symmetry.**

Plane of symmetry $= 3 + 6 = 9$

Axis of symmetry $= 3 + 4 + 6 = 13$

Centre of symmetry $= 1$

$\therefore$ Total elements of symmetry $= 9 + 13 + 1 = \mathbf{23}$

Unit Cell : For every crystal lattice, it is possible to select a group of lattice points which sets the pattern for a whole lattice. This three dimensional group of points is called unit cell of a crystal and is characterised by the distances a, b and c and angles α, β and γ. The whole crystal can be developed by a step wise shifting of the unit cells in all the three dimensions. In simple cubic there is only one atom, in body-centred cubic (bcc) there are two atoms and in face-centred cubic (fcc) there are four atoms. The array of points showing how molecules, atoms or ions are arranged in different sites in three dimensional space is referred as **space** lattice.

In various unit cells, there are three kinds of **lattice points :** Points located at the corners; points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corners and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell :

(i) A point that lies at the corner of unit cell is shared among eight unit cells and thus, it contributes for 1/8 of each such point to unit cell.

(ii) A point along an edge is shared by four unit cells and thus contribute for 1/4 of each such point to unit cell.

(iii) A face-centred point is shared by two unit cells and thus contributes for 1/2 of each such point to unit cell.

(iv) A body-centred point lies entirely within the unit cell and thus contributes for one each such point to unit cell.

Note : (a) The simple cubic unit cell has 8 atoms at eight corners. Each atom is shared by 8 unit cells.

$$\therefore \quad n = 8 \times \frac{1}{8} = 1$$

(b) The body centred cubic cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore \quad n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

(c) The face centred cubic unit cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore \quad n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

The coordination number : The number of nearest neighbours for any particular atom in a space lattice is called the coordination number. In diamond the coordination number is 4. In simple cubic crystal like NaCl it is 6. In bcc crystal like CsCl it is 8. Here Cs^+ is at the body-centre of a cube of Cl^- and Cl^- at the body-centre of cube of Cs^+. In cubic close packed and hexagonal close packed, the coordination number is 12.

The ratio of the radius of cation and anions (r^+ / r^-) : The coordination number of an ion in closed packed structures depends on the ratio of the radius of ion with respect to the radius of the ions surrounding it. In case of ionic solids, the radius ratio [r^+ / r^-] is the ratio of the cation to anion radius.

Minimum ionic radius ratio	Geometry	Coordination number
0.225 to 0.414	tetrahedral	4
0.414 to 0.732	octahedral	6
0.732 to above	cubic	8

Usually cations are smaller than anions and hence the cations usually fill the voids and anions surrounds them.

Crystal systems : The different possible geometrical shape of crystal lattice (or crystals) are called crystal systems.

On the basis of above facts and laws there are 230 crystal forms which are grouped on the basis of their symmetry into 32 classes. The 32 classes are then broadly referred to seven crystal systems (Fig. 7) given below in Table 1.

Table-1. Seven Crystal Systems

System	Axial distance	Axial angles	Maximum symmetry elements	*Examples*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Nine planes, thirteen axes	NaCl, KCl, CaF_2, ZnS, *diamond, alums*
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Five planes, five axes	TiO_2, ZnO_2, SnO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Three planes, three axes	Rhombic Sulphur, $BaSO_4$, KNO_3
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	One plane, one axis	$Na_2SO_4 \cdot 10H_2O$, $CaSO_4 \cdot 2H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, *monoclinic sulphur*
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Seven planes, seven axes	Mg, PbI_2, CdS, ZnO, HgS, *Graphite*
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	—do—	Calcite, $NaNO_3$, ICl
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	No plane, no axis	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, H_3BO_3

Cubic crystals have three patterns of Bravais lattice in which crystals are formed:

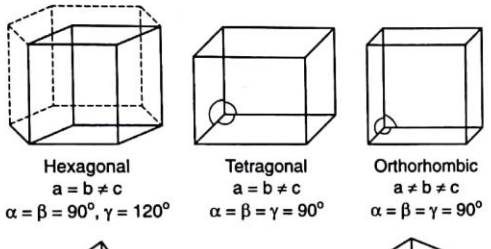


Fig. 7

(i) Simple cubic in which one atom (ion) is at the corner of a cube Fig. 8(a).

(ii) Face-centred cubic (fcc) in which the atoms are not only at the corner of the cube but there are atoms in the face of the cube also. Fig. 8 (b).

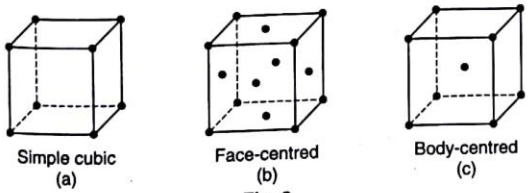


Fig. 8

(iii) Body-centred cubic (bcc) in which one atom is placed at the centre which is not shared by any other cube. *Fig. 8 (c).*

One can think of the atoms (ions) as spheres which are arranged in two different ways:

(i) Cubic close packing (ccp) Fig. 9 (a), (ii) Hexagonal close packing (hcp) Fig. 9 (b), (iii) Body-centred cubic packing (bccp) Fig. 9 (c).

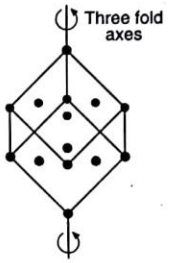


Fig. 9 (a) Cubic close packing

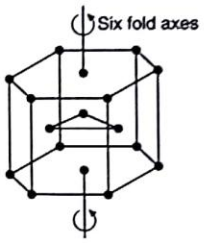


Fig. 9 (b) Hexagonal close packing

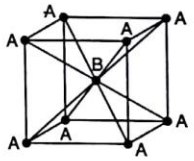


Fig. 9 (c) Body-centred close packing

Some Applications of Crystallographic Studies:

(i) Density of crystalline solids :

$$\text{Density of the unit cell} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell } (V)} \quad \ldots(1)$$

Also, Mass of the unit cell

$$= \text{No. of atoms in unit cell } (n) \times \text{Mass of each atom}$$

$$= \text{No. of atoms in unit cell } (n) \times \frac{\text{Atomic mass}}{\text{Av. No.}} \quad \ldots(2)$$

$\therefore$ By Eqs. (1) and (2),

$$\text{Density of unit cell} = \frac{n \times \text{atomic mass}}{\text{Av. no.} \times V} = \frac{n \times \text{atomic mass}}{\text{Av. no.} \times a^3} \quad \ldots(3)$$

Where volume of cubic unit cell = a^3 and a is edge length of unit cell.

(ii) Radii of the ion : If the edge length of the cubic cell is known, ionic radii for the ion in the crystal lattice can be calculated.

Where a is edge length of cubic cell.

Thus, radius of B^-

$$= \frac{\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2}}{2} = \frac{a}{2\sqrt{2}}$$

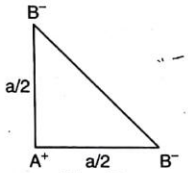


Fig. 10

(iii) Radii of metal atoms : If a is the length of unit cell, then

(a) For simple cubic lattice : Radius of metal atom = $\frac{a}{2}$

(b) For bcc lattice : Radius of metal atom = $\frac{\sqrt{3}a}{4}$

(c) For fcc lattice : Radius of metal atom = $\frac{a}{2\sqrt{2}}$

(iv) Packing density :

$$\text{Packing density} = \frac{\text{Volume of atom in unit cell}}{\text{Volume of unit cell}}$$

(a) In sc structure : Packing density = 0.52

(b) In fcc structure : Packing density = 0.74

(c) In bcc structure : Packing density = 0.68

The Bragg's equation : The diffraction pattern obtained during X-ray diffraction resulting from the scattering of X-rays by a regular arrangement of atoms or ions has been interpreted in terms of Bragg's equation :

$$n\lambda = 2d \sin\theta \quad \ldots(1)$$

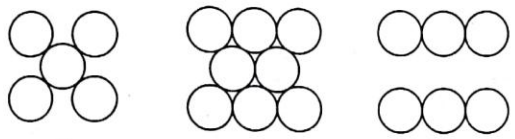
(Bragg's equation)

where n is an integer (1, 2, 3, ...); λ is the wavelength of X-rays used, d is the distance of separation between the planes of atoms, θ is the angle at which constructive interference occurs.

It is evident from Bragg's equation, if $2d < n\lambda$ then $\sin\theta > 1$ which is not possible.

• NUMERICAL PROBLEMS •

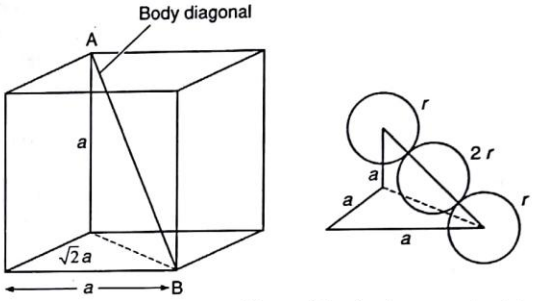
1. Calculate the number (n) of atoms contained within (a) cubic cell (b) a body-centred cubic cell (c) a face-centred cubic cell.
2. The figures given below show the location of atoms is three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **(IIT 2000)**



(i) (ii) (iii)

Fig. 11

3. A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound?
4. A solid made up of A and B atoms has atoms A in ccp arrangement. Atoms of B occupy all the octahedral voids and half the tetrahedral voids. Suggest the formula of compound.
5. In an ionic oxide, oxide ions are arranged in hcp array and positive ion occupy two thirds of octahedral void. Suggest the formula assuming metal as M.
6. In a close packed structure of mixed oxides, the lattice is composed of oxide ions, one eighth of tetrahedral voids are occupied by divalent cations while one half of octahedral voids are occupied by trivalent cations. What is the formula of the oxide?
7. In a crystal of an ionic compound, the anions B form a close packed lattice and the cations A occupy one half of the tetrahedral voids. What is the formula of the compound?
8. In a crystal of an ionic compound the ions B form the close packed lattice and the ions A occupy all the tetrahedral voids. What is the formula of the compound?
9. Calculate the coordination number of an atom is :
   (a) A premitive cubic unit cell
   (b) A bcc unit cell
   (c) A fcc unit cell
10. A closed packed structure of uniform spheres has the cell edge = 0.8 mm. Calculate the radius of molecule if it has:
    (a) single cubic lattice
    (b) bcc lattice
    (c) fcc lattice
11. Sodium metal crystallizes in a body-centred cubic lattice with the cell edge $a = 4.29$ Å. What is the radius of sodium atom? **(IIT 1994)**
12. The length of the unit cell edge of a body-centred cubic metal crystal is 352 pm. Calculate the radius of an atom of the metal.



