Day 6

Chemical Thermodynamics

Day 6

Outlines ...

- Zeroth Law of Thermodynamics
- First Law of Thermodynamics
- Work
- Enthalpy
- Heat
- Entropy Change (ΔS)
- Gibbs Helmholtz Equation
- Carnot Cycle

Thermodynamics

The study of heat or any other form of energy into or out of a system, due to some physical or chemical transformations, is called thermodynamics. It is based on four generalisations i.e., zeroth, first, second and third law of thermodynamics.

Fundamentals of Thermodynamics

The several terms used in thermodynamics are given below.

System

System is a part of universe under observation. It is basically a specific portion which is considered under thermodynamic studies.

On the basis of exchange of mass and energy, systems are of three types

(i) **Isolated System** In which neither matter nor energy can be exchanged with surroundings.

(ii) **Closed System** In which only energy can be exchanged with surroundings.

(iii) **Open System** In which energy and matter both can be exchanged with surroundings.

Surroundings

The part of the universe except system is called **surroundings**.

Thermodynamics Properties

(i) **Intensive Properties** Those properties, that depend on nature of matter but do not depend on quantity of the matter *e.g.*, pressure, temperature, specific heat, melting point etc.

(ii) **Extensive Properties** Those properties, that depend on quantity of the matter present in the system *e.g.*, internal energy, heat, total moles, volume, enthalpy, entropy, free energy etc.

(iii) **State Functions** Those macroscopic properties which depend only on the state of the system and not on how it is reached. *e.g.*, pressure, volume, temperature, ΔH, ΔE etc.

Force is extensive property but pressure is intensive property.

Processes

The state of a variable can be changed by means of a operation called **process**.

These are of following types.

(i) **Adiabatic Process** In which system does not exchange heat with its surrounding *i.e.*, $dQ = 0$.

(ii) **Isothermal Process** In which temperature remains fixed *i.e.*, $dT = 0$.

(iii) **Isobaric Process** In which change of state is brought about at constant pressure *i.e.*, $dp = 0$.

(iv) **Isochoric Process** In which volume of the system remains constant, *i.e.*, $dV = 0$.

(v) **Cyclic Process** This is the process in which a system undergoes a number of different states and finally returns to its initial state. For such a process, change in internal energy and enthalpy is zero *i.e.*, $dE = 0$ and $dH = 0$.

(vi) **Reversible Process** In this process, (quasistatic system), change taken place is infinitesimally slow and their direction at any point can be reversed by infinitesimal change in the state of the system. Reversible process is an ideal process and here, every intermediate state is in equilibrium with others, if any.

(vii) **Irreversible Process** In this process, is the one which can not be reversed. In this process amount of energy increases. All natural processes are irreversible in nature.

Thermodynamics Equilibrium

If macroscopic properties like temperature, pressure, etc., do not change with the time, the system is said to be in thermodynamic equilibrium.

- Mechanical equilibrium, *i.e.*, when no work is done on the system or by the system.
- Thermal equilibrium, *i.e.*, temperature remains constant throughout the system including the surroundings.
- Chemical equilibrium, *i.e.*, composition of the system remains constant and definite.

Internal Energy (E or U)

It is the total energy within the substance. It means sum of translational energy, vibrational energy, potential energy etc. We can only determine the change in internal energy. At constant temperature, internal energy change (ΔE) will be zero. Internal energy depends on temperature, pressure, volume and quantity of matter.

Zeroth Law of Thermodynamics *or* Law of Thermal Equilibrium

If the two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.

The law defines the temperature as the property which determines, whether the body is in thermal equilibrium or not.

First Law of Thermodynamics

Energy can neither be created nor destroyed although it may be converted from one form to another

$$\Delta E = q + W.$$

Sign convention

(i) If W is positive — work done on the system

(ii) If W is negative — work done by the system

(iii) If q is positive-when heat is supplied to the system

(iv) If q is negative-when heat is lost by the system.

Concept of Work

The work has done when gas expands or contracts against the external pressure. Work done is a path function not a state function as depends upon the path followed.

$$W = p_{ext} \times \Delta V$$

- For expansion

$$W = -p_{ext}(V_2 - V_1) \text{ [Here } V_2 > V_1]$$

- For compression

$$W = -p_{ext}(V_2 - V_1) \text{ [Here } V_2 < V_1]$$

- Maximum work done for reversible isothermal process

$$W_{rev} = -2.303\, nRT \log \frac{V_2}{V_1}$$

where, V_2 = final volume, V_1 = initial volume

Also, $W_{rev} = -2.303 nRT \log \frac{p_1}{p_2}$

- Maximum work done for irreversible isothermal expansion

Free expansion

If gas expands in vaccum, $p_{ext} = 0$, therefore, $W = 0$

Intermediate expansion

$p_{ext} < p_{gas}$, $W_{irr} = \int_{V_1}^{V_2} p_{ext} X dV$

xdv as $= -P_{ext}(V_2 - V_1)$

For isothermal irreversible expansion

$$q = -W = p_{ext}(V_2 - V_1)$$

Enthalpy

The total heat content of a system at constant pressure is called the **enthalpy of the system**. Indeed, it is the sum of internal energy and the product of pressure-volume work. It is an extensive quantity and represented by the symbol H. The equation is $H = E + pV$

$$\Delta H = \Delta E + p\Delta V$$

$$\Delta H = \Delta E + \Delta n_g RT$$

where, ΔH = enthalpy change

Δn_g = gaseous moles of products − gaseous moles of reactants.

If $\Delta n_g = 0$, then $\Delta H = \Delta U$; If $\Delta n_g > 0$ then $\Delta H > \Delta U$ and If $\Delta n_g < 0$ then, $\Delta H < \Delta U$.

For reaction involving solids and liquids only $\Delta H = \Delta E$.

Enthalpy also changes, when a substance undergoes phase transition.

Heat

Heat is defined as the quantity of energy, which flows between system and surroundings on account of temperature difference. It is also a path function, i.e., depends upon the path followed.

It is given as

$$H = ms\Delta t$$

where, m = mass of substance

s = specific heat

Δt = temperature difference.

» *Heat flowing into the system is taken as positive and heat flowing out of the system is taken as negative.*

» *Both work and heat appear only at the boundary of the system during a change in state. Both W and q are not state functions but quantity W + q is a state function.*

Heat Capacity

Heat capacity (C) of a system is defined as the amount of heat required to raise the temperature of the system by 1°C.

$$C = \frac{q}{\Delta T}$$

If the system consists of a single substance or a solution and weighs 1 mole, the heat capacity of the system is referred as **molar heat capacity.**

If the system consists of a single substance or a solution and weights 1 g, the heat capacity of the system is referred as **specific heat of the system.**

$$\sigma_L = C \times m \times \Delta T$$

where, m = mass of substance,

C = specific heat capacity.

Molar Heat Capacity in Different Cases

(i) In case of gases heat given to the system depends upon the condition of constant pressure (p) or constant volume (V).

Molar heat capacity at constant pressure

$$C_p = C_p \times M$$

Molar heat capacity, at constant volume, $C_V = C_V \times M$

(C_p and C_V are specific heats at constant pressure and volume respectively and M is molecular weight of gas.)

(iv) $C_p - C_V = R$ (R is the molar gas constant.)

$$C_p - C_V = \frac{R}{M}$$

(v) The molar heat capacity at constant volume,

$$C_V = \left(\frac{3}{2}\right)R$$

(vi) Molar heat capacity at constant pressure,

$$C_p = \left(\frac{3}{2}\right)R + R$$
$$= \left(\frac{5}{2}\right)R$$

(vii) Poisson's ratio, $\gamma = \frac{C_p}{C_V} = \left(\frac{5}{3}\right) = 1.66$

$\gamma = 1.66$ for monoatomic gases (like He, Ar)
$\gamma = 1.40$ for diatomic gases (like H_2, O_2, CO)
$\gamma = 1.33$ for triatomic gases (like H_2O, O_3)

Kirchhoff's Equation

According to this equation, the partial derivate of the change of enthalpy (or of internal energy) during a reaction, with respect to temperature, at constant pressure (or volume) equals the change in heat capacity at constant pressure (or volume).

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

and $$\Delta C_V = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$$

where, $\Delta C_p = \Sigma C_p$ of products $- \Sigma C_p$ of reactants
$\Delta C_V = \Sigma C_V$ of products $- \Sigma C_V$ of reactants

Entropy Change (ΔS)

Entropy is the measurement of randomness or disorder of the molecules.

"For a spontaneous process in an isolated system, the change in entropy is positive this statement is known as Second law of thermodynamics".

A process, which proceeds of its own accord without any outside help is termed as **spontaneous process**.

Entropy is a state function and depends only on initial and final states of the system. *i.e.*, $\Delta S = S_{\text{final}} - S_{\text{initial}}$.

Unit of entropy is joule per kelvin per mol.

Entropy is the measure of unavailable energy.

Unavailable energy = entropy × temperature.

$$\Delta S_{\text{universe}} > 0$$

"The entropy of a substance varies directly with the temperature. At absolute zero, the entropy of a pure crystal is zero. This statement is known as **Third law of thermodynamics**".

$\Delta S \geq 0$ favours the spontaneity

$\Delta S < 0$ favours the non-spontaneity

For a reversible change at constant temperature

$$\Delta S = \frac{q_{\text{rev}}}{T} = S_{\text{final}} - S_{\text{initial}}$$

q_{rev} = heat absorbed or evolved at absolute temperature, T

If $\Delta S > 0$, heat is absorbed and if $\Delta S < 0$, heat is evolved.

The change of matter from one state to another is called **phase transition.** The entropy changes at the time of phase transition are as follows

$$\Delta S_{\text{melting}} = \frac{\Delta H_{\text{fusion}}}{T_m}; (T_m = \text{melting point of susbstance})$$

$$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_b}; (T_b = \text{boiling point of substance})$$

$$\Delta S_{\text{sublimation}} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sub}}}; (T_{\text{sub}} = \text{sublimation temperature})$$

Third Law of Thermodynamics

This law was proposed by German chemist **Walther Nernst.** According to this law, "*The entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached*". It forms the basis from which entropies at other temperatures can be measured.

$$\lim_{T \to 0} S = 0$$

Gibbs Helmholtz Equation

The changes in the gibbs energy of a system as a function of temperature can be calculated by the equation known.

$$\Delta G = \Delta H - T\Delta S$$

where, ΔG = Gibbs free energy (measurement of useful work)

The following cases are considered for ΔG.

(i) $\Delta G > 0$, for non-spontaneous process
(ii) $\Delta G < 0$, for spontaneous process
(iii) $\Delta G = 0$, at equilibrium

- In determination of spontaneity, Gibbs energy criteria is better than entropy criteria because Gibbs energy refers to the system only while entropy refers to both system and surroundings $\Delta G = \Delta G° + 2.303\,RT \log Q$

  where, Q = reaction quotient
- At equilibrium, $\Delta G = 0$

$\therefore$ $$\Delta G° = -2.303\,RT \log K$$

K = equilibrium constant

$$\Delta G° = -n E°_{\text{cell}} F$$

where, n = number of electrons losed or gained

$E°_{\text{cell}}$ = standard electrode potential, 1F = 96500 C

Conversion of Heat into Work

(Carnot Cycle)

***Carnot** in 1824 gave an imaginary reversible cycle which demonstrates the maximum conversion of heat into work. He actually proposed a theoretical heat engine to show that its efficiency was based upon the temperatures, between which it operated. Infact, heat engine is a machine which can do work by using heat that flows out spontaneously from a high temperature source to a low temperature sink.*

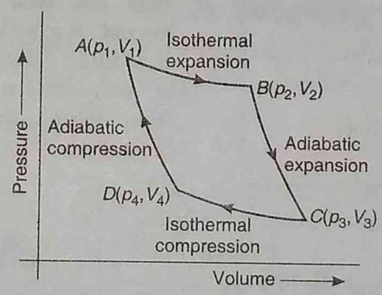
A Carnot cycle comprises four operations or processes:

(i)Isothermal reversible expansion

(ii)Adiabatic reversible expansion

(iii)Isothermal reversible compression

(iv)Adiabatic reversible compression



(a)Net work done in 1 cycle is $W = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3} \mathrm{V}$

(b) Neheat absorbed in the whole cycle is $q = R(T_2 - T_1) \ln \frac{V_2}{V_1}$

The ratio of the work obtained in a cyclic process (W) to the heat taken from a high efficiency reservoir is called the **efficiency of heat engine.** It is denoted by η.

$$\eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

The above relation shows that efficiency depends upon the temperature limits between which the cycle operates. The above relation was stated in the form of **Carnot theorem** by Carnot *i.e.*, "*Every perfect engine working reversibly between the same temperature limits has the same efficiency, whatever be the working substance.*"

Practice Zone DAY 6

1. When 1.8 g of steam at the normal boiling point of water is converted into water, at the same temperature, enthalpy and entropy changes respectively will be
[Given ΔH_{vap} for water $= 40.8\,kJ\,mol^{-1}$]
(a) -8.12 kJ, 11.89 JK^{-1} (b) 10.25 kJ, 12.95 JK^{-1}
(c) -4.08 kJ, -10.93 JK^{-1} (d) 10.93 kJ, -4.08 JK^{-1}

2. When the heat of a reaction at constant pressure is -2.5×10^3 cal and entropy change for the reaction is 7.4 cal deg^{-1}, it is predicted that the reaction at 25°C is
(a) reversible (b) spontaneous
(c) non-spontaneous (d) irreversible

3. Which of the following does not have zero entropy even at absolute zero?
CO, CO_2, NaCl, NO
(a) CO, CO_2 (b) CO, NO
(c) CO_2, NaCl (d) NaCl

4. In which case, a spontaneous reaction is possible at any temperature?
(a) ΔH(–ve), ΔS + (ve) (b) ΔH(–ve), ΔS – (ve)
(c) ΔH + (ve), ΔS + (ve) (d) None of these

5. For two moles of an ideal gas
(a) $(C_V - C_p) = -2R$ (b) $(C_p - C_V) = 0$
(c) $(C_p - C_V) = R$ (d) $(C_p - C_V) = R/2$

6. What will be the change of entropy $\Delta_r S°$ at 298 K for the reaction in which urea is formed from NH_3 and CO_2?
$$2NH_3(g) + CO_2(g) \longrightarrow NH_2CONH_2(aq) + H_2O(l)$$
[Given the standard entropy of $NH_2CONH_2(aq)$, $CO_2(g)$, $NH_3(g)$ and $H_2O(l)$ are 174.0, 213.7, 192.3 and 69.9 $JKmol^{-1}$ respectively]
(a) 200 $JK^{-1}\,mol^{-1}$ (b) -35.44 $JK^{-1}\,mol^{-1}$
(c) -354.4 $JK^{-1}\,mol^{-1}$ (d) 425.2 $JK^{-1}\,mol^{-1}$

7. 1 mole of CO_2 gas at 300 K is expanded under adiabatic conditions such that its volume becomes 27 times. What is work done? ($\gamma = 1.33$ and $C_V = 6\,cal\,mol^{-1}$ for CO_2)
(a) 900 cal (b) 1000 cal
(c) 1200 cal (d) 1400 cal

8. Internal energy and pressure of a gas of unit volume are related as
(a) $p = \frac{2}{3}E$ (b) $p = \frac{E}{2}$
(c) $p = \frac{3}{2}E$ (d) $p = 2E$

9. Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10.0 kcal/mol. What will be the change in internal energy (ΔE) of 3 mole of liquid at same temperature?
(a) 30 kcal (b) –54 kcal
(c) 27.0 kcal (d) 50 kcal

10. 1 mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The ΔE for this process is ($R = 2$ cal K^{-1} mol^{-1})
(a) 270 cal (b) zero
(c) 10 L atm (d) 181.7 cal

11. The pressure-volume work for an ideal gas can be calculated by using the expression $W = -\int_{V_i}^{V_f} p_{ex}\,dV$. The work can also be calculated from the pV – plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibility from volume V_i to V_f. Choose the correct option. **[NCERT Exemplar]**
(a) W (reversible) = W (irreversible)
(b) W (reversible) < W (irreversible)
(c) W (reversible) > W (irreversible)
(d) W (reversible) = W (irreversible) + $p_{ex}\Delta V$

12. 2 moles of an ideal gas at 27°C are expanded reversibly from 2 L to 20 L. Find entropy change.
($R = 2$ cal / mol K)
(a) 0 (b) 4
(c) 9.2 (d) 92.0

13. At 27° C, latent heat of fusion of a compound is 2930 J/mol. Entropy change during fusion is
(a) 9.77 J/mol K
(b) 0.977 J/mol K
(c) 9.07 J/mol K
(d) None of the above

14. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following. **[NCERT Exemplar]**

(a) $q = 0, \Delta T \neq 0, W = 0$ (b) $q \neq 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T = 0, W = 0$ (d) $q = 0, \Delta T < 0, W \neq 0$

15. For an isomerisation reaction $A \rightleftharpoons B$, the temperature dependence of equilibrium constant is given by

$$\log_e K = 4.0 - \frac{2000}{T}$$

The value of $\Delta S°$ at 300 K is therefore,

(a) $4R$ (b) $5R$ (c) $400\,R$ (d) $2000\,R$

16. A carnot engine operates between temperature T and 400 K ($T > 400$ K). If efficiency of engine is 25%, the temperature T is

(a) 666.0 K (b) 498.5 K
(c) 533.3 K (d) 500.0 K

17. Which correctly represents the physical significance of Gibbs energy change?

(a) $-\Delta G = W_{\text{compression}}$
(b) $-\Delta G = W_{\text{expansion}}$
(c) $\Delta G = -W_{\text{expansion}} = W_{\text{non-expansion}}$
(d) $\Delta G = W_{\text{expansion}}$

18. Water is brought to boil under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporised. Calculate the molar internal energy change at boiling point (373.15 K).

(a) 37.5 kJ mol^{-1} (b) 3.75 kJ mol^{-1}
(c) 42.6 kJ mol^{-1} (d) 4.26 kJ mol^{-1}

19. An ideal gas expands in volume from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 Nm^{-2}. The work done is

(a) 900 kJ (b) –900 kJ
(c) 270 kJ (d) –900 J

20. When 1 mole of a gas is heated at constant volume, temperature is raised from 298 K to 308 K. Heat supplied to the gas is 500 J. Then, which statement is correct?

(a) $q = -W = 500\,J$, $\Delta E = 0$ (b) $q = W = 500\,J$, $\Delta E = 0$
(c) $q = \Delta E = 500\,J$, $W = 0$ (d) $\Delta E = 0, q = W = -500\,J$

21. The molar heat capacity of water at constant pressure is 75 J $K^{-1}mol^{-1}$. When 1.0 kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is

(a) 1.2 K (b) 2.4 K (c) 4.8 K (d) 6.8 K

22. At 1 atm pressure, $\Delta S = 75$ J K^{-1} mol^{-1}; $\Delta H = 30$ kJ mol^{-1}. The temperature of the reaction at equilibrium is

(a) 400 K (b) 330 K
(c) 200 K (d) 110 K

23. What is the entropy change (in J K^{-1} mol^{-1}), when one mole of ice is converted into water at 0°C ? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C.)

(a) 20.13 (b) 2.013 (c) 2.988 (d) 21.98

24. In which process net work done is zero?

(a) Cyclic (b) Isobaric
(c) Adiabatic (d) Free expansion

25. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

(a) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$; +ve
(b) ΔS_{system} be zero
(c) $\Delta S_{\text{system}} - \Delta S_{\text{surrounding}}$; + ve
(d) $\Delta S_{\text{surrounding}}$; zero

26. The van't Hoff reaction isotherm is

(a) $\Delta G = RT \log K_p$
(b) $-\Delta G = RT \ln K_p$
(c) $\Delta G = RT^2 \ln K_p$
(d) None of the above

27. The direct conversion of A to B is difficult, hence it is carried out by the following shown path

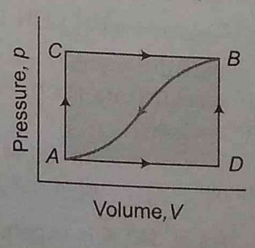
$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

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, then $\Delta S_{(A \to B)}$ is

(a) + 100 eu (b) + 60 eu
(c) – 100 eu (d) – 60 eu

Directions (Q. Nos. 28 to 30) *When a system is taken from state A to state B along the path ACB as shown, 80 J of heat flows into the system and the system does 30 J of work.*



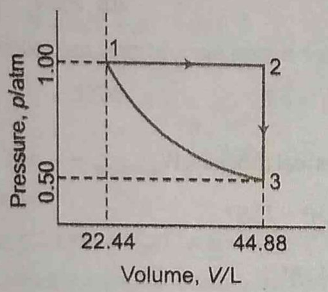
28. How much heat flows into the system along path ADB, if the work done is 10 J?

(a) 80 J (b) 40 J
(c) 50 J (d) 60 J

29. When the system is returned from state B to A along the curved path, work done on the system is 20 J. Does the system absorb or liberate heat, and how much?
(a) System liberates heat, −70 J (b) System absorbs heat, 70 J
(c) System absorbs heat, 90 J (d) System liberates heat, −90 J

30. If $E_D - E_A = 40$ J, heat absorbed in the process DB is
(a) 50 J (b) + 30 J (c) + 60 J (d) + 10 J

Directions (Q. Nos. 31 and 32) *A sample consisting of 1 mole of a monoatomic perfect gas* $\left(C_V = \frac{3}{2}R\right)$ *is taken through the cycle as shown*



31. Temperature at points 1, 2 and 3 are respectively
(a) 273 K, 546 K, 273 K (b) 546 K, 273 K, 273 K
(c) 273 K, 273 K, 273 K (d) 546 K, 546 K, 273 K

32. ΔE for the process $(1 \rightarrow 2)$ is
(a) 0.00 J (b) $+3.40 \times 10^3$ kJ
(c) −3.40 J (d) -3.40×10^3 J

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. Statement I The thermodynamic function, which determines the spontaneity of a process is the free energy. For a process to be spontaneous, the change in free energy must be negative.