13. Chromium metal crystallizes with a body-centred cubic lattice. The length of the unit cell edge is found to be 287pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3? **(IIT July 1997)**
14. At room temperature, sodium crystallizes in a body-centred cubic lattice with $a = 4.24$ Å. Calculate theoretical density of sodium (Atomic mass of Na = 23).
15. Lithium borohydride crystallizes in an orthorhombic system with 4 molecule per unit cell. The unit cell dimensions are $a = 6.8$ Å, $b = 4.4$ Å and $c = 7.2$ Å. If the molar mass is 21.76, calculate the density of crystal.
16. An ionic compound AB has a rock salt structure with $A:B = 1:1$. The formula mass of AB is $6.023y$ amu and the closest $A - B$ distance is $y^{1/2}$ nm.
    (a) Calculate the density of lattice.
    (b) If the observed density of lattice is found to be 20 kg m^{-3}, then predict the type of defect. **(IIT 2004)**
17. A compound CuCl has face-centred cubic structure. Its density is 3.4 g cm^{-3}. What is the length of unit cell?
18. A fcc element (atomic mass = 60) has a cell edge of 400 pm. What is its density?
19. A metal crystallizes into two cubic phases, face-centred cubic (fcc) and body-centred cubic (bcc) whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of fcc and bcc. **(IIT 1999)**
20. The density of KCl is 1.9893 g cm^{-3} and the length of a side unit cell is 6.29082 Å as determined by X-ray diffraction. Calculate the value of Avogadro's number.
21. The edge length of unit cell of a metal having molar mass 75 g mol^{-1} is 5 Å which crystallizes in cubic lattice. If

the density is 2 g/cm^3, calculate the radius of metal atom ($N_A = 6 \times 10^{23}$). **(IIT 2006)**

22. The density of solid argon is 1.65 g/mL at –233°C. If the argon atom is assumed to be sphere of radius 1.54×10^{-8} cm, what percentage of solid argon is apparently empty space? (Atomic mass of Ar = 40)
23. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? **(IIT May 1997)**
24. The unit cell edge length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.
25. If the radius of the octahedral void is r and radius of the atom in close packing is R, derive relation between r and R.
26. An element crystallizes in fcc lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure. **(IIT 2005)**
27. A solid compound AB has NaCl structure. If the radius of the cation is 100 pm (picometer) what is the radius of cation B ? 1 pm = 10^{-12} m.
28. In a compound AB, the ionic radii of A^+ and B^- are 88 pm and 200 pm respectively. What is the coordination number of A^+?
29. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of element.
30. Calculate the concentration of cation vacancies if NaCl is doped with 10^{-3} mole % of $SrCl_2$.
31. In the cubic crystal of CsCl ($d = 3.97$ g cm^{-3}) the eight corners are occupied by Cl^- with a Cs^+ at the centre and *vice-versa*. Calculate the distance between the neighbouring Cs^+ and Cl^- ions. What is the radius ratio of the two ions? [Atomic mass of Cs = 132.91 and Cl = 35.45]
32. You are given marbles of diameter 10 mm. They are to be placed such their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangement of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area. **(IIT 2003)**
33. Calculate the wavelength of X-rays which produces a diffraction angle 2θ equal to 16.80° for a crystal. Assume first order diffraction with interparticle distance in crystal of 0.2 nm.
34. The angle of diffraction 2θ for a first order nature was found to be 27°8′ using X-rays of wavelength 2.29 Å. Calculate the distance between two diffracted planes.
35. In diamond lattice, all lattice points and alternate tetrahedral voids are occupied by the carbon atoms. If diamond crystallizes in fcc form with edge length 'a', find out the:
    (a) number of next nearest neighbours in diamond lattice
    (b) distance between the next nearest neighbours.
36. A metallic element crystallises into a lattice containing a sequence of layers of $AB\ AB\ AB$. Any packing of spheres leaves out voids in the lattice. Calculate?
    (a) Coordination number.
    (b) Packing fraction and % by volume of this empty lattice space. **(IIT 1996)**
    (c) Base area of unit cell.
    (d) Volume of unit cell.

SOLUTIONS (Numerical Problems)

1. (a) The cubic unit cell has 8 atoms at eight corners. Each atom is shared by 8 unit cells.

$$\therefore \quad n = 8\times\frac{1}{8} = 1$$

(b) The body-centred cubic cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore \quad n = \left(8\times\frac{1}{8}\right)+1 = 2$$

(c) The face-centred cubic unit cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore \quad n = 8\times\frac{1}{8}+\left(6\times\frac{1}{2}\right) = 4$$

2. (i) Face plane
(ii) Face diagonal plane
(iii) Diagonal plane.

3. A atoms are at eight corners of the cube.

Therefore, the number of A atoms in the unit cell $= \frac{8}{8} = 1$

B atoms are at the face-centre of six faces

Therefore, its share in the unit cell $= \frac{6}{2} = 3$

The formula is $\boldsymbol{AB_3}$.

4. **For ccp or hcp array of A :**
No. of octahedral voids for each atom of $A = 1$
No. of tetrahedral voids for each atom of $A = 2$
Since, B occupy all the octahedral voids and half of the tetrahedral voids, thus one atom of B for octahedral void and one atom of B for tetrahedral void for each A atom is involved or the formula will be $\boldsymbol{AB_2}$.

5. **For ccp or hcp array of oxide ion :**
No. of octahedral voids for each oxide ion = 1
Since $\frac{2}{3}$ of octahedral voids are occupied by metal ion
Thus each oxide ion has $\frac{2}{3}$ metal ion or whole number ratio of oxide and metal ion is $1 : \frac{2}{3}$ or $3 : 2$. Thus formula is $\boldsymbol{M_3O_2}$.

6. Number of oxide ions (O) per unit cell = 1
Number of tetrahedral voids per ion in lattice = 2
Number of divalent cation $(A) = \frac{1}{8}\times 2 = \frac{1}{4}$
Number of octahedral voids per ion in lattice = 1
Number of trivalent cations $(B) = 1\times\frac{1}{2} = \frac{1}{2}$
Formula $= A_{1/4}B_{1/2}O = \boldsymbol{AB_2O_4}$

7. In a close packed array of B ion the number of tetrahedral voids per ion of B is **two.** Since, half of the tetrahedral voids is occupied by the cations A the number of cations is the same as that of the anion in the crystal and the formula of the compound is $\boldsymbol{AB}$.

8. In closed packed array of B ion the number of tetrahedral voids per ion of B is two. Since, tetrahedral voids are occupied by A ions, there are two A ions per B ion in the crystal. Therefore, the formula of the compound is $\boldsymbol{A_2B}$.

9. (a) In a primitive cubic unit cell, each atom has 6 equally spaced nearest neighbour atoms. Thus, coordination number = **6.**
(b) Considering the atom in the centre of the bcc unit cell, we find that it is surrounded by 8 nearest neighbour atoms situated at the corners of the cube. Thus, coordination number = **8.**
(c) Coordination number for a face-centred atom in an fcc unit cell is, evidently, equal to **12.**

10. (a) $r = \frac{a}{2} = \frac{0.8}{2} = \mathbf{0.4\ mm}$

(b) $r = \frac{\sqrt{3}\,a}{4} = \frac{0.8\times\sqrt{3}}{4} = \mathbf{0.3464\ mm}$

(c) $r = \frac{a}{2\sqrt{2}} = \frac{0.8}{2\sqrt{2}} = \mathbf{0.2828\ mm}$

11. Radius of Na (if bcc lattice) $= \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}\times 4.29}{4} = \mathbf{1.8574\ Å}$

12. In a bcc unit cell, the atoms touch each other along the body diagonal. So, if the radius of the atom is r, then

Body diagonal $= r+2r+r = 4r$

From the geometry of a cube

Body diagonal $= \sqrt{3}\times$ edge length $= \sqrt{3}\,a$

Then, $4r = \sqrt{3}\times a$ or radius of metal atom $= \frac{\sqrt{3}}{4}\times a$

$$r = \frac{\sqrt{3}}{4}\times a = \frac{\sqrt{3}}{4}\times 352 = \mathbf{152.4\ pm}$$

13. For bcc lattice $r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4}\times 287 = \mathbf{124.27\ pm}$

Now, $\text{Density} = \frac{n\times\text{atomic mass}}{V\times\text{Av. no.}} = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. no.}}$

$n = 2$ for bcc; $a = 287\times10^{-10}$ cm

$$\therefore \quad D = \frac{2\times 51.99}{(287\times10^{-10})^3\times 6.023\times10^{23}} = \mathbf{7.30\ g/mL}$$

14. A body-centred cubic unit cell contains 8 atoms at the 8 corners and one in the centre

$\because$ Total number of atoms per unit cell $= 8\times\frac{1}{8}+1 = 2$

$$\therefore \text{Density} = \frac{n\times\text{atomic mass}}{\text{Av. no.}\times a^3}$$

$$= \frac{2\times 23}{6.023\times10^{23}\times(4.24\times10^{-8})^3}$$

$$= \mathbf{1.002\ g\ cm^{-3}}$$

15. $\because \quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}}$

$n = 4$, $M = 21.76\,\text{g mol}^{-1}$,

Av. no. $= 6.023\times10^{23}$ and $V = a\times b\times c$

$\therefore \quad V = 6.8\times10^{-8}\times4.4\times10^{-8}\times7.2\times10^{-8}$

$= 2.154\times10^{-22}\,\text{cm}^3$

$\therefore$ Density $= \dfrac{4\times21.76}{2.154\times10^{-22}\times6.023\times10^{23}} = \mathbf{0.6709\ g\ cm^{-3}}$

16. (a) AB has rock salt ($A:B = 1:1$) structure, *i.e.*, fcc structure ($n = 4$) and formula mass of BB is 6.023 y g having closest distance $A-B$ $y^{1/3}$ nm. Therefore edge length of unit cell

$$a = 2(A^+ + B^-) = 2\times y^{1/3}\times10^{-9}\ \text{m}$$

$$\therefore \text{Density of } AB = \frac{n\times\text{ molar mass}}{\text{Av. no.}\times V} = \frac{n\times\text{molar mass}}{6.023\times10^{23}\times a^3}$$

$$= \frac{4\times6.023\times y\times10^{-3}}{6.023\times10^{23}\times(2y^{1/3}\times10^{-9})^3}$$

(molar mass in kg mol^{-1})

$$= \mathbf{5.0\ kg\ m^{-3}}$$

(b) The observed density of AB is 20 kg m^{-3} which is higher than calculated density 5.0 kg m^{-3} and thus AB has either interstitial impurity defect or substitutional impurity defect.