Statement II The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must be always positive if it is spontaneous.

34. Statement I Spontaneous process is an irreverssible process and may be reversed by some external agency.

Statement II Decrease in enthalpy is a contributory factor for spontaneity.

35. Statement I Two bodies at thermal equilibrium may or may not have equal heat.

Statement II Two bodies at thermal equilibrium have same temperature.

36. Statement I As solid changes to liquid and then to vapour state, entropy increases.

Statement II As going from solid to liquid and then to vapour state, disorder increases.

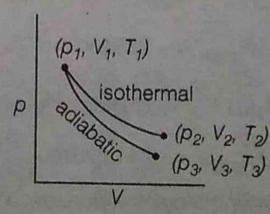
37. The enthalpy of vaporisation of liquid diethyl ether $(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35°C). What will be the ΔS for conversion of liquid to vapour and vapour to liquid respectively?
(a) + 84.41 and −84.41 JK^{-1} mol^{-1}
(b) + 80.90 and −68.83 JK^{-1} mol^{-1}
(c) − 84.41 and + 90.63 JK^{-1} mol^{-1}
(d) + 68.83 and −84.41 JK^{-1} mol^{-1}

38. 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. The increase in internal energy of process is
(a) 305.85 J (b) 394.95 J
(c) 405.83 J (d) −463.28 J

39. The heat of sublimation of iodine is 24 cal g^{-1} at 50°C. If specific heat of solid iodine and its vapours are 0.055 and 0.031 cal g^{-1} respectively, the heat of sublimation of iodine at 100°C is
(a) 22.8 cal g^{-1} (b) 25.2 cal g^{-1}
(c) −22.8 cal g^{-1} (d) −25.2 cal g^{-1}

40. For a reaction $M_2O(s) \longrightarrow 2M(s) + \frac{1}{2}O_2(g)$,
$\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm. The temperature upto which the reaction would not be spontaneous is
(a) $T < 400.08$ K (b) $T < 273.15$ K
(c) $T < 428.57$ K (d) $T < 473.50$ K

41. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement is incorrect?



(a) $T_1 = T_2$ (b) $T_3 > T_1$
(c) $W_{(isothermal)} > W_{(adiabatic)}$ (d) $\Delta U_{(isothermal)} > \Delta U_{(adiabatic)}$

AIEEE & JEE Main Archive

42. 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 σ_L and w for the process will be [$R = 8.314$ J/mol K)
(ln 7.5 = 2.01) **[JEE Main Online 2013]**

(a) $\sigma_L = -208$ J, $w = -208$ J (b) $\sigma_L = -208$J, $w = +208$ J
(c) $\sigma_L = +208$J, $w = +208$J (d) $\sigma_L = +208$J, $w = -208$J

43. Given,

Reaction	Energy change (in kJ)
$Li(s) \longrightarrow Li(g)$	161
$Li(g) \longrightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \longrightarrow F(g)$	77
$F(g) + e^- \longrightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \longrightarrow LiF(s)$	−1047
$Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$	−617

Bases on data provided, the value of electron gain enthalpy of fluorine would be **[JEE Main Online 2013]**

(a) -300 kJ mol^{-1} (b) -350 kJ mol^{-1}
(c) -328 kJ mol^{-1} (d) -228 kJ mol^{-1}

44. A piston filled with 0.04 mole 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 log 7.5 = 2.01) **[JEE Main Online 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

45. Electron gain enthalpy with negative sign of fluorine is less than that of chlorine due to **[JEE Main Online 2013]**

(a) high ionization enthalpy of fluorine
(b) smaller size of chlorine atom
(c) smaller size of fluorine atom
(d) bigger size of 2p orbital of fluorine

46. Given, (a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

$$\Delta H^\circ_{298\,K} = -285.9\,\text{kJmol}^{-1}$$

(b) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$;

$$\Delta H^\circ_{298\,K} = -241.8\,\text{kJmol}^{-1}$$

the molar enthalpy of vaporization of water will be **[JEE Main Online 2013]**

(a) 241.8 kJ mol^{-1} (b) 22.0 kJ mol^{-1}
(c) 44.1 kJ mol^{-1} (d) 527.7 kJ mol^{-1}

47. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2, \Delta_r G = +940 \text{ kJ mol}^{-1}$$

The potential difference needed for the electrolytic reduction of aluminium oxide at 500°C should be atleast **[JEE Main Online 2013]**

(a) 4.5 V (b) 3.0 V
(c) 5.0 V (d) 2.5 V

48. The incorrect expression among the following is **[AIEEE 2012]**

(a) $\frac{\Delta G_{\text{system}}}{\Delta G_{\text{total}}} = -T$

(b) In isothermal process, $W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$

(c) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

(d) $K = e^{-\Delta G^\circ/RT}$

49. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is **[AIEEE 2011]**

(a) 38.3 J mol^{-1} K^{-1} (b) 35.8 J mol^{-1} K^{-1}
(c) 32.3 J mol^{-1} K^{-1} (d) 42.3 J mol^{-1} K^{-1}

50. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,$$ **[AIEEE 2010]**

$$\Delta_r G = +966 \text{ kJ mol}^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least

(a) 4.5 V (b) 3.0 V (c) 2.5 V (d) 5.0 V

51. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

(a) $T_e > T$ (b) $T > T_e$ **[AIEEE 2010]**
(c) T_e is 5 times T (d) $T = T_e$

52. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is **[AIEEE 2009]**

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K standard Gibbs energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are − 166.2, − 237.22 and − 394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is − 726 kJ mol^{-1}, efficiency of the fuel cell will be

(a) 80% (b) 87% (c) 90% (d) 97%

53. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1} respectively. For the reaction,

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3,\ \Delta H = -30\text{ kJ}$$

to be at equilibrium, the temperature will be **[AIEEE 2008]**

(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K

54. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

Given, $\Delta_r H^\circ_{298\,K} = -54.07$ kJ mol^{-1}

$\Delta_r S^\circ_{298\,K} = 10$ JK^{-1} mol^{-1}

and $R = 8.314$ JK^{-1} mol^{-1}

$= 2.303 \times 8.314 \times 298$

$= 5705$ **[IIT JEE 2007]**

(a) 5 (b) 10
(c) 95 (d) 100

55. For the process,

$H_2O(l)$ (1 bar, 273 K) $\rightarrow H_2O(g)$ (1 bar, 373 K),

The correct set of thermodynamic parameters is **[IIT JEE 2007]**

(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0,\ \Delta S = -ve$
(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

56. $(\Delta H - \Delta E)$ for the formation of carbon monoxide (CO) from its elements at 298 K is ($R = 8.314$ JK^{-1} mol^{-1}) **[AIEEE 2006]**

(a) -2477.57 J mol^{-1} (b) 2477.57 J mol^{-1}
(c) -1238.78 J mol^{-1} (d) 1238.78 J mol^{-1}

57. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas? **[IIT JEE 2006]**

(a) $4R/2$
(b) $3R/2$
(c) $5R/2s$
(d) Zero

58. 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? **[AIEEE 2006]**

(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 processes

59. When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm, changes volume from 1 L to 2 L. The final temperature in kelvin would be **[IIT JEE 2005]**

(a) $\frac{T}{2^{2/3}}z$ (b) $T + \frac{2}{3 \times 0.0821}$
(c) T (d) $T - \frac{2}{3 \times 0.0821}$

60. For a spontaneous reaction the ΔG, equilibrium constant (K) and E°_{cell} will be respectively. **[AIEEE 2005]**

(a) $-ve, >1, -ve$ (b) $-ve, <1, -ve$
(c) $+ve, >1, -ve$ (d) $-ve, >1, +ve$

61. Spontaneous adsorption of a gas on solid surface is an exothermic process because **[IIT JEE 2004]**

(a) ΔH increases for system (b) ΔS increases for gas
(c) ΔS decreases for gas (d) ΔG increases for gas

62. A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2, work done is found to be $J(q_1 + q_2)$. This is in accordance with **[AIEEE 2002]**

(a) first law of thermodynamics
(b) second law of thermodynamics
(c) Joules equivalent law
(d) None of the above

63. In thermodynamics, a process is called reversible when **[IIT JEE 2001]**

(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

Answers

1. (c)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (a)	**9.** (c)	**10.** (b)
11. (b)	**12.** (c)	**13.** (a)	**14.** (c)	**15.** (a)	**16.** (c)	**17.** (b)	**18.** (a)	**19.** (d)	**20.** (c)
21. (b)	**22.** (a)	**23.** (d)	**24.** (d)	**25.** (a)	**26.** (b)	**27.** (b)	**28.** (b)	**29.** (b)	**30.** (d)
31. (a)	**32.** (b)	**33.** (a)	**34.** (b)	**35.** (b)	**36.** (a)	**37.** (a)	**38.** (b)	**39.** (a)	**40.** (c)
41. (b)	**42.** (d)	**43.** (c)	**44.** (a)	**45.** (c)	**46.** (c)	**47.** (d)	**48.** (d)	**49.** (a)	**50.** (b)
51. (a)	**52.** (d)	**53.** (a)	**54.** (a)	**55.** (d)	**56.** (d)	**57.** (c)	**58.** (c)	**59.** (d)	**60.** (d)
61. (c)	**62.** (c)	**63.** (c)							

Hints & Solutions

1. $\Delta H_{\text{condensation}}$ for 1.8 g of steam

$$= (-40.8) \times \frac{1.8}{18} = -4.08\ \text{kJ}$$

$$\Delta S = \frac{\Delta H}{T_b} = \frac{-4.08 \times 10^3}{373.15} = -10.93\ \text{JK}^{-1}$$

2. Heat at constant pressure means enthalpy, *i.e.*,

$$\Delta H = -2.5 \times 10^3\ \text{cal}$$
$$\Delta S = 7.4\ \text{cal deg}^{-1}$$
$$T = 298\ \text{K}$$
$$\Delta G = \Delta H - T\Delta S$$
$$= -2.5 \times 10^3 - 298 \times 7.4 = -4705\ \text{cal}$$

Hence, the process is spontaneous.

3. CO and NO molecules in solid states at 0 K adopt a nearly random arrangement indicating a positive value of entropy. It is due to their dipole moment which results in disorder.

4. For a spontaneous process, $\Delta G = -\text{ve} = \Delta H - T\Delta S$

$\therefore$ $\Delta H = -\text{ve},\ \Delta S = +\text{ve}$

5. C_p and C_V are the terms for molar capacities.

6. For the given change

$$\Delta_r S^\circ = \Sigma n_P S_P^\circ - \Sigma n_R S_R^\circ$$
$$= S^\circ_{NH_2CONH_2} + S^\circ_{H_2O} - [2 \times S^\circ_{NH_3} + S^\circ_{CO_2}]$$
$$= 174.0 + 69.9 - [2 \times 192.3 + 213.7]$$
$$= -354.4\ \text{JK}^{-1}\ \text{mol}^{-1}$$

7. For adiabatic condition $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$

$$\frac{T_2}{T_1} = \left(\frac{1}{27}\right)^{1.33-1} = \left(\frac{1}{27}\right)^{0.33} = \left(\frac{1}{27}\right)^{1/3} = \frac{1}{3}$$

$$T_2 = 300 \times \frac{1}{3} = 100\ \text{K}$$

Thus, $T_2 < T_1$, hence cooling takes place due to expansion under adiabatic condition.

$$\Delta E = q + W = W$$

($\because q = 0$ for adiabatic change.)

Sign of ΔE is negative because the gas expands.

$$W = -\Delta E = -C_V(T_2 - T_1)$$
$$= -6(100 - 300) = 1200\ \text{cal}$$

8. $p \times 1 = RT$

Internal energy, $E = \frac{3}{2}RT = \frac{3}{2}p$

$$p = \frac{2}{3}E$$

9. $\Delta H = \Delta E + \Delta n_g RT$

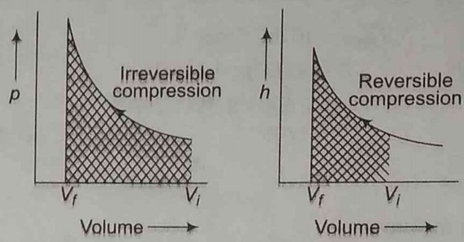
Given, $\Delta H = 30$ kcal for 3 mol

$\Delta n_g = 3$ because, liquid $\rightleftharpoons$ vapour

$$30 = \Delta E + 3 \times 2 \times 500 \times 10^{-3}$$
$$\Delta E = 27\ \text{kcal}$$

10. For isothermal process, $\Delta E = 0$

11.



Area under the curve is more in irreversible compression than the area under curve of reversible compression. Thus, $W_{\text{irreversible}} < W_{\text{reversible}}$

12. $\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 \times 2 \times 2 \log \frac{20}{2} = 9.2$

13. $\Delta S = \frac{\Delta H_f}{T} = \frac{2930}{300} = 9.773\ \text{J K}^{-1}\ \text{mol}^{-1}$

14. In free expansion, $W = 0$ while in adiabatic process, $\sigma_L = 0$,

$$\Delta u = \sigma_L + W = 0$$

This suggests that internal energy remains constant. Therefore, $\Delta T = 0$. Expansion of an ideal gas under adiabatic conditions in a vacuum leads to no absorption/evolution of heat. Thus, no external work is done for the separation of gaseous molecules.

15. Variation of K with temperature is given by

$$\log K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Given, $\log K = 4.0 - \frac{2000}{T}$

On comparing, $\frac{\Delta S^\circ}{R} = 4$

or $\Delta S^\circ = 4R$

16. $\eta\ (\text{efficiency}) = \frac{T_2 - T_1}{T_2}$

$$0.25 = \frac{T - 400}{T}$$

$\therefore$ $T = 533.3\ \text{K}$

17. A decrease in Gibbs energy results in useful work done by the system, *i.e.*, work of expansion $(-W_{\text{expansion}})$ or $-\Delta G = W_{\text{expansion}}$

18. ΔH = work done $= i \times V \times t$ J $= 0.50$ A $\times 12$ V $\times 300$ s

$= 1800$ J $= +1.8$ kJ

Molar enthalpy of vaporisation,

$$\Delta H_m = \frac{\Delta H}{\text{moles of } H_2O} = \frac{\Delta H}{n_{H_2O}} = \frac{1.8 \text{ kJ}}{\frac{0.798}{18}} = 40.6 \text{ kJ mol}^{-1}$$

$$\Delta H_m = \Delta E_m + p\,\Delta V$$
$$\Delta H_m = \Delta E_m + \Delta n_g RT$$
$$\Delta H_m = \Delta E_m + RT \quad [\Delta n_g = 1 \text{ for } H_2O\,(l) \rightleftharpoons H_2O\,(g)]$$

Molar internal energy change,

$$\Delta E_m = \Delta H_m - RT$$
$$= 40.6 - 8.314 \times 10^{-3} \times 373.15 = 37.5 \text{ kJ mol}^{-1}$$

19. Work done by gas $= -p_{ext} \times$ change in volume

$$= -10^5(10^{-2} - 10^{-3}) = -10^5 \times 0.009 = -900 \text{ J}$$

20. At constant volume, $p\Delta V = 0$,

$\therefore \quad q = \Delta E$

21.
$$Q = mC_p\Delta T$$
$$1000 = \frac{100}{18} \times 75 \times \Delta T$$
$$\Delta T = 2.4 \text{ K}$$

22.
$$\Delta G = \Delta H - T\Delta S$$

At equilibrium, $\Delta G = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{75} = 400 \text{ K}$$

23. $\Delta S_f = \dfrac{\Delta H_f}{T} = \dfrac{6 \times 10^3}{273} = 21.98$ J

24. $W = -p\Delta V$ (p = zero in vacuum)

$\therefore \quad W = 0$

25. For a spontaneous process,

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ be positive.

26. $\Delta G = -RT \ln K_p = -2.303\,RT \log K_p$

27.

	ΔS
$A \to C$	50 eu
$C \to D$	30 eu
$D \to B$	–20 eu
$A \to B$	60 eu

28.
$$\Delta E(ACB) = 80 - 30 = 50 \text{ J}$$
$$\therefore \quad Q(ADB) = \Delta E - W = 50 - 10 = 40 \text{ J}$$

29.
$$W(B \to A) = 20 \text{ J}$$
$$Q = ?$$
$$\Delta E = Q + W$$
$$50 = Q - 20$$
$$Q = 70 \text{ J}$$

i.e., system absorbs heat.

30.
$$\Delta E(ADB) = \Delta E(A \to D) + \Delta E(D \to B)$$
$$50 \text{ J} = 40 + \Delta E(D \to B)$$
$$\Delta E(D \to B) = 10 \text{ J}$$
$$Q(D \to B) + W(D \to B) = 10 \text{ J}$$
$$Q(D \to B) + 0 = 10 \text{ J} \qquad (\because V = \text{constant})$$
$$Q(D \to B) = 10 \text{ J}$$

31. At point (1), pressure is 1 atm and volume is 22.4 L for one mole which indicates NTP states. Thus, temperature is 273 K. At point (2), pressure is again 1 atm but volume is doubled, so that temperature is also doubled. At point (3), pressure is halved but volume is doubled, so that temperature is 273 K.

32. $\Delta E = nC_V\Delta T$

$$= 1 \times \frac{3}{2} \times 8.314 \times 273 = 3.4 \times 10^3 \text{ kJ}$$

33. Statement II is the correct explanation for statement I.

34. Both the statements are correct but statement II is not the correct explanation for statement I.

35. Both are facts.

36. Statement II is the correct explanation for statement I.

37. $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T} = \dfrac{26 \times 10^3}{308} = +84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\Delta S_{cond} = \frac{\Delta H_{cond}}{T} \qquad [\because \Delta H_{cond} = -26 \text{ kJ}]$$
$$= -\frac{26 \times 10^3}{308} = -84.41 \text{ JK}^{-1} \text{ mol}^{-1}$$

38. Work is done against constant pressure and thus, irreversible.

Given, $\quad \Delta V = 6 - 2 = 4$ L

$p = 1$ atm

$$W = p \times dV = -1 \times 4 \text{ L atm}$$
$$= -\frac{1 \times 4 \times 1.987}{0.0821} \text{cal}$$

$(\because 0.0821 \text{ L atm} = 1.987 \text{ cal}) = -96.81$ cal

$$= -96.81 \times 4.184 \text{ J} = -405.04 \text{ J}$$

From first law of thermodynamics

$$q = \Delta E - W$$
$$\Delta E = q + W = 800 - 405.04 = 394.95 \text{ J}$$

39. Kirchhoff's equation,

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$
$$\Delta H_2 - \Delta H_1 = \Delta C_p\,(T_2 - T_1)$$
$$\Delta H_2 - 24 = (0.031 - 0.055)(100 - 50)$$
$$\Delta H_2 = 22.8 \text{ cal g}^{-1}$$

40. For a non-spontaneous reaction,

$$\Delta G = +\text{ve}$$
$$\Delta G = \Delta H - T\Delta S$$

$\therefore \Delta H - T\Delta S$ should be +ve.

or

$$\Delta H > T\Delta S$$

which is possible if $T < \dfrac{\Delta H}{\Delta S}$

Given, $\Delta H = 30 \times 10^3$ J mol^{-1}

$\Delta S = 70$ JK^{-1} mol^{-1}

$$T < \frac{30 \times 10^3}{70}$$

$$T < 428.57 \text{ K}$$

41. (a) Since, change of state (p_1, V_1, T_1) to (p_2, V_2, T_2) is isothermal therefore, $T_1 = T_2$ (correct statement)

(b) Since, change of state (p_1, V_1, T_1) to (p_3, V_3, T_3) is an adiabatic expansion, it brings about cooling of gas, therefore, $T_3 < T_1$. Thus, it is incorrect.

(c) Work done is the area under the curve of p-V diagram. As obvious from the given diagram, magnitude of area under the isothermal curve is greater than that under adiabatic curve, hence $W_{\text{isothermal}} > W_{\text{adiabatic}}$ (correct statement)

(d) $\Delta U = nC_V \Delta T$

In isothermal process, $\Delta U = 0$ as $\Delta T = 0$

In adiabatic process,

$\Delta U = nC_v (T_3 - T_1) < 0$ as $T_3 < T_1$

$\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$ (correct statement)

42. In isothermal reversible expansion, $\Delta U = 0$, thus, $\sigma_L = -W$

Therefore, $W = -208$ J

43. From Born-Haber cycle,

$$Q = S + I + D + \text{EA} + U$$

$$-617 = 161 + 520 + 77 + \text{EA} - 1047$$

[$\because$ Here, S = sublimation energy, I = ionisation energy, D = dissociation energy, EA = electron gain enthalpy and U = lattice energy.

$\therefore$ EA $= 289 - 617$

$= -328$ kJ mol^{-1}

44. The process is isothermal expansion, hence

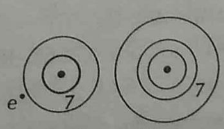
$q = -W$.

$\Delta E = 0$

$q = +208$ J

$W = -208$ J (*expansion work*)

45. Due to smaller size and high repulsive force within the outermost orbit of fluorine its electron gain enthalpy is less negative.