17. Molecular mass of CuCl = 99

$n = 4$ for face-centred cubic cell

$$\because \quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}} = \frac{4\times99}{a^3\times6.023\times10^{23}}$$

or $$3.4 = \frac{4\times99}{a^3\times6.023\times10^{23}}$$

$$\therefore \quad a = 5.783\times10^{-8}\,\text{cm} = \mathbf{5.783\ Å}$$

18. $\because$ $\text{Density} = \dfrac{n\times\text{atomic mass}}{V\times\text{Av. no.}} = \dfrac{n\times\text{atomic mass}}{a^3\times\text{Av. no.}}$

Given, Atomic mass = 60,

$$a = 4\times10^2\,\text{pm} = 4\times10^2\times10^{-12}\ \text{m}$$

$$= 4\times10^{-10}\times10^2\,\text{cm} = 4\times10^{-8}\ \text{cm}$$

($\because$ 1 pm $= 10^{-12}$ m)

Also, $n = 4$ for face-centred cubic lattice

$$\therefore \quad \text{Density} = \frac{4\times60}{(4\times10^{-8})^3\times6.023\times10^{23}} = \mathbf{6.23\ g\ cm^{-3}}$$

19. fcc unit cell length = 3.5 Å

bcc unit cell length = 3.0 Å

$$\text{Density in fcc} = \frac{n_1\times\text{atomic mass}}{V_1\times\text{Av. no.}}$$

$$\text{Density in bcc} = \frac{n_2\times\text{atomic mass}}{V_2\times\text{Av. no.}}$$

$$\frac{D_{\text{fcc}}}{D_{\text{bcc}}} = \frac{n_1}{n_2}\times\frac{V_2}{V_1}$$

Now, n_1 for fcc = 4; Also, $V_1 = a^3 = (3.5\times10^{-8})^3$

n_2 for bcc = 2; Also, $V_2 = a^3 = (3.0\times10^{-8})^3$

$$\frac{D_{\text{fcc}}}{D_{\text{bcc}}} = \frac{4\times(3.0\times10^{-8})^3}{2\times(3.5\times10^{-8})^3} = \mathbf{1.259}$$

20. KCl has face-centred cubic structure $\therefore$ $n = 4$

Given, Density = 1.9893 g cm^{-3}

$$a = 6.29082\times10^{-8}\ \text{cm}$$

$$\because \quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}} = \frac{n\times\text{molar mass}}{a^3\times\text{Av. no.}}$$

$$\therefore \quad 1.9893 = \frac{4\times74.5}{(6.29082\times10^{-8})^3\times N}$$

$$\therefore \quad N = \mathbf{6.017\times10^{23}}$$

21. $$\text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. No.}}$$

$a = 5\times10^{-8}$ cm, $d = 2$ g/cm^3

$$\therefore \quad 2 = \frac{n\times75}{(5\times10^{-8})^3\times6\times10^{23}} \quad \therefore\ n = 2$$

i.e., the metal crystallizes in bcc, thus,

$$\text{radius} = \frac{\sqrt{3}}{4}\times a = \frac{\sqrt{3}}{4}\times5 = 2.165\ \text{Å} = \mathbf{216.5\ pm}$$

22. Volume of one atom of Ar $= \dfrac{4}{3}\pi r^3$

Also, No. of atoms in 1.65 g or one mL $= \dfrac{1.65}{40}\times6.023\times10^{23}$

$\therefore$ Total volume of all atoms of Ar in solid state

$$= \frac{4}{3}\pi r^3\times\frac{1.65}{40}\times6.023\times10^{23}$$

$$= \frac{4}{3}\times\frac{22}{7}\times(1.54\times10^{-8})^3\times\frac{1.65}{40}\times6.023\times10^{23}$$

$$= 0.380\ \text{cm}^3$$

Volume of solid argon = 1 cm^3

$$\therefore \quad \%\ \text{empty space} = \frac{[1-0.380]}{1}\times100 = \mathbf{62\%}$$

23. $$\text{Density of NaCl} = \frac{n\times\text{atomic mass}}{\text{Av. no.}\times a^3}$$

$$= \frac{4\times58.5}{6.023\times10^{23}\times(5.64\times10^{-8})^3}$$

$$= \mathbf{2.16\ g/cm^3}$$

24. The distance between Li^+ and Cl^- ion can be derived as half of the edge length of cube

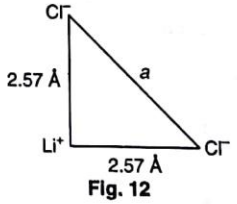


Fig. 12

$$\therefore \quad d_{Li^+-Cl^-} = \frac{5.14}{2} = 2.57\ \text{Å}$$

$$\therefore \quad d_{Cl^--Cl^-} = \sqrt{(2.57)^2+(2.57)^2} = 3.63\ \text{Å}$$

$$\text{The radius of } Cl^- = \frac{d_{Cl^--Cl^-}}{2} = \frac{3.63}{2}$$

$$= \mathbf{1.815\ Å}$$

25. Consider an octahedral void (Fig. 13) represented by the shaded portion (the spheres present below and above the void are not shown). Now suppose the length of each arm of the square will be $2R$ (R is radius of atom). Let r be the radius of void. For right angle triangle ABC.

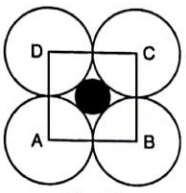


Fig. 13

$$AC = \sqrt{[(AB)^2 + (BC)^2]}$$
$$= \sqrt{[(2R)^2 + (2R)^2]} = \sqrt{8}R$$

Also, $AC = R + R + 2r = 2r + 2R = 2(r + R)$

or $\sqrt{8}R = 2\sqrt{2}R = 2(r + R)$ or $r = \sqrt{2}R - R$

$$r = [\sqrt{2} - 1]R = \mathbf{0.414 \times R}$$

26. Either octahedral voids $\left(\frac{r_1}{r_2} = 0.414\right)$ or tetrahedral voids $\left(\frac{r_1}{r_2} = 0.225\right)$ are occupied by interstitial sites in fcc where r_1 is radius of atom in interstitial sites and r_2 is radius of atom arranged in fcc.

Since in fcc atoms along face diagonal are touching, thus,

$$4r_2 = \sqrt{2}\,a$$

Required diameter of interstitial sites $= 2r_1 = 2 \times 0.414 r_2$

$$= \frac{2 \times 0.414 \times \sqrt{2}\,a}{4} = \frac{2 \times 0.414 \times \sqrt{2} \times 400}{4}$$

$$= \mathbf{117.1\ pm}$$

27. The number of units of AB in a unit cell (fcc) = 4

Radius of cation $A^+ = 100\,\text{pm} = 100 \times 10^{-10}$ cm

Radius of r^+/r^- for octahedral coordination = 0.414

Hence, Radius of the anion $(B^-) = \frac{100}{0.414} = \mathbf{241.5\ pm}$

28. Radius ratio $= \frac{r^+}{r^-} = \frac{88}{200} = 0.44$

The radius ratio lying in between 0.414 and 0.732 and thus represents for octahedral voids. Also B^- is larger than A^+ and thus B^- forms closed packed structure and A^+ occupies the void space. Thus, coordination number of cation A^+ in AB is **six.**

29. No. of atoms in unit cell = 1 + 2 = 3

Volume of unit cell $= 24 \times 10^{-24}\,\text{cm}^3$

Density $= 7.2\ \text{g cm}^{-3}$

$\because$ $\text{Density} = \frac{n \times \text{atomic mass}}{V \times \text{Av. no.}}$

$\therefore$ $7.2 = \frac{3 \times \text{atomic mass}}{24 \times 10^{-24} \times 6.023 \times 10^{23}}$

$\therefore$ Atomic mass = 34.69

$\because$ 34.69 g has no. of atoms $= 6.023 \times 10^{23}$

$\therefore$ 200 g has no. of atoms $= \frac{6.023 \times 10^{23} \times 200}{34.69}$

$$= \mathbf{3.4722 \times 10^{24}\ atoms}$$

30. Doping of $SrCl_2$ to NaCl brings in replacement of two Na^+ ion by each Sr^{2+} ion, but each Sr^{2+} occupies only one lattice point. This produces one cation vacancy.

Thus, doping of 10^{-3} mole of $SrCl_2$ in 100 mole NaCl will produce cation vacancies $= 10^{-3}$

$\therefore$ 100 mole NaCl will have cation vacancies after doping $= 10^{-3}$

$\therefore$ 1 mole NaCl will have cation vacancies $= \frac{10^{-3}}{100} = 10^{-5}$

$\therefore$ Total cationic vacancies $= 10^{-5} \times$ Av. no. $= \mathbf{6.02 \times 10^{18}}$

31. In a unit cell, there are one Cs^+ and $\frac{1}{8} \times 8 = 1\,Cl^-$, *i.e.*, one CsCl molecule

$\because$ $\text{Density} = \frac{n \times \text{molar mass}}{V \times \text{Av. no.}} = \frac{n \times \text{molar mass}}{a^3 \times \text{Av. no.}}$

$\therefore$ $3.97 = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$

$a = 4.13 \times 10^{-8}$ cm

$\therefore$ $a = 4.13$ Å

For a cube of side length 4.13 Å, diagonal

$= \sqrt{3} \times 4.13 = 7.15$ Å

As it is a bcc with Cs^+ at centre (radius r^+) and Cl^- at corners (radius r^-) so,

$2r^+ + 2r^- = 7.15$ or $r^+ + r^- = 3.57$ Å

i.e., Distance between neighbouring Cs^+ and Cl^- = 3.57 Å

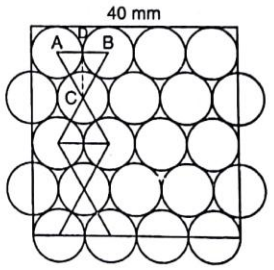
Now assume two Cl^- ions touch each other so,

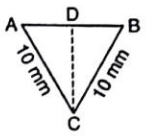
Length of unit cell $= 2r^- = 4.13$ Å $\therefore$ $r^- = 2.06$ Å

$\therefore$ $r^+ = 3.57 - 2.06 = 1.51$

$\therefore$ $r^+/r^- = 1.51/2.06 = \mathbf{0.73}$

32.





$CD = 10 \sin 60 = 10\frac{\sqrt{3}}{2}$

$= 5\sqrt{3}$

Area of square having spherical marbles in it

$= 40 \times 10^{-1} \times 40 \times 10^{-1}\,\text{cm}^2 = 16\,\text{cm}^2$

The maximum number of spheres of 10 mm diameter in hcp packing can be seen in Fig. 1.

Total length covered by spheres

$= 5 + 4 \times CD = 5 + 4 \times 10 \sin 60$

$= 5 + 4 \times 5\sqrt{3} = 40$ mm

Maximum number of spheres $(s) = \underset{\text{(Full)}}{14} + \underset{\text{(Half)}}{8} = 18$

$\therefore$ Number of spheres per $\text{cm}^2 = \frac{18}{16} = \mathbf{1.125}$

33. $\because \quad n\lambda = 2d\sin\theta$

Given, $n = 1$; $d = 0.2\times10^{-9}$ m, $\theta = \frac{16.80}{2} = 8.40^\circ$

Thus, $\lambda = \frac{2\times0.2\times10^{-9}\times\sin 8.4}{1} = \mathbf{5.84\times10^{-11}\,m}$

34. $\because \quad n\lambda = 2d\sin\theta$

Given, $n = 1$; $\lambda = 2.29\times10^{-10}$ m; $\theta = \frac{27°8'}{2} = 13°34'$

$\therefore \quad 1\times2.29\times10^{-10} = 2\times d\times\sin 13°34'$

$\therefore \quad d = \mathbf{4.88\times10^{-10}\,m}$

35. (a) Nearest neighbours are atoms at lattice points and tetrahedral voids.

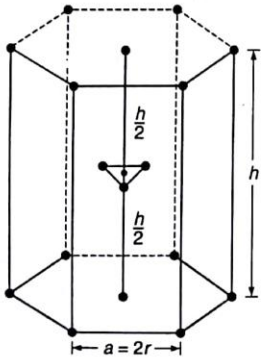
Thus, next nearest neighbours are atoms at **lattice points.**

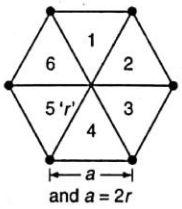
$\therefore$ Number of next nearest neighbours = 12

(b) Distance between next nearest neighbour (for fcc)

$$= \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}} = \mathbf{0.707}a$$

36. (a) The given packing (*AB AB AB*...) is three dimensional close packing as shown in given figure. In this arrangement three atoms are arranged in the body centred position in such a way, so that it forms equilateral triangle and twelve atoms are placed at 12 corners and two atoms at two face centres.





(i) $\therefore$ **No. of atoms per unit cell** $= \frac{1}{6}\times12 + \frac{1}{2}\times2 + 3 = 6$

(ii) Thus, **coordination number** of three dimensional hcp lattice becomes 12, *i.e.*, 6 from own layer and 3 from above and 3 from lower layer.

(b) Packing fraction : Each corner atom would be common to 6 other unit cells. If r is the radius of each sphere, then

$$\text{packing fraction} = \frac{6\times\frac{4}{3}\pi r^3}{V}$$

where V = volume of hexagon = Area of base (A) $\times$ height (h)

$$\therefore \text{ Packing fraction} = \frac{6\times\frac{4}{3}\pi r^3}{6\sqrt{3}r^2\times4r\times\sqrt{\frac{2}{3}}} = \frac{\pi}{3\sqrt{2}}$$

$$= \mathbf{0.74} \quad \text{or} \quad \mathbf{74\%}$$

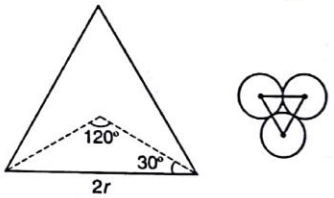
(c) Base Area (A) of unit cell : Base area of hcp unit cell is given by :

$$A = 6\times\frac{\sqrt{3}}{4}\times a^2$$

$$A = \frac{3\sqrt{3}}{2}a^2$$

$$A = \frac{3\sqrt{3}}{2}\times4r^2 = 6\sqrt{3}r^2$$

(d) Calculation of height : $\cos 120° = \frac{x^2+x^2-(2r)^2}{2x^2}$



or $$-\frac{1}{2} = \frac{2x^2-4r^2}{2x^2} = \frac{x^2-2r^2}{x^2} \quad \text{or} \quad 3x^2 = 4r^2$$

$\therefore \quad x = \frac{2r}{\sqrt{3}}$

Now $$\left(\frac{h}{2}\right)^2 = a^2 - x^2$$

$$\frac{h^2}{4} = (2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2 \quad \text{or} \quad \frac{h^2}{4} = \frac{8r^2}{3}$$

$\therefore \quad h^2 = \frac{32r^2}{3}$ or $h = 4r\times\sqrt{\frac{2}{3}}$

SINGLE INTEGER ANSWER PROBLEMS

1. If radius ratio is less than 0.155, the co-ordination no. is .....
2. In pentagonal bipyramidal structure, the co-ordination no. is .....
3. Number of second nearest neighbours in body centred lattice is .....
4. Co-ordination no. of Cs^+ in CsCl is .....
5. Number of Al atoms per unit cell of Al in its crystal lattice is .....
6. The ratio of co-ordination no. of Al and no. of Al atoms per unit cell in fcc lattice is .....
7. FeO crystallises in NaCl type lattice. The crystal is however non-stoichiometric as $Fe_{0.96}O$ and deficient in iron. Some cation sites are vacant and some contain Fe^{3+} so that it becomes electrically neutral. The % of cation sites vacant are .....
8. A crystal of sodium hydride has fcc unit cell of H^- ions with Na^+ ions at the body centres of unit cell and in the centre of edges. The no. of H^- that touch each Na^+ is .....
9. In HCP arrangement of atoms, co-ordination no. of atoms in the middle layer is .....
10. The number of tetrahedral voids present in bcc lattice is .....
11. If the distance between $Cs^+ - Cl^-$ in CsCl lattice is $2\sqrt{3}$ Å, the edge length of cube is .....
12. The no. of octahedral sites per square are in a ccp (fcc) structure .....
13. If edge length of a bcc crystallized Fe is $8\sqrt{3}$, the atomic radius is .....
14. A mineral having the formula AB_2 crystallises in cubic close packed lattice, with A atoms occupying the lattice point. The ratio of co-ordination no. of A and B is .....
15. Lattice energy of NaCl is −186 kcal/mol and solution enthalpies of cation and anion respectively are −97 and −85 kcal / mol. The enthalpy of solution of NaCl in kcal is .....
16. Number of regular hexagonal faces in a truncated tetrahedron is .....
17. Number of regular trigonal faces in a truncated tetrahedron is .....
18. Number of square faces in a truncated octahedron is :
19. A compound AB has rock salt structure with $A:B = 1:1$. The formula mass of AB is 6.023 Y amu and the closest A-B distance is $y^{1/3}$ nm. The density of lattice in 5×10^{-a} g / cm^3. The value of a is .....
20. A metal crystallises in two cubic faces fcc and bcc, where unit cell lengths are 4.0 and 2.0Å respectively. The ratio of density in bcc and fcc is .....
21. The ratio of co-ordination no. of A and B is 1 : 3, then the ratio of no. of atoms of A and B in unit cell is .....
22. The number of nearest neighbours in an atom/ion for an octahedral hole of a closed packed structure is .....
23. The ratio of number of nearest neighbour and no. of atoms per unit cell in a simple cubic structure is .....
24. The ratio of number of nearest neighbour and no. of atoms per unit cell in a fcc structure is .....
25. The ratio of number of nearest neighbour and no. of atoms per unit cell in a bcc structure is .....
26. The ratio of co-ordination number of cation and anion in fluorite CaF_2 is .....
27. The ratio of co-ordination number of anion and cation in antifluorite Na_2O is .....
28. Ice crystallises in a hexagonal lattice having volume of the unit cell as 132×10^{-24} cm^3. If density of ice is 0.92 g cm^{-3} at a given temperature, then number of H_2O molecule per unit cell is .....
29. When the radius ratio of r_M/r_X of a crystal lies in the range of 0.414 – 0.732, the co-ordination number of M is .....
30. Silver (atomic mass = 108 g mol^{-1}) has a density of 10.5 g/cm^3. The number of silver atoms on a surface area of 10^{-12} m^2 can be expressed in scientific notations as $Y\times10^X$. The value of X is : **(IIT 2010)**
31. Co-ordination number of Al in the crystalline state of $AlCl_3$ is : **(IIT 2009)**
32. Number of hexagonal faces that are present in a truncated octahedron. **(IIT 2011)**
33. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8g cm^{-3}, then the number of atoms present in 256 g of the crystal is $N\times10^{24}$. The value of N is : **[JEE (Main) 2017]**

ANSWERS

1. Two 2. Seven 3. Six 4. Eight 5. Four 6. Three 7. Four 8. Six 9. Six 10. Four 11. Four 12. One
13. Six 14. Two 15. Four 16. Four 17. Four 18. Six 19. Three 20. Four 21. Three 22. Six 23. Six 24. Three
25. Four 26. Two 27. Two 28. Four 29. Six 30. Seven 31. Four 32. Eight 33. Two

OBJECTIVE PROBLEMS (One Answer Correct)

1. Na and Mg crystallise in bcc and fcc type crystals, the ratio of number of atoms present in unit cell of their respective crystal is :
(a) 1 (b) 0.5
(c) 3 (d) 4

2. In a closed packed structure of mixed oxides, the lattice is composed of mixed oxides ions. One eighth of tetrahedral voids are occupied by divalent cations (A^{2+}) while one half of octahedral voids are occupied by trivalent cation (B^{3+}). The formula of mixed oxide is :
(a) A_2BO_3 (b) AB_2O_3
(c) A_2BO_4 (d) AB_2O_4

3. An ionic solid A^+B^- crystallises as a bcc structure. The distance between cation and anion in the lattice is 338 pm. The edge length of cell is :
(a) 338 pm (b) 390.3 pm
(c) 292.7 pm (d) 507 pm

4. An ionic solid A^+B^- crystallises as a fcc structure. If the edge length of cell is 508 pm and radius of anion is 144 pm, the radius of cation is :
(a) 110 pm (b) 364 pm
(c) 220 pm (d) 288 pm

5. The density of an ionic compound (molar mass 58.5) is 2.165 kg m^{-3} and the edge length of unit cell is 562 pm, then the closest distance between A^+B^- and rank of unit cell is:
(a) 281 pm, 4 (b) 562 pm, 2
(c) 562 pm, 4 (d) 281 pm, 2

6. The γ-form of iron has fcc structure (edge length 386 pm) and β-form has bcc structure (edge length 290 pm). The ratio of density in γ-form and β-form is :
(a) 0.9788 (b) 1.02
(c) 1.57 (d) 0.6344

7. The internuclear distance in NaCl is 0.282 nm and density of solid NaCl (molar mass 58.5) is 2.17×10^3 kg m^{-3}. If a unit cell of NaCl has 4 formula units, the Avogadro's number is :
(a) 6.01×10^{23} (b) 6.02×10^{23}
(c) 6.03×10^{23} (d) 6.04×10^{23}

8. The bcc structure of an element has density 7.12 kg/m^3 and edge length of unit cell is 2.88 Å. The number of atoms present in 288 g of element is :
(a) 3.4×10^{22} (b) 3.4×10^{23}
(c) 3.4×10^{24} (d) 3.4×10^{21}

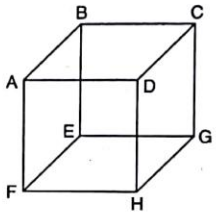
9. The edge length of unit cell of a metal (molar mass 24) having cubic structure 4.53 Å. If the density of metal is 1.74 g/cm^3, the radius of metal is : (Av. No. $=6\times10^{23}$)
(a) 180 pm (b) 160 pm
(c) 140 pm (d) 190 pm

10. The ratio of packing density in fcc, bcc and cubic structure is respectively :
(a) 1 : 0.92 : 0.70 (b) 0.70 : 0.92 : 1
(c) 1 : 0.70 : 0.92 (d) 0.92 : 0.70 : 1