High repulsion

46. Molar enthalpy of vaporization $= 285.9 - 241.8$

$= 44.1$ kJ mol^{-1}

47. $\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2;\ \Delta_r G = +940$ kJ mol^{-1}

Half cell reactions are $\frac{2}{3}Al_2^{3+} + 4e^- \longrightarrow \frac{4}{3}Al$

$$2O^{2-} \longrightarrow O_2 + 4e^-$$

$$\frac{2}{3}Al_2^{3+} + 2O^{2-} \longrightarrow \frac{4}{3}Al + O_2$$

Number of electrons involved, $n = 4$

We know that, $\Delta_r G = nF E_{\text{cell}}$

$$E_{\text{cell}} = \frac{\Delta_r G}{nF} = \frac{940 \times 10^3 \text{ J mol}^{-1}}{4 \times 96500} = 2.5 \text{ V}$$

48. (a) $\Delta G = \Delta H - T\,\Delta S$

For a system, total entropy change $= \Delta S_{\text{total}}$

$$\Delta H_{\text{total}} = 0$$

$\therefore$ $\Delta G_{\text{system}} = -T\,\Delta S_{\text{total}}$

$\therefore$ $\dfrac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

Thus, (a) is correct.

(b) For isothermal reversible process, $\Delta E = 0$

By first law of thermodynamics

$$\Delta E = q + W$$

$\therefore$ $W_{\text{reversible}} = -q = -\int_{V_i}^{V_f} p\,dV$

$$W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$$

Thus, (b) is correct

(c) $\Delta G = \Delta H° - T\,\Delta S°$

$\Delta G° = -RT \log K$

$\therefore$ $-RT \log K = \Delta H° - T\,\Delta S°$

$\therefore$ $\log K = -\left(\dfrac{\Delta H° - T\,\Delta S°}{RT}\right)$

Thus, (c) is incorrect.

(d) $\Delta G° = -RT \log K$

$\therefore$ $\log K = -\dfrac{\Delta G°}{RT}$

$\therefore$ $K = e^{-\Delta G°/RT}$

Thus, (d) is also correct

49. Entropy change for n moles of isothermal expansion of an ideal gas from volume V_1 to volume V_2 is

$$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 8.3143 \log \frac{100}{10}$$

$$= 38.296 \text{ J mol}^{-1} \text{ K}^{-1}$$

50. $\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2$

$$\Delta G = +966 \text{ kJ mol}^{-1} = 966 \times 10^3 \text{ J mol}^{-1}$$
$$\Delta G = -nFE_{cell}$$
$$966 \times 10^3 = -4 \times 96500 \times E_{cell}$$
$$E_{cell} = 2.5 \text{ V}$$

51. $\Delta G = \Delta H - T\Delta S$

At equilibrium, $\Delta G = 0$

For a reaction to be spontaneous ΔG should be negative, so T should be greater than T_e.

52. Percentage efficiency of the fuel cell
$$= \frac{\Delta G}{\Delta H} \times 100$$

The concerned reaction is
$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta G_r = \Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, l) - \Delta G_f(CH_3OH, l) - \frac{3}{2}\Delta G_f(O_2, g)$$
$$= -394.4 + 2(-237.2) - (-166.2) - 0$$

Thus, percentage efficiency 702.6.

53. $\Delta_r S° = S°_{XY_3} - \left[\frac{1}{2}S°_{X_2} + \frac{3}{2}S°_{Y_3}\right]$
$$= 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right]$$
$$= 50 - (30 + 60) = -40 \text{ JK}^{-1} \text{ mol}^{-1}$$
$$\Delta_r G° = \Delta_r H° - T\Delta_r S° \text{ (At equilibrium, } \Delta_r G° = 0)$$
$$\therefore \quad T = \frac{\Delta_r H°}{\Delta_r S°} = \frac{-30{,}000 \text{ J mol}^{-1}}{-40 \text{ JK}^{-1} \text{ mol}^{-1}} = 750 \text{ K}$$

54. $\Delta G° = \Delta H° - T\Delta S° = -2.303\, RT \log_{10} K$
$$\therefore \ -2.303\, RT \log_{10} K = \Delta H° - T\Delta S°$$
$$i.e., \quad -2.303 \times 8.314 \times 298 \times \log_{10} K = [-54.07 \times 1000] - [298 \times 10]$$
$$-5705 \log_{10} K = -54070 - 2980$$
$$-5705 \log_{10} K = -57050$$
$$\text{or} \quad \log_{10} K = 10$$

55. $H_2O(l)$ and $H_2O(g)$ both exist together at same temperature and pressure,
$$H_2O(l) \rightleftharpoons H_2O(g)$$
In the state of equilibrium, $\Delta G = 0$ and conversion of liquid into gas increases disorderness.

Hence, entropy $\Delta S = +$ve,

56. $$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$
$$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$$
$$\Delta H - \Delta E = \Delta n_g RT$$
$$= \frac{1}{2} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$
$$= 1238.78 \text{ J mol}^{-1}$$

57. The molar heat capacity for any process is given by following expression $C = C_V + \frac{R}{1-\gamma}$ when $pV^\gamma =$ constant

and $C_p / C_V = \gamma$

Here, $\frac{p}{V} = 1$, *i.e.*, pV^{-1} constant
$$C = \frac{3}{2}R + \frac{R}{1-(-1)} = \frac{3}{2}R + \frac{R}{2} = \frac{4}{2}R$$

58. $T_{f(\text{irreversible})} > T_{f(\text{reversible})}$

It is an adiabatic expansion and $W_{(rev)}$ is maximum.

59. For adiabatic change, $\Delta E = \Delta W$
$$\Delta E = nC_V(T_2 - T)$$
$$\Delta W = -p(V_2 - V_t)$$
$$nC_V(T_2 - T) = -p(V_2 - V_t) = -1(2-1)$$
$$n \times \frac{R}{(\gamma - 1)} \times (T_2 - T) = -1$$
$n = 1, \gamma = \frac{5}{3}$ for monoatomic gas, $R = 0.0821$ L atm K^{-1} mol^{-1}
$$1 \times \frac{0.0821}{\frac{5}{3} - 1} \times (T_2 - T) = -1$$
$$T_2 = T - \frac{2}{3 \times 0.0821}$$

60. $$\Delta G° = -2.303\, RT \log K_{eq} = -nFE°_{cell}$$
If a cell reaction is spontaneous (proceeding in forward side), it means $K_{eq} > 1$ and $E°_{cell} = +$ve
$$\Delta G° = -\text{ve}$$

61. For spontaneous adsorption process, standard Gibbs free energy (ΔG) must be negative as well as the degree of randomness of gas molecule on the surface of solid decreases. For exothermic process, ΔH must be negative; $\Delta H = \Delta G + T\Delta S$

$T\Delta S$ is negative, hence during this adsorption ΔS decreases.

62. Joule's law suggests
$$J = \frac{\text{Mechanical work done by the system}, W}{\text{Net heat given to the system}, Q}$$
Hence, $J = \frac{W}{q_1 + q_2}$
$$W = J(q_1 + q_2)$$
is constant with Joules law of equivalence.

63. In thermodynamics, a process is called **reversible**, when the surroundings are always in equilibrium with the system.

Day 7

Thermochemistry

Day 7 Outlines ...

Concept of Thermochemistry

The energy and heat associated with chemical reactions are considered under thermochemistry. A reaction may release or absorb energy and phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings.

Chemical Reactions

Chemical reactions are invariably associated with transfer of energy and most frequently, energy transfer in chemical reactions takes place in the form of heat. Reactions may be exothermic or endothermic. Both the reactions are given below

(i) **Exothermic** reactions transfer heat to the surroundings.

$$4Al\,(s) + 3O_2\,(g) \longrightarrow 2Al_2O_3\,(s);\ \Delta H = -1676\ kJ$$

(ii) **Endothermic** reactions transfer heat from the surroundings.

$$N_2(g) + O_2\,(g) \longrightarrow 2NO\,(g);\ \Delta H = +90.4\ kJ$$

Thermochemical Standard States

A thermochemical standard state of a substance is its most stable state under 1 atm pressure (standard pressure) and 298 K (standard temperature). Under these conditions, any parameter is designated by $\Delta H^\circ, \Delta E^\circ, \Delta S^\circ$ etc. For a pure substance in the liquid or solid phase, the standard state is pure liquid or solid.

For a gas, the standard state is the gas at a pressure of one atmosphere. In a mixture of gases, its partial pressure must be one atmosphere.

For a substance in solution, the standard state refers to one molar concentration.

Heat *or* Enthalpy of Reaction

It is the amount of heat absorbed or evolved at constant pressure, when the quantities of substance indicated by thermochemical equation have completely reacted. It is denoted by ΔH_r, *e.g.*,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g); \Delta H_r = -890.3 \text{kJ}$$

$$\Delta H_r^\circ = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$$

or

$$\Delta H_r^\circ = H_{\text{products}} - H_{\text{reactants}}$$

(i) If $H_{\text{products}} = H_{\text{reactants}}$; $\Delta H = 0$

(ii) If $H_{\text{products}} > H_{\text{reactants}}$; $\Delta H = +\text{ve}$, reaction is said to be endothermic.

(iii) If $H_{\text{products}} < H_{\text{reactants}}$; $\Delta H = -\text{ve}$, reaction is said to be exothermic.

Factors Influencing Enthalpy of Reaction

Various factors that affect the enthalpy of reaction are

(i) Physical state of reactants and products

(ii) Allotropic forms of elements involved

(iii) Chemical composition of reactants and products

(iv) Amount of reactants

(v) Temperature

(vi) Medium of reaction

Types of Standard Enthalpy of Reactions

The types of standard enthalpy of reactions are given below

1. Standard Enthalpy of Formation (ΔH_f°)

It is the standard enthalpy change for the formation of one mole of a compound from its elements, e.g.,

$$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g); \Delta H_f^\circ = -74.8 \text{ kJ}$$

Enthalpy of formation of an element at standard state by convention is taken as zero, e.g., enthalpy of formation of Mg, Al, Na, H_2, O_2 etc., is taken as zero.

The enthalpy of the chemical reaction is given by

$$\Delta_r H^\circ = \Delta_f H_P^\circ - \Delta_f H_R^\circ$$

Here, $\Delta_f H^\circ_P$ = standard enthalpy of formation for products

$\Delta_f H_r^\circ$ = standard enthalpy of formation for reactants

2. Standard Enthalpy of Combustion (ΔH_c°)

It is the standard enthalpy change per mole of a substance, when it undergoes complete combustion. e.g.,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$$

$\Delta H_c^\circ = -192 \text{kcal}$ *ΔH combustion is always negative but for certain reactions it is positive. For example,*

$$N_2 + O_2 \longrightarrow 2NO, \Delta H = \text{positive}$$

$$F_2 + \frac{1}{2}O_2 \longrightarrow OF_2, \Delta H = \text{positive}$$

3. Enthalpy of Neutralisation (ΔH_n°)

It is the amount of heat liberated when 1 g equivalent of an acid is completely neutralised by 1 g equivalent of a base. ΔH_n is constant for strong acid and strong base, *i.e.*, $\Delta H_n = -13.7 \text{ kcal mol}^{-1}$ or $-57.27 \text{ kJ mol}^{-1}$

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l);$$

$$\Delta H_n = -57.3 \text{ kJ mol}^{-1}$$

For a weak acid against a strong base or weak base, the numerical value of ΔH_n is always less than 13.7 due to the fact that here the heat is used up in ionisation of weak acid or weak base.

The absolute value of heat of neutralization of HF is more than 57.3 kJ. This is due to very high heat of hydration of fluoride ion.

4. **Standard Enthalpy of Atomisation (ΔH_a°)**

It is the energy required, when one mole of the molecule breaks into its atoms. In case of diatomic molecules (X_2), the enthalpy of atomisation, bond dissociation enthalpy and bond enthalpy are same thing.

5. **Standard Enthalpy of Solution (ΔH_{sol}°)**

It is the standard enthalpy change, when one mole of substance dissolves in a specified amount of solvent.

$$\Delta H_{sol}^\circ = \Delta H_{lattice} - \Delta H_{hydration}$$

- *Integral and differential heats of solution are not same.*
- *Integral heat of solution is the enthalpy change when 1 mole of solute is dissolved in a pure solvent to form a solution of desired concentration.*
- *Differential heat of solution is the enthalpy change when 1 mole of solute is dissolved in such a large volume of solution so that no enthalpy change occurs on further dilution.*
- *If the solubility of a substance is known at two different temperatures, the mean molar enthalpy of solution over this temperature range can be calculated by applying an equation similar to van't Hoff equation;*

$$\frac{\log S_1}{\log S_2} = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where, S_1 and S_2 are solubilities at T_1 and T_2 temperatures respectively.

6. **Lattice Enthalpy (U)**

It is the enthalpy change, which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

7. **Enthalpy of Hydration (ΔH_{hyd})**

It is the enthalpy change, when one mole of anhydrous or partially hydrated salt combines with required number of moles of water to form a specific hydrate.

$$CuSO_4\,(s) + 5H_2O\,(l) \longrightarrow CuSO_4 \cdot 5H_2O\,(s);$$
$$\Delta H_{hydration} = -78.21\,\text{kJ mol}^{-1}$$

During dissolution, physical state of the compound changes while during hydration, there is no change in the physical state of compound.

8. **Standard Enthalpy of Hydrogenation ($\Delta H^\circ_{hydrogenation}$)**

It is the amount of enthalpy change that takes place when one mole of unsaturated organic compound is completely hydrogenated.

9. **Standard Enthalpy of Dilution (ΔH_{dil}°)**

The standard enthalpy change, when 1 mole of a substance is diluted to such an extent that on further dilution no heat is evolved or absorbed is termed as standard heat of dilution.

10. **Standard Enthalpy of Fusion (ΔH_{fusion}°)**

It is the enthalpy change that accompanies melting of one mole of a solid substance.

11. **Standard Enthalpy of Vaporisation (ΔH_{vap}°)**

It is the amount of heat required to convert one mole of liquid into its vapour state.

$$\Delta H_{vap}^\circ = -\Delta H_{cond}^\circ$$

12. **Standard Enthalpy of Sublimation (ΔH_{sub}°)**

At standard conditions, change in enthalpy, when one mole of a solid substance sublimes is called the standard enthalpy of sublimation.

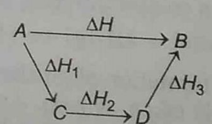
13. **Enthalpy of Transition**

It is the enthalpy change when one mole of the substance undergoes transition from one allotropic form to another.

Hess's Law

The enthalpy change in a particular reaction is always constant and is independent of the path by which the reaction takes place.

In other words, the total heat change (ΔH) accompanying a chemical reaction is the same whether, the reaction takes place in one step or in more steps.



According to Hess's law ;

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Some applications of Hess's law are

- In determination of heat of formation,
- In determination of heat of transition.

Bond Energy

When a bond is formed between two atoms in gaseous state to form a molecule, some heat is always evolved which is called bond energy or bond formation energy.

Bond dissociation energy is the amount of energy required to break/dissociate bond of a particular type present in one molecule of the compound, while bond energy is taken as the average value of dissociation energies of same type of bonds present in one mole.

Since, a chemical reaction involves the breaking of old bonds in reactants and formation of new bonds in products, the enthalpy change of a reaction,

$$\Delta H_r = \text{Sum of BE of reactants} - \text{Sum of BE of products}$$

In a polyatomic molecule containing two or more covalent bonds between same atoms (*e.g.*, CH_4), the term average bond energy is preferred in place of bond dissociation energy. For CH_4, average BE of C—H bond

$$= \frac{\text{Heat of dissociation of } CH_4}{4}$$

Bond dissociation enthalpy values are exothermic, if bond formation occurs whereas bond energy values are endothermic, if bond dissociation occurs.

Factors Affecting Bond Enthalpy

- **Size of atoms** Smaller the size of atom, more closer are atoms to each other during bonding, hence larger is the bond enthalpy. *e.g.*, bond enthalpy of halogens follows the following order F—F < Cl—Cl > Br—Br > I—I
- Bond enthalpy of fluorine is smaller than chlorine because of the high degree of lone pair repulsions in F_2 due to its smaller size.
- **Electronegativity** Larger the electro negativity difference between two atoms, more is the polarity in bond and thus, more is the bond strength as well as bond enthalpy. *e.g.*, F—H > O—H > N—H
(Bond enthalpy decreases)
- **Bond length** Shorter the bond length, more is the bond dissociation enthalpy.
- **Number of bonding electrons** As the number of electrons involved in bond increases, strength of the bond increases. This increases the bond enthalpy. *e.g.*, C≡C > C═C > C—C
(Bond enthalpy decreases)

Calorimetry

The experimental measurement of the heat of reaction or enthalpy change is known as calorimetry.

In laboratory, heat changes in physical and chemical processes are measured with a calorimeter which is an insulated container $q = mc\Delta t = C\,\Delta t$ (Heat capacity, $C = mc$)

where, m is the mass of the substance in grams, c is the specific heat and C is the heat capacity.

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

For endothermic change, q is positive and for exothermic change, q is negative.

Constant Volume Calorimetry

Heat of combustion is measured by placing a known mass of a compound in a constant volume bomb calorimeter which is filled with oxygen at about 30 atm pressure. On ignition of the sample electrically, there is evolution of heat which can be calculated by recording the rise in temperature of water.

Heat lost by the sample = Heat gained by the water

$$q_{\text{combustion}} = -[q_{\text{water}} + q_{\text{bomb}}] = -[m_{\text{water}} \times c_{\text{water}} + m_{\text{bomb}} \times c_{\text{bomb}}] \times \Delta t$$

$$q_{\text{combustion}} = \Delta E_{\text{combustion}} \text{(combustion in bomb calorimeter at constant } V)$$

Therefore, $\Delta H_{\text{combustion}} = \Delta E + \Delta n_g RT$

The calorific value of a fuel or food is the amount of heat in calories or joules produced from the complete combustion of one gram of the fuel or the food. *Calorific value* $= \dfrac{\Delta H_{\text{comb}}}{\text{molecular mass}}$

Practice Zone DAY 7

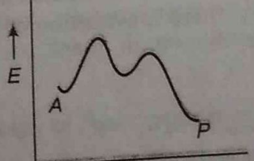
1. Heat produced in calories by the combustion of one gram of carbon is called
(a) heat of combustion of carbon
(b) heat of formation of carbon
(c) calorific value of carbon
(d) heat of product of carbon

2. Enthalpy of sublimation of a substance is equal to [NCERT Exemplar]
(a) enthalpy of fusion + enthalpy of vapourisation
(b) enthalpy of fusion
(c) enthalpy of vapourisation
(d) twice the enthalpy of vapourisation

3. Enthalpy of solution of NaOH (solid) in water is -41.6kJ mol^{-1}. When NaOH is dissolved in water, the temperature of water
(a) increases
(b) decreases
(c) does not change
(d) fluctuates indefinitely

4. The temperature of a bomb calorimeter rose by 1.6 K when a current of 3.2 A is passed for 27s from a 12 V source. Which of the following statements is true?
(a) The calorimeter constant is 648 JK^{-1}
(b) This calorimeter constant will be same if the calorimeter is open
(c) The information is insufficient for calculating calorimeter constant
(d) The calorimeter constant is independent of calorimeter content

5. Consider the following reaction and corresponding. energy diagram : $A \rightarrow P$



Which of the following statements is incorrect?
(a) It is a two step reaction
(b) First step is slower than second step
(c) A is more unstable compared to P
(d) All steps are exothermic

6. If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 250°C and 1 atm pressure be 52, −394 and −286 kJ mol^{-1} respectively, the enthalpy of combustion of $C_2H_4(g)$ will be
(a) 1412 kJ mol^{-1}
(b) −1412 kJ mol^{-1}
(c) +141.2 kJ mol^{-1}
(d) −141.2 kJ mol^{-1}

7. $C + O_2 \longrightarrow CO_2;$ $\Delta H = x$

$CO + \frac{1}{2}O_2 \longrightarrow CO_2;$ $\Delta H = y$

Then, the heat of formation of CO is
(a) $x - y$
(b) $y - 2x$
(c) $x + y$
(d) $2x - y$

8. Equal volumes of methanoic acid and sodium hydroxide are mixed, if x is the heat of formation of water, heat evolved in neutralisation is
(a) more than x
(b) equal to x
(c) twice of x
(d) less than x

9. If the heat of neutralisation for a strong acid-base reaction is −57.1 kJ, what would be the heat released when 350 cm^3 of 0.20 M of a dibasic strong acid is mixed with 650 cm^3 of 0.10 M monoacidic base?
(a) 57.1 kJ
(b) 3.71 kJ
(c) −57.1 kJ
(d) 0.317 kJ

10. The heat evolved in the combustion of methane is given by the following equation

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$ $\Delta H = -890.3$ kJ

How many grams of methane would be required to produce 445.15 kJ of heat of combustion?
(a) 4 g
(b) 8 g
(c) 12 g
(d) 16 g

11. In a calorimeter, the temperature of the calorimeter increases by 6.12 K, the heat capacity of the system is 1.23 kJ/g /deg. What is the molar heat of decomposition for the ammonium nitrate?
(a) −7.53 kJ/mol
(b) −398.1 kJ/mol
(c) −16.1 kJ/mol
(d) −602 kJ/mol

12. The heat of combustion of carbon to CO_2 is −393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is
(a) +315 kJ
(b) −31.5 kJ
(c) −315 kJ
(d) +31.5 kJ

13. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104.58 and 103 kcal respectively. The enthalpy of formation of HCl gas would be

(a) –44 kcal (b) 44 kcal (c) –22 kcal (d) 22 kcal

14. Given that,

$$C(g) + 4H(g) \longrightarrow CH_4(g); \qquad \Delta H = -166 \text{ kJ}$$

The bond energy of C—H will be

(a) –416kJ/mol (b) –41.6kJ/mol
(c) 832kJ/mol (d) None of these

15. The amount of heat absorbed by 70.09 of water for their complete vapourisation is **[NCERT Exemplar]**

(a) 23, 352J (b) 7000 J
(c) 15,813J (d) 158, 200J

16. The entropy values (in $JK^{-1} mol^{-1}$) of $H_2(g) = 130.6$, $Cl_2(g) = 223.0$ and $HCl(g) = 186.7$ at 298 K and 1 atm pressure, then entropy change for the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \text{ is}$$

(a) +540.3 (b) +727.3 (c) –166.9 (d) +19.8

17. The following is (are) endothermic reactions

(i) combustion of methane
(ii) decomposition of water
(iii) dehydrogenation of ethane to ethylene
(iv) conversion of graphite to diamond

(a) (i), (ii) (b) (ii), (iii)
(c) (iii), (iv) (d) (ii), (iii), (iv)

18. Combustion of glucose takes place according to the equation,

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O; \Delta H = -72 \text{ kcal}$$

How much energy will be required for the production of 1.6 g of glucose (molecular mass of glucose = 180) ?