11. If R is the radius of the octahedral voids and r is the radius of the atom in close packing, then :
(a) $\frac{r}{R}=2.41$ (b) $\frac{r}{R}=4.76$
(c) $\frac{r}{R}=3.22$ (d) $\frac{r}{R}=9.1$

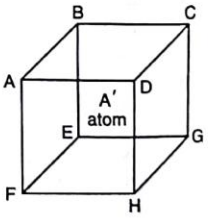
12. A metal crystallises in bcc lattice. The % fraction of edge length not covered by atom is:
(a) 10.4% (b) 13.4%
(c) 12.4% (d) 11.4%

13. In the cubic lattice given below the three distances between the atoms $A-B$, $A-C$ and $A-G$ are respectively :



(a) $a, \sqrt{2}a, \sqrt{3}a$ (b) $a, \sqrt{3}a, \sqrt{2}a$
(c) $\frac{a}{2}, \frac{a}{\sqrt{2}}, \frac{\sqrt{3}a}{2}$ (d) $a, \frac{\sqrt{3}a}{2}, \sqrt{2}a$

14. In body-centred cubic lattice given below, the three distances AB, AC and AA' are:
(a) $a, \sqrt{2}a, \frac{\sqrt{3}a}{2}$
(b) $a, \frac{\sqrt{3}a}{2}, \sqrt{2}a$
(c) $\frac{\sqrt{3}a}{2}, \sqrt{2}a, a$
(d) $a, \frac{a}{\sqrt{2}}, \frac{\sqrt{3}a}{2}$



15. Two ionic solids AB and CB crystallise in the same lattice. If $\frac{r_{A^+}}{r_{B^-}}$ and $\frac{r_{C^+}}{r_{B^-}}$ are 0.50 and 0.70 respectively, then the ratio of edge length of AB and CD is :
(a) 0.68 (b) 0.78
(c) 0.88 (d) 0.98

16. A molecule A_2B (molar mass = 166.4) occupies triclinic lattice with $a=5$ Å, $b=8$ Å and $c=4$ Å. If density of AB_2 is 5.2 g cm^{-3}, the number of molecules present in one unit cell is:

(a) 2 (b) 3
(c) 4 (d) 5

17. Silicon dopped with gp. 13 and gp. 15 members elements is respectively called ... semiconductor.
(a) *p*-type, *n*-type (b) *n*-type, *p*-type
(c) *p*-type (d) *n*-type

18. Na and Mg crystallise in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respectively crystal is:
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

19. How many unit cells are present in a cubic shaped ideal crystal of NaCl of mass 1.0 g?
(a) 1.28×10^{21} unit cells (b) 1.71×10^{21} unit cells
(c) 2.57×10^{21} unit cells (d) 5.14×10^{21} unit cells

20. What type of crystal defect is indicated in the diagram given below?

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-
Cl^-	□	Cl^-	Na^+	□	Cl^-
Na^+	Cl^-	□	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+	□	Na^+

(a) Frenkel and Schottky defects
(b) Schottky defect
(c) Interstitial defect
(d) Frenkel defect

21. The volume of atoms present in a face-centred cubic unit cell of a metal (r is atomic radius) is:
(a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$
(c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

22. In a *p*-type semiconductor, the majority carriers of current are:
(a) protons (b) electrons
(c) holes (d) neutrons

23. Among which the magnetic susceptibility does not depend upon temperature?
(a) Diamagnetism (b) Paramagnetism
(c) Ferromagnetism (d) Ferrite

24. Copper and silicon are cooled from 300 K to 60 K, the conductivity:
(a) decrease in Cu but increase in Si
(b) increase in Cu but decrease in Si
(c) increase in both
(d) decrease in both

25. Zn converts from molten state to its solid state in hcp structure. The number of nearest atoms is:
(a) 4 (b) 6
(c) 8 (d) 12

26. Forbidden energy gap for Si is approximately:
(a) 1 eV (b) 6 eV
(c) 0 eV (d) 3 eV

27. In a semiconductor at room temperature:
(a) the valence band is partially empty and conduction band is partially filled
(b) the valence band is completely filled and the conduction band is partially filled
(c) the valence band is completely filled
(d) the conduction band is completely filled

28. Si is used more as semiconductor than Ge because:
(a) Si is cheaper than Ge
(b) It is found in abundance
(c) Less leakage of current in Si
(d) All of the above

29. Above Curic temperature:
(a) A ferromagnetic substance becomes ferromagnetic
(b) A ferromagnetic substance becomes paramagnetic
(c) A paramagnetic substance becomes diamagnetic
(d) A diamagnetic substance becomes paramagnetic

30. The fraction of total volume occupied by the atoms present in a simple cube is:
(a) $\frac{\pi}{6}$ (b) $\frac{\pi}{3\sqrt{2}}$
(c) $\frac{\pi}{4\sqrt{2}}$ (d) $\frac{\pi}{4}$

31. Percentage of free space in a body centred cubic unit cell is:
(a) 34% (b) 28%
(c) 30% (d) 32%

32. In which of the following pairs of structures, tetrahedral as well as octahedral voids are noticed?
(a) hc, fcc (b) hcp, sc
(c) hcp, ccp (d) bcc, hcp

33. In a cubic unit cell 7 of the 8 corners are occupied by atom A and centres of faces are occupied by atom B. The general formula of compound is:
(a) A_7B_6 (b) A_7B_{24}
(c) $A_{24}B_7$ (d) A_6B_7

34. Anions A form hexagonal closest packing and cation B occupy only 2/3 of octahedral voids in it, the general formula of compound is:
(a) BA (b) BA_2
(c) B_2A_3 (d) B_3A_2

35. In NaCl crystal, the number of next nearest neighbours of each Na^+ is:
(a) $8Cl^-$ (b) $12Na^+$
(c) $12Cl^-$ (d) $24Cl^-$

36. When anion leaves the normal sites an electron occupies interstitial sites in a crystal lattice it is called:
(a) Schottky defect (b) Frenkel defect
(c) Metal excess defect (d) Metal deficiency

37. Certain crystals produce electric signals on applying pressure. This phenomenon is:
(a) Ferro electricity (b) Ferri electricity
(c) Piezo electricity (d) Pyro electricity

38. Co-ordination no. of $AlCl_3$ in crystalline state is:
(a) 4 (b) 6
(c) 5 (d) 8

39. Carbon, Silicon and Germanium have four valency electrons each. These are characterised by conduction bond separated by energy bond gaps respectively equal to $(E_g)_C$, $(E_g)_{Si}$ and $(E_g)_{Ge}$. The correct statement is:
(a) $(E_g)_C = (E_g)_{Si} = (E_g)_{Ge}$
(b) $(E_g)_C > (E_g)_{Si} > (E_g)_{Ge}$
(c) $(E_g)_C < (E_g)_{Ge} > (E_g)_{Si}$
(d) $(E_g)_{Si} < (E_g)_{Ge} > (E_g)_C$

40. In a solid lattice, the cation left a lattice site and is located at an interstitial position. The lattice defect is:
(a) Interstitial defect (b) Vacancy defect
(c) Frenkel defect (d) Schottky defect

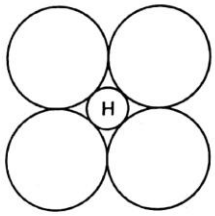
41. Schottky defect in crystals is observed when:
(a) unequal no. of cations and anions are missing from crystal lattice
(b) equal no. of cations and anions are missing from crystal lattice
(c) an atom leaves its normal site and occupies an interstitial site
(d) density of crystal is increased

42. The metallic lustre exhibited by sodium is explained by:
(a) diffusion of sodium ions
(b) oscillation of loose electrons
(c) excitation of free protons
(d) existence of body centred cubic lattice

43. CsBr has b.c.c structure with edge length 4.3Å. The shortest inter ionic distance in between Cs^+ and Br^- (in Å) is:
(a) 3.72 (b) 1.86
(c) 7.44 (d) 4.3

44. The co-ordination number of a metal crystallizing in a hexagonal close-packed structure is :
(a) 12 (b) 4
(c) 8 (d) 6

45. The radius (R) of atoms forming a closed packed structure in the given figure is 2×10^{-8} cm.



The maximum radius of atom occupying the octahedral hole (H) is :
(a) 8.28×10^{-9} cm (b) 0.414×10^{-8} cm
(c) 0.225×10^{-8} cm (d) 4.5×10^{-8} cm

46. Which of the following crystal does not possess any symmetry ?
(a) $K_2Cr_2O_7$ (b) $CuSO_4 \cdot 5H_2O$
(c) H_3BO_3 (d) Either of these

47. The energy gap between conduction band and valence band is zero in :
(a) Na (b) Diamond
(c) Si (d) Ge

48. Which one is the incorrect statement ?
(a) $FeO_{0.98}$ has non-stoichiometric metal deficiency defect
(b) Density decreases in case of crystals with Schottky's defect
(c) NaCl(s) is insulator, silicon is semiconductor, silver is conductor, quartz is piezo electric crystal
(d) Frenkel defect is favoured in those ionic compounds in which sizes of cations and anions are almost equal

SOLUTIONS (One Answer Correct)

1. (b) No. of atoms in bcc = 2
No. of atoms in fcc = 4
$\therefore$ Ratio $= \frac{2}{4} = 0.5$

2. (d) Number of tetrahedral voids per ion in lattice = 2
Number of $A^{2+} = \frac{1}{8}\times 2 = \frac{1}{4}$
Number of octahedral voids per ion in lattice = 1
Number of $B^{3+} = 1\times\frac{1}{2} = \frac{1}{2}$
$\therefore$ Formula AB_2O_4

3. (b) $r^+ + r^- = \sqrt{3}\times\frac{a}{2}$
$\therefore \quad a = \frac{2}{\sqrt{3}}\times 338 = 390.3\text{ pm}$

4. (a) $r^+ + r^- = \frac{a}{2}$ for fcc

5. (a) $d = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. No.}}$ or
$$2.165 = \frac{n\times 58.5}{(562\times10^{-10})^3\times 6\times10^{23}}$$
$\therefore\ n = 4$ rank of unit cell
$\therefore\ AB$ has fcc structure,
$\therefore \quad d_{A^+-B^-} = \frac{a}{2}$

6. (a) $\frac{d_r}{d_B} = \frac{d_{fcc}}{d_{bcc}} = \frac{n_r\times(a_B)^3}{n_B\times(a_r)^3} = \frac{4}{2}\times\left(\frac{290}{386}\right)^3 = 0.9788$

7. (a) $d = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. No.}}$ and $r^+ + r^- = \frac{a}{2}$

8. (c) $\text{Density} = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. No.}}$
$$\therefore \text{ Atomic mass} = \frac{\text{Density}\times a^3\times\text{Av. No.}}{n}$$
$$= \frac{7.12\times(2.88\times10^{-8})^3\times 6.023\times10^{23}}{2} = 51.22$$
$$\therefore \text{ No. of atoms} = \frac{6.023\times10^{23}\times 2.88}{51.22} = 3.386\times10^{24}$$

9. (b) $d = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. No.}}$
$\therefore\ n = 4$ and metal crystallises in fcc. Then $r = \frac{a}{2\sqrt{2}}$

10. (a) Packing density in fcc, bcc and sc are 0.74, 0.68 and 0.52 respectively.