(a) 0.064 kcal (b) 0.64 kcal
(c) 6.4 kcal (d) 64 kcal

19. 2.1 g of Fe combines with S evolving 3.77 kJ. The heat of formation of FeS in kJ/mol is

(a) –1.79 (b) –100.5
(c) –3.77 (d) None of these

20. The 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 the reaction,

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g), \text{ is}$$

(a) 524.1 (b) 41.2 (c) –262.5 (d) –41.2

21. Heat of formation of H_2O is –188 kJ/mol and H_2O_2 is –286 kJ/mol. The enthalpy change for the reaction,

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \text{ is}$$

(a) 196 kJ (b) –196 kJ
(c) 984 kJ (d) –984 kJ

22. Which of the reactions defines ΔH_f°?

(a) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$
(c) $N_2(l) + 3H_2(g) \longrightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

23. ΔH for combustion of ethane and ethyne are – 341.1 and –310.0 kcal respectively. What will be the ratio of calorific values of ethane and ethyne respectively?

(a) 1 : 0.95 (b) 0.65 : 2 (c) 0.95 : 1 (d) 0.002 : 1

24. The enthalpy of dissolution of $BaCl_2(s)$ and $BaCl_2 \cdot 2H_2O(s)$ are –20.6 and 8.8 kJ per mol respectively. The enthalpy of hydration for, $BaCl_2(s) + 2H_2O \longrightarrow BaCl_2 \cdot 2H_2O(s)$, is

(a) 29.4 kJ (b) –29.4 kJ
(c) –11.8 kJ (d) 38.2 kJ

25. The enthalpy of combustion of H_2, cyclohexene and cyclohexane are –241, –3800 and –3920 kJ mol^{-1} respectively. Heat of hydrogenation of cyclohexene is

(a) 121 kJ mol^{-1} (b) –121 kJ mol^{-1}
(c) +242 kJ mol^{-1} (d) –242 kJ mol^{-1}

26. $\Delta_f u^\circ$ for the formation of $CH_4(g)$ at certain temperature is –393 kJ mol^{-1}. The value of $\Delta_f H^\circ$ is :

(a) zero (b) $< \Delta_f u^\circ$
(c) $> \Delta_f u^\circ$ (d) equal to $\Delta_f u^\circ$

27. The H_f° of O_3, CO_2, NH_3 and HI are 142.2, –393.3, –46.2 and +25.9 kJ per mol respectively. The order of their increasing stabilities will be

(a) O_3, CO_2, NH_3, HI (b) CO_2, NH_3, HI, O_3
(c) O_3, HI, NH_3, CO_2 (d) NH_3, HI, CO_2, O_3

Directions (Q. Nos. 28 and 29)

(a) *A student heated a sample of a metal weighing 32.6 g to 99.83°C and put it into 100.0 g of water at 23.62°C in a calorimeter. The final temperature was 24.41°C. The student calculated the specific heat of the metal, but neglected to use the heat capacity of the calorimeter. The specific heat of water is 4.184 J/g°C, what was his answer? The metal was known to be chromium, molybdenum or tungsten. By comparing the value of the specific heat to those of the metals (Cr – 0.460 ; Mo – 0.250 ; W – 0.135 J/g°C), the student identified the metal.*

(b) *The student at the next laboratory, did the same experiment, obtained the same data, and used the heat capacity of the calorimeter in his calculations. The heat capacity of the calorimeter was 410 J/°C.*

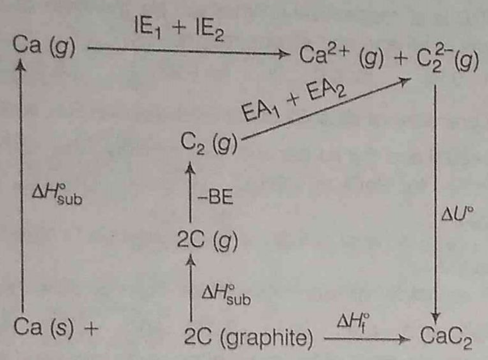
28. Metal identified by first student was

(a) Cr (b) Mo
(c) W (d) None of these

29. Metal identified by the student in the next laboratory was

(a) Cr (b) Mo
(c) W (d) None of these

Directions (Q. Nos. 30 to 32) *The Born-Haber cycle for the formation of* CaC_2 *can be constructed as*



30. Using the Born-Haber cycle, determine ΔU (lattice energy) of CaC_2 given

$$\Delta H_f^\circ = -60 \text{ kJ mol}^{-1}, \Delta H_{sub}^\circ \text{ Ca(s)} = 180 \text{ kJ mol}^{-1}$$

$$IE_1 \text{ (Ca)} = 600 \text{ kJ mol}^{-1}, IE_2 \text{ (Ca)} = 1150 \text{ kJ mol}^{-1}$$

$$EA_1 (C_2) = -315 \text{ kJ mol}^{-1}, EA_2(C_2) = 410 \text{ kJ mol}^{-1}$$

$$BE (C_2) = 614 \text{ kJ mol}^{-1}$$

$$\Delta H_{sub}^\circ \text{ C (gr)} = 717 \text{ kJ mol}^{-1}$$

(a) -1707 kJ mol^{-1} (b) -2845 kJ mol^{-1}
(c) -2905 kJ mol^{-1} (d) -1206 kJ mol^{-1}

31. Which is the most stable compound?

(a) NaCl (b) $MgCl_2$
(c) KCl (d) RbCl

32. Calculate the electron affinity of bromine atom from the following data :

Lattice energy of sodium bromide = -736 kJ mol^{-1}

$$\Delta H_f^\circ \text{ (NaBr)} = -376 \text{ kJ mol}^{-1}$$

$\Delta H_{298\text{ K}}$ of sublimation of sodium = 109 kJ mol^{-1}

$$\text{BE (Br – Br)} = 192 \text{ kJ mol}^{-1}$$

Ionisation enthalpy of sodium = 490 kJ mol^{-1}

(a) -436 kJ mol^{-1}
(b) -335 kJ mol^{-1}
(c) -353 kJ mol^{-1}
(d) None of the above

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.
(e) Statement I and II are false.

33. Statement I The enthalpy of formation of $H_2O(l)$ is greater than that of H_2O (g).

Statement II The enthalpy change for condensation reaction, *i.e.*, $H_2O(g) \rightarrow H_2O$ (l) is negative.

34. Statement I For a certain reaction, heat of combustion at constant pressure (q_v) is always greater than that at constant volume (q_v).

Statement II Combustion reactions are invariably accomplished by increase in number of moles.

35. Statement I The heat of neutralization of a strong acid with strong base is equal to the heat of ionisation of water.

Statement II H^+ ions from an acid combines rapidly with $OH^\ominus$ ions from base to form water while water ionises to a very small extent.

36. Statement I Heat of neutralisation for HF is -68.552 kJ / eq whereas for HCl it is -57.26 kJ / eq.

Statement II The acid HF is weak acid.

37. A cooking gas cylinder is assumed to contain 11.2 kg *iso*-butane. The combustion of *iso*-butane is given by

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l),$$
$$\Delta H = -2658 \text{ kJ}$$

If a family needs 15,000 kJ of energy per day for cooking, how long would the cylinder last?

[Assuming that 30% of the gas is wasted due to incomplete combustion.]

(a) 34 days (b) 30 days (c) 31 days (d) 24 days

38. 1.0 L sample of mixture of CH_4 and O_2 measured at 25°C and 740 torr, was allowed to react at constant pressure in a calorimeter, together with its contents had a heat capacity of 1260 cal K^{-1}. The complete combustion of CH_4 to CO_2 and water caused a temperature rise in calorimeter of 0.667 K. What will be the mol % of CH_4 in the original mixture? [Heat of combustion of CH_4 is -210.8 kcal.]

(a) 25% (b) 15% (c) 40% (d) 10%

39. When 1 mole of oxalic acid is treated with excess of NaOH in dilute aqueous solution, 106 kJ of heat is liberated. The enthalpy of ionisation of the acid is

(a) 4.3 kJ mol^{-1}
(b) – 4.3 kJ mol^{-1}
(c) – 8.6 kJ mol^{-1}
(d) 8.6 kJ mol^{-1}

40. An athlete takes 20 breathes per minute at room temperature. The air inhaled in each breathe is 200 mL which contains 20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all the oxygen consumed is used for converting glucose into $CO_2(g)$ and $H_2O(l)$, how much glucose will be burnt in the body in one hour?

(a) 25.29 g
(b) 29.25 g
(c) 50.00 g
(d) 15.68 g

41. What will be the enthalpy change for the combustion of cyclopropane at 298 K? The enthalpies 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}.

(a) 844.63 kJ
(b) – 844.63 kJ
(c) – 2091.32 kJ
(d) 1893.44 kJ

AIEEE & JEE Main Archive

42. Given that

(i) $\Delta_f H°$ of N_2O is 82 kJ mol^{-1}

(ii) Bond energies of $N{\equiv}N$, $N{=}N$, $O{=}O$ and $N{=}O$ are 946, 418, 498 and 607 kJ mol^{-1} respectively. The resonance energy of N_2O is **[JEE Main Online 2013]**

(a) –88 kJ
(b) –66 kJ
(c) –62 kJ
(d) –44 kJ

43. Which of the following statements/relationships is not correct in thermodynamic changes? **[JEE Main Online 2013]**

(a) $\Delta U = 0$ (isothermal reversible expansion of a gas)
(b) $W = -nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(c) $q = -nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(d) For a system, at constant volume, heat involved completely changes to internal energy

44. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar **[JEE Main Online 2013]**

(a) Ca < S < Ba < Se < Ar
(b) S < Se < Ca < Ba < Ar
(c) Ba < Ca < Se < S < Ar
(d) Ca < Ba < S < Se < Ar

45. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $C{\equiv}C$ bond in C_2H_2.