11. (a) $AC = \sqrt{AB^2 + BC^2}$
$= \sqrt{(2r)^2 + (2r)^2}$
$r + r + 2R = 2\sqrt{2}\,r$
$\therefore \quad 2R = 2(\sqrt{2}r - r)$
$R = (\sqrt{2}-1)r, \quad \frac{R}{r} = 0.41, \quad \therefore\ \frac{r}{R} = 2.41$

12. (b) In bcc $r = \frac{\sqrt{3}a}{4}$
Also, edge length of unit cell = a
radius of atom = r
$\therefore$ Edge length not covered by atom = $a - 2r$
or $= a - \frac{\sqrt{3}}{2}\cdot a = a\left[\frac{2-\sqrt{3}}{2}\right]$
$\therefore$ Percentage fraction not covered
$$= \frac{a\left[\frac{2-\sqrt{3}}{2}\right]}{a}\times 100 = 0.134\times 100 = 13.4\%$$

13. (a) Edge length = $AB = AD = BC = CD = a$
Also, $AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$
$AG = \sqrt{AC^2 + CG^2} = \sqrt{2a^2 + a^2} = \sqrt{3}a$

14. (a) Edge length = $AB = AD = BC = CD = a$
$\therefore \quad AC = \sqrt{AB^2 + BC^2} = \sqrt{2}\,a$
Now, $AA'^2 + A'G^2 = \left(\frac{\sqrt{3}a}{2}\right)^2$
$\therefore \quad 2AA'^2 = \frac{3a}{4}$ or $AA' = \frac{\sqrt{3}a}{2}$

15. (c) $\frac{r_{A^+}}{r_{B^-}} = 0.50$ and $\frac{r_{C^+}}{r_{B^-}} = 0.70$
$\therefore \quad \frac{r_{A^+} + r_{B^-}}{r_{B^-}} = 1 + 0.5 = 1.5 \quad \frac{r_{C^+} + r_{B^-}}{r_{B^-}} = 1.70$
$\therefore \quad \frac{r_{A^+} + r_{B^-}}{r_{C^+} + r_{B^-}} = \frac{1.5}{1.7}$
$\therefore \quad a_{AB} = 2(r_{A^+} + r_{B^-})$
$a_{CB} = 2(r_{C^+} + r_{B^-})$
$\therefore \quad \frac{a_{AB}}{a_{CB}} = \frac{1.5}{1.7} = 0.88$

16. (b) Volume of unit cell
$= a\times b\times c = 5\times10^{-8}\times 8\times10^{-8}\times 4\times10^{-8}$
$= 1.6\times10^{-22}\text{ cm}^3$
Mass of unit cell $= 1.6\times10^{-22}\times 5.2 = 8.32\times10^{-22}$ g
Number of molecules in one unit cell
$$= \frac{8.32\times10^{-22}\times 6\times10^{23}}{166.4} = 3$$

17. (a) Follow text.

18. (d) No. of unit cell in bcc is 2 and fcc is 4.

19. (c) $n = 4$ for fcc;
Also, no. of atoms in 1g NaCl $= \frac{6.023\times10^{23}}{58.5}$

No. of unit cell present in 1g NaCl

$$= \frac{6.023\times10^{23}}{58.5\times4} = 2.57\times10^{21} \text{ unit cell}$$

20. (b) These defect are produced when one +ve and one –ve ion are missing from their respective position removed.

21. (d) Volume of atom in a cell $= \frac{4}{3}\pi r^3 \times n$ ($n = 4$ for fcc)

$$= \frac{4}{3}\pi r^3 \times 4 = \frac{16}{3}\pi r^3$$

22. (c) In *p*-type semiconductors, conduction occurs by "+ve" majority carriers (*i.e.*, by holes).

23. (a) Diamagnetism is independent of temperature.

24. (b) Copper is conductor and thus resistance decreases (conductance increase) and silicon is semiconductor and so resistance increases (conductance decreases) on cooling.

25. (d) In hcp, unit cell is hexagonal and co-ordination number 12.

26. (a) E_g for Si = 1.1 eV ; E_g for Ge = 0.7 eV

27. (a) In semiconductors at room temperature, some of the electrons of valence bond gain sufficient energy to go in conduction bond.

28. (d) All are facts.

29. (b) It is a fact.

30. (a) — do —

31. (d) — do —

32. (c) These are facts.

33. (b) No. of atoms A at corners $= 7\times\frac{1}{8} = \frac{7}{8}$

No. of atoms B at faces $= 6\times\frac{1}{2} = 3$

$\therefore$ $A_{7/8}B_3$ or A_7B_{24}

34. (c) No. of anion A^- in unit cell $= 6$

No. of cation B^- in unit cell $= 6\times\frac{2}{3} = 4$

$\therefore$ B_4A_6 or B_2A_3

35. (b) It is a fact.

36. (c) — do —

37. (c) — do —

38. (a) In solid state it exists as Al_2Cl_6.

39. (b) Carbon is insulator, Si is semiconductor with higher energy bond gap, while Ge is semiconductor with smaller energy bond gap.

40. (c) It is a fact.

41. (b) — do —

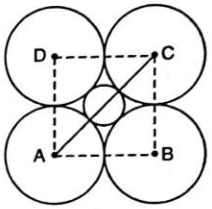
42. (b) Follow metallic bonding.

43. (a) For bcc : $r = \frac{\sqrt{3}}{4}\times a = \frac{\sqrt{3}}{4}\times 4.3 = 1.86$ Å

$\therefore$ shortest inter ionic distance $= 2r = 3.72$ Å.

44. (a) In hcp structure co-ordination no. of metal is 12.

45. (a) Given radius of spheres is $R(2\times10^{-8}$ cm). Let radius of void be r.



The octahedral void.

In the triangle ABC

$$AC^2 = (AB)^2 + (BC)^2 = (2R)^2 + (2R)^2$$

$$[R + 2r + R]^2 = 8R^2$$

$$2R + 2r = 2\sqrt{2}R$$

$\therefore$ $\frac{R+r}{R} = \sqrt{2}$

$$1 + \frac{r}{R} = \sqrt{2}$$

$$\frac{r}{R} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$

$\therefore$ $r = 0.414R = 0.414\times2\times10^{-8} = 8.28\times10^{-9}$

46. (d) All are triclinic crystals having no symmetry.

47. (a) Conduction bond and valence bonds overlaps in metals.

48. (a,d) $FeO_{0.98}$ has a non-stoichiometric molecule having metal excess defect (compare this molecule with FeO) and not metal deficiency defect. Frenkel defect is favoured in those ionic compounds if there is a large difference between sizes of cation and anions.

PREVIOUS YEARS PROBLEMS

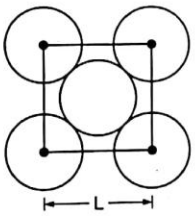
1. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axis are removed, then the resultant stoichiometry of the solid is : **(IIT 2001)**
   (a) AB_2 (b) A_2B
   (c) A_4B_3 (d) A_3B_4

2. A substance A_xB_y crystallises in face-centred cubic (fcc) lattice in which atoms A occupy each corner of the cube and atoms B occupy the centre of each face of the cube. The composition of A_xB_y is : **(IIT 2002)**
   (a) AB_3 (b) A_4B_3
   (c) A_3B (d) cannot be specified

3. The pyknometer density of NaCl crystal is $2.165\times10^3\ kg\ m^{-3}$ while its X-ray density is $2.178\times10^3\ kg\ m^{-3}$. The fraction of unoccupied sites in NaCl crystal is: **(IIT 2003)**
   (a) 5.96×10^{-2} (b) 5.96×10^{-1}
   (c) 5.96×10^{-3} (d) 5.96

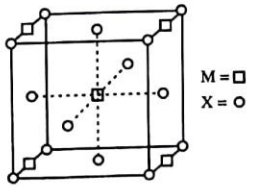
4. In which of the following crystals alternate tetrahedral voids are occupied? **(IIT 2005)**
   (a) NaCl (b) ZnS
   (c) CaF_2 (d) Na_2O

5. The packing efficiency of the two dimensional square unit cell shown below is : **(IIT 2010)**



   (a) 39.27% (b) 68.02%
   (c) 74.05% (d) 78.54%

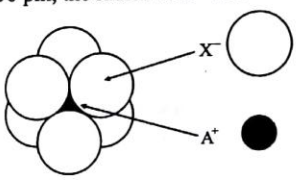
6. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown in figure. The empirical formula of the compound is : **(IIT 2012)**



   (a) MX (b) MX_2
   (c) M_2X (d) M_5X_{14}

7. Which of the following exists as covalent crystals in the solid state? **[JEE (Main) 2013]**
   (a) Sulphur (b) Phosphorus
   (c) Iodine (d) Silicon

8. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is :



   [JEE (Advanced-I) 2013]
   (a) 104 pm (b) 125 pm
   (c) 183 pm (d) 57 pm

9. CsCl crystallises in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct? **[JEE (Main) 2014]**
   (a) $r_{Cs^+} + r_{Cl^-} = 3a$ (b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
   (c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3a}$

10. Sodium metal crystallizes in a body-centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately : **[JEE (Main) 2015]**
    (a) 1.86 Å (b) 3.22 Å
    (c) 5.72 Å (d) 0.93 Å

11. If the unit cell of a mineral has cubic packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holed occupied by magnesium ions m and n respectively, are : **[JEE (Advanced) I 2015]**
    (a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$
    (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

12. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be : **[JEE (Main) 2017]**
    (a) $2a$ (b) $2\sqrt{2}a$
    (c) $\sqrt{2}a$ (d) $\frac{a}{\sqrt{2}}$

SOLUTIONS (Previous Year Problems)

1. (d) Na in NaCl has 8 corner and 6 face atoms. If we remove face-centred atom of one axis, two face atoms are removed. Thus, A is at 8 corner and B is at 4 faces.

No. of A atoms per unit cell $= 8\times\frac{1}{8}+4\times\frac{1}{2}=3$

No. of B atoms per unit cell $= 12\times\frac{1}{4}+1=4$

Thus, formula is A_3B_4.

2. (a) A at fcc thus $A=\frac{8}{8}=1$ and B at centre thus $B=\frac{1}{2}\times 6=3$. Thus formula is AB_3.

3. (c) Fraction not occupied $=\frac{(m/e_1)-(m/e_2)}{(m/e_2)}$

$$=\frac{\left(\frac{1}{e_1}\right)-\left(\frac{1}{e_2}\right)}{\left(\frac{1}{e_2}\right)}=\frac{e_1-e_2}{e_1}=\frac{e_2}{e_1}-1$$

$$=\frac{2.178}{2.165}-1=0.006$$

4. (b) In ZnS structure, sulphide ions occupy all the lattice points while Zn^{2+} ions are present in alternate tetrahedral voids.

5. (d) Packing efficiency $=\frac{u}{V}=\frac{2\pi r^2}{L^2}$

$\because$ $r=\frac{L}{2\sqrt{2}}$

$\therefore$ $\text{P.E.}=\frac{2\pi L^2}{(2\sqrt{2})^2\cdot L^2}=\frac{\pi}{4}=0.7854$

6. (b) M_pX_q has ccp structure, therefore,

$X=8\times\frac{1}{8}+6\times\frac{1}{2}=4$

$M=4\times\frac{1}{4}+1=2$

So, unit cell formula of the compound is M_2X_4 and the empirical formula of the compound is MX_2.

7. (d) Silicon (Si) : Covalent solid
Sulphur : Molecular solid
Phosphorus (P_4) : Molecular solid
Iodine (I_2) : Molecular solid

8. (a) The figure represents an octahedral void

$\frac{r_{A^+}}{r_{X^-}}=0.414$

$r_{A^+}=0.414\times 250=104$ pm

9. (c) For bcc if edge length is a, then

$$r_{Cs^+}+r_{Cl^-}=\frac{\sqrt{3}}{2}a$$

10. (a) For bcc unit cell : $r=\frac{\sqrt{3}}{4}.a$

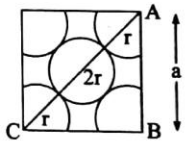
$\therefore$ $r=\frac{\sqrt{3}}{4}\times 4.29=1.85$ Å

11. (a) Effective number of $O^{-2}=4$
Effective number of $Al^{+3}=4m$
Effective number of $Mg^{+2}=8m$
$\Rightarrow$ By charge balance $12m+16n=8$
$3m+4n=2$
Possible value of m and n which satisfy the above equation are

$$m=\frac{1}{2};\ n=\frac{1}{8}$$

i.e., $3\times\frac{1}{2}+4\times\frac{1}{8}=2$

12. (d) In fcc, one of the face is like



From ΔABC,

$$2a^2=16r^2$$

or $$r^2=\frac{1}{8}a^2$$

or $$r=\frac{a}{2\sqrt{2}}$$

Distance of closest approach $=2r=\frac{a}{\sqrt{2}}$.

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. In which of the following systems primitives $a \neq b \neq c$?
   (a) Orthorhombic (b) Monoclinic
   (c) Triclinic (d) Hexagonal
2. In which of the following systems interfacial angles $\alpha = \gamma = 90°$ but $\beta \neq 90°$?
   (a) Monoclinic (b) Rhombohedral
   (c) Triclinic (d) Hexagonal
3. The space in which atoms are not present in unit cell is?
   (a) In sc 48% (b) In fcc 26%
   (c) In bcc 32% (d) In hexagonal 26%
4. Which of the following having their radius ratio between 0.414 to 0.732, *i.e.*, for NaCl structure have their radius ratio not in this range but possess NaCl type structure?
   (a) LiBr (b) KCl
   (c) RbCl (d) BaO
5. If radius of anion is 0.20 nm, the maximum radius of cations which can be filled in respective voids are correctly matched in :
   (a) $r^+ = 0.0828$ nm for tetrahedral void
   (b) $r^+ = 0.045$ triangular void
   (c) $r^+ = 0.1464$ nm for octahedral void
   (d) none of the above
6. Which of the following statements are correct?
   (a) Dislocation of ion from lattice site to interstitial site is called Frenkel defect
   (b) Missing of +ve and –ve ions from their respective position producing a pair of holes is called Schottky defect
   (c) Presence of ions in the vacant interstitial sites along with lattice point is called interstitial defect
   (d) Non stoichiometric NaCl is yellow solid
7. Select the correct statements :
   (a) The conductance through electrons is called *p*-type conduction
   (b) The conductance through positive holes is called *p*-type conduction
   (c) The conductance through electrons is called *n*-type conduction
   (d) The band gap in Germanium is small
8. Select the correct statements :
   (a) Solid with F-centres are paramagnetic
   (b) Ferrimagnetic character of Fe_3O_4 at room temperature changes to paramagnetic character at 850 K
   (c) Anti ferrimagnetic V_2O_3 changes to paramagnetic at 150 K
   (d) Non stoichiometric Cu_2O is *p*-type semiconductor
9. Which of the following statements are correct ?
   (a) The coordination number of each type of ion in CsCl crystal is 8
   (b) A metal that crystallises in bcc structure has a coordination number of 12
   (c) A unit cell of ionic crystal shares some of its ion with other unit cells
   (d) The length of the unit cell in NaCl is 552 pm ($\gamma_{Na^+} = 95$ pm, $\gamma_{Cl^-} = 181$ pm)
10. Select the correct statements about three dimensional hcp system :
    (a) Number of atoms in hcp unit cell is six
    (b) The volume of hcp unit cell is $24\sqrt{2}\,r^3$
    (c) The empty space in hcp unit cell is 26%
    (d) The base area of hcp unit cell is $6\sqrt{3}\,r^2$
11. If the limiting radius ratio $\left(\frac{r^+}{r^-}\right)$ lies in the range 0.225 to 0.414, there is:
    (a) tetrahedral void (b) coordination no. 4
    (c) zinc blene structure (d) NaCl type structure
12. The correct statement(s) regarding defects in solids is(are): **(IIT 2009)**
    (a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
    (b) Frenkel defect is a dislocation defect
    (c) Trapping of an electron in the lattice leads to the formation of F-center
    (d) Schottky defects have no effect on the physical properties of solids
13. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is(are) : **[JEE (Advanced) II 2016]**
    (a) The number of the nearest neighbours of an atom present in the topmost layer is 12
    (b) The efficiency of atom packing is 74%
    (c) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
    (d) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c) Follow text.
2. (a,b) —do—
3. (a,b,c,d) —do—
4. (a,b,c,d) $\frac{r^+}{r^-}$ for LiBr, KCl, RbCl and BaO are 0.34, 0.38, 0.77 and 0.83 respectively.
5. (a,b,c) $\frac{r^+}{r^-}$ = 0.732, 0.414, 0.225 Maximum for octahedral, tetrahedral and triangular voids.
6. (a,b,c,d) Non stoichiometric NaCl has F-centres due to anion vacancy defect.
7. (b,c,d) Follow text. **Concepts of Physical Chemistry** by **P. Bahadur**, Prakash publications, Muzaffarnagar.
8. (a,b,c,d) —do—
9. (a,c,d) In bcc coordination number is 8.
10. (a,b,c,d) Follow solution of Numerical problem 36 on page 623?
11. (a,b,c) These are facts.
12. (b,c) Frenkel defect is created when an ion leaves its correct lattice site and occupies an interstitial site, *i.e.*, dislocation. The holes left due to Schottky defect when negative ions are apart from their lattice are occupied by electrons and are called F-centres.
13. (b, c, d)
    For any atom in top most layer, coordination number is not 12 since there is no layer above top most layer and thus (a) is wrong. (b) and (c) are facts
    $\because \quad \sqrt{2}a = 4R$
    So $\quad a = 2\sqrt{2}R$

COMPREHENSION BASED PROBLEMS

Comprehension 1: In crystalline solids atoms or molecules are arranged in a regular and long range order fashion in a three dimensional pattern. These have sharp melting point, flat faces, sharp edges, bounded by well defined planes. A large number of unit cells, each of which possess a definite geometry bounded by plane faces give rise to the formation of a crystal. A point at the corner of unit cell contributes for 1/8 of each such point to unit cell. A point along an edge contribute for 1/4 of each such point to unit cell. A body centred point contributes for 1 each such points to unit cell. Co-ordination number is the number of nearest neighbours that each ion is surrounded by an oppositely charged ions. Radius of unit cell in sc, fcc and bcc is $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ and $\frac{\sqrt{3}a}{4}$ where a is edge length of cell.

[1] A mineral having the formula AB_2 crystallises in the cubic closed packed lattice, with A^{2+} atoms occupying the lattice points and B^- tetrahedral voids. The co-ordination number of A, B and fraction of the tetrahedral sites occupied by B atom respectively are:
(a) 8, 4, 100% (b) 4, 8, 100%
(c) 8, 6, 57% (d) 6, 8, 57%

[2] An alloy of Cu and gold crystallises in a cubic lattice in which the gold atoms occupy the lattice points at the corners of cube and copper atoms occupy the centre of each face. The formula of this compound is:
(a) $AuCu_3$ (b) AuCu
(c) $AuCu_2$ (d) $CuAu_3$

[3] Packing factors for a body centred cubic and simple cubic structure are:
(a) 0.68, 0.524 (b) 0.524, 0.68
(c) 0.48, 0.52 (d) 0.52, 0.48

[4] In solid NH_3, each NH_3 molecule has six other NH_3 molecules as nearest neighbours. ΔH of sublimation of NH_3 at the melting point is 30.8 kJ/mol and the estimated ΔH of sublimation in absence of H-bonding is 14.3 kJ/mol. The strength of H-bond in NH_3 ion kJ/mol is:
(a) 5.5 (b) 11.0
(c) 16.5 (d) 2.75

[5] The fraction of Ni^{2+} and Ni^{3+} ions in $Ni_{0.98}O_{100}$ is:
(a) 96, 4 (b) 90, 10
(c) 4, 96 (d) 10, 90

[6] An element (density 6.8 g/cm^3) occurs in bcc structure with cell edge of 290 pm. The number of atoms present in 200 g of element is:
(a) 24×10^{23} (b) 24×10^{24}
(c) 24×10^{22} (d) 24×10^{20}

Comprehension 2 : In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal closepacked (hcp), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

[1] The number of atoms in this hcp unit cell is: **(IIT 2008)**
(a) 4 (b) 6
(c) 12 (d) 17

[2] The volume of this hcp unit cell is :
(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$
(c) $12\sqrt{2}r^3$ (d) $\frac{64}{3\sqrt{3}}r^3$

[3] The empty space in this hcp unit cell is:
(a) 74% (b) 47.6%
(c) 32% (d) 26%

SOLUTIONS

Comprehension 1

[1] (a) AB_2 has bcc structure, A^{2+} possess face centred cubic lattice. B^- ions occupy all the (100%) tetrahedral voids. Thus each A^{2+} is in contact with $8B^-$ and each B^- with $4A^{2+}$ ions.

[2] (a) An atoms/unit cell $= \frac{1}{8}\times 8 = 1$

Cu atoms/unit cell $= \frac{1}{2}\times 6 = 3$

$\therefore$ empirical formula is $AuCu_3$.

[3] (a) **Body centred cubic :** $r = \frac{\sqrt{3}a}{4}$;

The unit cell of body centred cubic has 2 atoms on the average

$\therefore$ Volume of atoms $= 2\times\frac{4}{3}\pi r^3$

$$= 2\times\frac{4}{3}\times\pi\times\left[\frac{\sqrt{3}a}{4}\right]^3 = \frac{\sqrt{3}}{8}\pi a^3$$

Volume of unit cell $= a^3$

$\therefore$ Packing factor $= \frac{\sqrt{3}}{8}\frac{\pi a^3}{24} = 0.68$

Simple cubic : $r = \frac{a}{2}$; The unit cell of sc has one atom.

$\therefore$ Volume of atoms $= \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{4\pi a^3}{24}$

Volume of unit cell $= a^3$

$\therefore$ Packing factor $= \frac{4}{24}\frac{\pi a^3}{a^3} = 0.524$

[4] (a) Total strength of H-bonds = 30.8 – 14.4 = 16.4 kJ/mol. There are 6 nearest neighbours, but each H-bond involves 2 molecules. Thus, total H-bond $= \frac{6}{2} = 3$

$\therefore$ H-bond energy $= \frac{16.4}{3} = 5.5$ kJ

[5] (a) Let Ni^{2+} be a and Ni^{3+} be $(100-a)$, then

$$a\times 2+(1-a)\times 3 = \frac{2\times 1.0}{0.98}$$

$\therefore$ $a = 95.9\%$

[6] (a) Density $= \frac{n\times\text{atomic mass}}{\text{Av. no.}\times a^3}$ or

$$\frac{2\times A}{6.023\times 10^{23}\times(290\times 10^{-10})^3} = 6.8$$

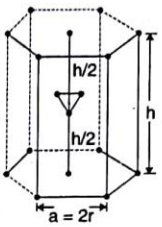
$\therefore$ $A = 50$

$\therefore$ no. of atoms in 200 g $= \frac{6.023\times 10^{23}\times 200}{50}$

$$= 24\times 10^{23}$$

Comprehension 2

In three dimensional closest packing of hcp or ccp (although both are different) only 74% of the available space is occupied by spheres. The remaining 26% space which is vacant, constitutes **interstitial voids** or **interstices sites** or **interstices**. The given packing (*AB AB AB*...) is three dimensional close packing as shown in given figure. In this arrangement three atoms are arranged in the body centred position in such a way, so that it forms equilateral triangle an twelve atoms are placed at 12 corners and two atoms at two face centres.



(i) **No. of atoms per unit cell**

$= \frac{1}{6}\times 12+\frac{1}{2}\times 2+3 = 6$

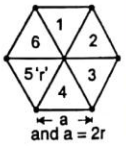
(ii) Thus **co-ordination number** of three dimensional hcp lattice becomes 12, *i.e.*, 6 from own layer and 3 from above and 3 from lower layer.

(iii) **Base Area (A) of unit cell :** Base area of hcp unit cell is given by:

$$A = 6\times\frac{\sqrt{3}}{4}\times a^2$$

$$A = \frac{3\sqrt{3}}{2}a^2$$

$$A = \frac{3\sqrt{3}}{2}\times 4r^2 = 6\sqrt{3}r^2$$



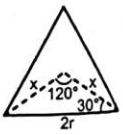
(iv) **Height of unit cell:**

$$\cos 120° = \frac{x^2+x^2-(2r)^2}{2x^2}$$

$$\text{or } -\frac{1}{2} = \frac{2x^2-4r^2}{2x^2} = \frac{x^2-2r^2}{x^2}$$

$$\text{or } 3x^2 = 4r^2$$

$$\therefore\ x = \frac{2r}{\sqrt{3}}$$



$$\text{Now } \left(\frac{h}{2}\right)^2 = a^2-x^2$$

$$\frac{h^2}{4} = (2r)^2-\left(\frac{2r}{\sqrt{3}}\right)^2 \text{ or } \frac{h^2}{4} = \frac{8r^2}{3}$$

$$\therefore\ h^2 = \frac{32r^2}{3} \text{ or } h = 4r\times\sqrt{\frac{2}{3}}$$



(v) **Packing fraction :** Each corner atom would be common to 6 other unit cell. If r is the radius of each sphere, then

$$\text{Packing fraction} = \frac{6\times\frac{4}{3}\pi r^2}{v}$$

where, v = volume of hexagon

= Area of base (A) × height (h)

$$\therefore\ \text{Packing fraction} = \frac{6\times\frac{4}{3}\pi r^2}{6\times\sqrt{3}r^2\times 4r\times\sqrt{\frac{2}{3}}} = \frac{\pi}{3\times\sqrt{2}}$$

$$= 0.74 \text{ or } 74\%$$

(vi) $V = h\times\text{area} = 6\sqrt{3}r^2\times 4r\times\sqrt{\frac{2}{3}} = 24\sqrt{2}r^3$

[1] (b), [2] (a), [3] (d)

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanation **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) **S** is correct but **E** is wrong
(b) **S** is wrong but **E** is correct
(c) Both **S** and **E** are correct and **E** is correct explanation of **S**
(d) Both **S** and **E** are correct but **E** is not correct explanation of **S**

1. S : Initially the term pseudo solid was given for solids, which were easily distorted by bending and compression forces. They even tend to flow slowly under its own mass and lose shape.
E : These characteristics are shown by pseudo solids as in pitch, glass and thus, the name pseudo solid was replaced by super cooled liquids.

2. S : The close packing of atoms in cubic structure is in the order fcc > bcc > sc.
E : Packing density $= \frac{\text{Volume of unit cell}}{a^3}$

3. S : In hexagonal close packing voids are between three touching spheres whose centres lie at the corners of an equilateral triangle.
E : In hexagonal close packing voids are called square voids.

4. S : Bragg's equation has no solution, if $n = 2$ and $\lambda > d$.
E : Bragg's equation is: $n\lambda = 2d \sin\theta$.

5. S : 6 : 6 co-ordination at normal temperature and pressure changes to 8 : 8 co-ordination at high pressure.
E : Pressure influences the structure of solids.

6. S : 8 : 8 co-ordination of CsCl at low temperature changes to 6 : 6 co-ordination at 760 K.
E : Temperature also influences the structure of solids.

7. S : Solids containing F-centres are paramagnetic.
E : F-centres solids possess holes occupied by unpaired electrons.

8. S : Solids having more F-centres possess intense colours.
E : Excess of Na^+ in NaCl solid having F-centres makes it appear to pink.

9. S : The conductance through electrons is called *n*-type conduction and if through positive holes, it is called *p*-type conduction.
E : Doping involves preparation of semi-conductors by the presence of impurities in the intrinsic semi-conductor.

10. S : A crystal having fcc structure is more closely packed than a crystal having bcc structure.
E : Packing fraction for fcc structure is double that of bcc structure.

11. S : In any ionic solid (*MX*) with Schottky defects, number of positive and negative ions are same.
E : Equal number of cation and anion vacancies are present.

12. S : bcc arrangement is less closely packed than ccp arrangement.
E : In ccp 74% of the available space is occupied by spheres but in bcc only 68% of the space is occupied by spheres.

13. S : Ferromagnetic substances are strongly attracted by magnetic field.
E : Ferromagnetism arises due to spontaneous alignment magnetic moments of ions or atoms in the same direction.

14. S : For ionic solids exhibiting Frenkel defects, the density remains unaltered.
E : Doping of group 14 elements with suitable elements of group 13 produces *p*-type of semiconductors.

15. S : In rock salt structure, all the octahedral voids in the close packing of anions are occupied by cations.
E : In rock salt structure, the distance of closest approach between two anions equal to half the face diagonal of unit cell.

16. S : Co-ordination number of CsCl changes from 8 : 8 to 6 : 6 on heating.
E : The crystal structure of CsCl changes to NaCl on heating.

17. S : Equivalent conducting power of H^+ and OH^- ion is maximum and abnormally high among all the ions.
E : There occurs a proton jump from one water molecule to other leading to grothus type conductance.

18. S : Band gap in germanium is small.
E : The energy spread of each germanium atomic energy level is infinitesimally small. **[IIT 2007]**

ANSWERS (Statement Explanation Problems)

1. (d) Both are facts.
2. (c) Explanation is correct reason for statement.
3. (a) In hexagonal close packing voids are triangular voids.
4. (c) If $n = 2$ and $\lambda > d$, then $\sin\theta > 1$, which is not possible.
5. (c) Explanation is correct reason for statement.
6. (c) —do—
7. (c) —do—
8. (a) Excess Na^+ in NaCl solid at F-centres develops yellow colour.
9. (d) Both are facts.
10. (a) Packing fraction in fcc = 74%
    Packing fraction in bcc = 67.9%
11. (c) Explanation is correct reason for statement.
12. (d) Both statement and explanation are correct but the reason is different.
13. (c) Explanation is correct reason for statement.
14. (d) Both statement and explanation are correct but reason for the statement is different.
15. (d) Both statement and explanation are correct but reason for the statement is different.
16. (c) Explanation is correct reason for statement.
17. (c) The given statement and its explanation are correct.
18. (a) Follow text.

MATCHING TYPE PROBLEMS

Type I : Only One Match Possible

1.

List A	List B
(A) Schottky defect	1. NaCl and $SrCl_2$
(B) Frenkel defect	2. Defects produced by heating Na in Cl_2
(C) F-centres	3. NaCl
(D) Metal deficiency	4. AgCl

Type II : More Than One Match Are Possible

2.

List A	List B
(A) Simple cubic and face-centred cubic parameters	(P) have these cell
(B) Cubic and rhombohedral	(Q) are two crystal system
(C) Cubic and tetragonal	(R) have only two crystallographic angles of 90°
(D) Hexagonal and monoclinic	(S) belong to same crystal system

Type III : Only One Match From Each List

3.

List A	List B	List C
1. Cubic	a. $a = b \neq c$	A. $\alpha = \beta = \gamma = 90°$
2. Tetragonal	b. $a \neq b \neq c$	B. $\alpha = \gamma = 90° \neq \beta$
3. Orthorhombic	c. $a = b = c$	C. $\alpha \neq \beta \neq \gamma \neq 90°$
4. Monoclinic		D. $\alpha = \beta = 90°; \gamma = 120°$
5. Triclinic		
6. Rhombohedral		
7. Hexagonal		

4.

List A	List B	List C
1. sc	a. $a = 2.31r$	A. $\frac{\pi}{6}$
2. fcc	b. $a = 2.828r$	B. $\frac{\pi}{3\sqrt{2}}$
3. bcc	c. $a = 2r$	C. $\frac{\sqrt{3}\pi}{8}$

5.

List A	List B
(A) Cubic	1. Simple or primitive
(B) Tetragonal	2. Body centred
(C) Orthorhombic	3. Face centred
(D) Monoclinic	4. End centred

ANSWERS

1. A– 3; B–4; C–2; D–1
2. A – P, S; B – P, Q; C – Q; D – Q,R
3. 1 – c–A; 2–a –A; 3–b–A; 4 –b–B; 5–b – C; 6 – c–B; 7–a–D
4. 1 – c–A; 2–b–B; 3–a– C
5. A– 1,2,3; B–1,2; C–1,2; D–4