The energy is (take the bond energy of a C—H bond as 350 kJ mol^{-1}) **[IIT JEE 2012]**

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g); \quad \Delta H = 225 \text{ kJ mol}^{-1}$$
$$2C(s) \longrightarrow 2C(g); \quad \Delta H = 1410 \text{ kJ mol}^{-1}$$
$$H_2(g) \longrightarrow 2H(g); \quad \Delta H = 330 \text{ kJ mol}^{-1}$$

(a) 1165 kJ mol^{-1}
(b) 837 kJ mol^{-1}
(c) 865 kJ mol^{-1}
(d) 815 kJ mol^{-1}

46. The standard ethalpy of formation of NH_3 is – 46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_2 is – 712 kJ mol^{-1}, the average bond enthalpy of N—H bond in NH_3 is **[AIEEE 2010]**

(a) – 964 kJ mol^{-1}
(b) – 352 kJ mol^{-1}
(c) + 1056 kJ mol^{-1}
(c) – 1102 kJ mol^{-1}

47. On the basis of the following thermochemical data [$\Delta fG° H^+(aq) = 0$]

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq); \quad \Delta H = 57.32 \text{ kJ}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta H = 286.02 \text{ kJ}$$

The value of enthalpy of formation of OH^- ion at 25°C is **[AIEEE 2009]**

(a) – 22.88 kJ
(b) – 228.88 kJ
(c) + 228.88 kJ
(d) – 343.52 kJ

48. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{disso}H°} Cl(g) \xrightarrow{\Delta_{eg}H°} Cl^-(g) \xrightarrow{\Delta_{hyd}H°} Cl^-(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$

[Using the data $\Delta_{disso}H°_{Cl_2} = 240$ kJ mol^{-1},

$\Delta_{eg}H° = -349$ kJ mol^{-1},

$\Delta_{hyd}H°_{Cl^-} = -381$ kJ mol^{-1}] will be **[AIEEE 2008]**

(a) –850 kJ mol^{-1}
(b) + 120 kJ mol^{-1}
(c) + 152 kJ mol^{-1}
(d) – 610 kJ mol^{-1}

49. Assuming that water vapour is an ideal gas, the internal energy change (ΔE), when 1 mole of water is vaporised at 1 bar pressure and 100°C, (Given : molar enthalpy of vaporisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and $R = 8.3$ J mol^{-1} K^{-1}) will be **[AIEEE 2007]**

(a) 4.100 kJ mol^{-1}
(b) 3.7904 kJ mol^{-1}
(c) 37.904 kJ mol^{-1}
(d) 41.00 kJ mol^{-1}

50. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement, if N_2 is added at equilibrium condition? **[IIT JEE 2006]**

(a) The equilibrium will shift to forward direction because according to second law of thermodynamics, the entropy must increases in the direction of spontaneous reaction.

(b) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$; where, G is Gibbs free energy per mole of the gaseous species measured at the partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.

(c) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.

(d) Catalyst will not alter the rate of either of the reactions.

51. The enthalpy changes for the following processes are listed below

$$Cl_2(g) \longrightarrow 2Cl(g), 242.3 \text{ kJ mol}^{-1}$$
$$I_2(g) \longrightarrow 2I(g), 151.0 \text{ kJ mol}^{-1}$$
$$ICl(g) \longrightarrow I(g) + Cl(g), 211.3 \text{ kJ mol}^{-1}$$
$$I_2(s) \longrightarrow I_2(g), 62.76 \text{ kJ mol}^{-1}$$

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation of ICl (g) is **[AIEEE 2006]**

(a) -14.6 kJ mol^{-1} (b) -16.8 kJ mol^{-1}
(c) $+16.8$ kJ mol^{-1} (d) $+244.8$ kJ mol^{-1}

52. The standard enthalpy of formation (ΔH_f°) at 298 K for methane, $CH_4(g)$ is -74.8 kJ mol^{-1}. The addition information required to determine the average energy for C–H bond formation would be **[AIEEE 2006]**

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of hydrogen molecule, H_2

53. Consider the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$; carried out at constant temperature and pressure. If ΔH and ΔE are the enthalpy and internal energy changes for the reaction, which of the following expressions is true? **[AIEEE 2005]**

(a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$ (d) $\Delta H = 0$

54. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1:1: 0.5 and ΔH_f for the formation of XY is -200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **[AIEEE 2005]**

(a) 400 kJ mol^{-1} (b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1} (d) None of these

55. The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is **[AIEEE 2004]**

(a) 110.5 kJ (b) 676.5 kJ
(c) -676.5 kJ (d) -110.5 kJ

56. If at 298 K, the bond energies of C—H, C—C, C=C and H—H bonds are 414, 347, 615 and 435 kJ mol^{-1} respectively, the value of enthalpy change for the reaction,

$$H_2C{=}CH_2(g) + H_2(g) \longrightarrow H_3C{-}CH_3(g)$$

at 298 K will be **[AIEEE 2003]**

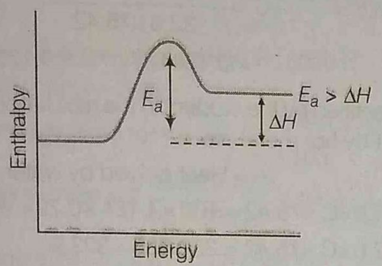
(a) +250 kJ (b) -250 kJ
(c) +125 kJ (d) -125 kJ

Answers

1. (c)	2. (a)	3. (a)	4. (a)	5. (d)	6. (b)	7. (a)	8. (d)	9. (b)	10. (b)
11. (d)	12. (c)	13. (c)	14. (b)	15. (d)	16. (d)	17. (d)	18. (b)	19. (b)	20. (b)
21. (a)	22. (b)	23. (c)	24. (b)	25. (b)	26. (b)	27. (c)	28. (c)	29. (b)	30. (c)
31. (b)	32. (b)	33. (a)	34. (c)	35. (b)	36. (b)	37. (d)	38. (d)	39. (d)	40. (b)
41. (c)	42. (a)	43. (c)	44. (c)	45. (d)	46. (b)	47. (b)	48. (d)	49. (c)	50. (b)
51. (c)	52. (a)	53. (b)	54. (d)	55. (d)	56. (d)				

Hints & Solutions

1. Heat produced by complete combustion of one gram of carbon is called its calorific value.
2. Enthalpy of sublimation of a compound is sum of the enthalpy of fusion and enthalpy of vapourisation.
3. Since, the process is exothermic, heat is evolved due to this temperature of water increases



4. $Q = It = 3.2 \times 27$

   Energy produced $= QV = 3.2 \times 27 \times 12 = 1036.8$ J

   Calorimeter constant $= \dfrac{1036.8}{1.6} = 648\ JK^{-1}$

   It is C_V and different from C_p.
5. Two peaks and a trough indicate that it is a two step process. Activation energy of first step is greater than that for second step, hence first step is a slower one. Ground state potential energy of P is less than A hence P is more stable and A is more unstable. F is irst step is endothermic while the second step is exothermic.
6. $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

$$\Delta H_{reaction} = [2 \times \Delta H_f^\circ(CO_2) + 2 \times \Delta H_f^\circ(H_2O)] - [\Delta H_f^\circ(C_2H_4) + 3 \times \Delta H_f^\circ(O_2)]$$
$$= [2(-394) + 2(-286)] - [52 + 0]$$
$$= -1412 \text{ kJ}$$

7.
$$C + O_2 \longrightarrow CO_2\ ;\ \Delta H = x$$
$$CO + \frac{1}{2}O_2 \longrightarrow CO_2\ ;\ \Delta H = y$$
$$\overline{C + \frac{1}{2}O_2 \longrightarrow CO\ ;\ \Delta H = x - y}$$

8. As methanoic acid is a weak acid, heat of neutralisation is less than x.
9. Millimoles of dibasic strong acid

   $= M \times V = 0.20 \times 350 = 70$ mmol

   $\therefore$ Amount of H^+ ions in the acid $= 2 \times 70 = 140$ mmol

   Similarly, amount of OH^- ions in monobasic strong base

   $= 0.10 \times 650 \times 1 = 65$ mmol

   [Here, OH^- is the miting reactant].

   $\because$ 1 mole of OH^- ions produces $= 57.1$ kJ heat

   65×10^{-3} moles of OH^- ions will produce

   $= 57.1 \times 65 \times 10^{-3} = 3.71$ kJ
10. CH_4 required $= \dfrac{445.15 \times 16}{890.3} = 8$ g
11. Molecular weight of $NH_4NO_3 = 80$

    Heat evolved $= 1.23 \times 6.12$

    Molar heat of decomposition $= 1.23 \times 6.12 \times 80$

    $= 602\ kJ\ mol^{-1}$

    (as heat is evolved)

    $= -602\ kJ\ mol^{-1}$
12. $C + O_2 \longrightarrow CO_2;\ \Delta H = -393.5$ kJ/mol

    $\because$ Heat released during the formation of 44 g of CO_2

    $= -393.5$ kJ

    Heat released during the formation of 1 g of CO_2

    $= \dfrac{-393.5}{44}$ kJ

    Heat released during the formation of 35.2 g (given) of CO_2

    $= -\dfrac{393.5 \times 35.2}{44} = -315$ kJ
13. $\dfrac{1}{2}H_2 + \dfrac{1}{2}Cl_2 \longrightarrow HCl$

$$\Delta H = \Sigma BE_{reactants} - \Sigma BE_{products}$$
$$= \left[\frac{1}{2}BE(H_2) + \frac{1}{2}BE(Cl_2)\right] - BE(HCl)$$
$$= \left[\left(\frac{1}{2} \times 104\right) + \left(\frac{1}{2} \times 58\right)\right] - 103$$
$$= (52 + 29) - 103 = -22 \text{ kcal}$$

14. The bond energy C—H $= -166/4 = -41.5\ kJ\ mol^{-1}$
15. (a) The heat absorbed, Q is given by

    Q = mass × latent heat of vaporisation (L_v)

    mass = 70.0 g = 0.07 kg

    $L_v = 2260$ kJ

    $\therefore\ Q = 0.07 \times 2260 = 158.2$ kJ $= 158200$ J
16. $\Delta S^\circ = 2S^\circ_{HCl} - (S^\circ_{H_2} + S^\circ_{Cl_2})$

    $= 2 \times 186.7 - (130.6 + 223.0) = 19.8\ JK^{-1}\ mol^{-1}$
17. (ii), (iii) and (iv) are endothermic reactions because they proceeds by the absorption of heat.
18. ΔH per 1.6g $= \dfrac{72 \times 1.6}{180} = 0.64$ kcal
19. ΔH/ mol of FeS $= \dfrac{3.77 \times 56}{2.1} = 100.5$
20. $C + O_2 \longrightarrow CO_2(g)\ ;\ \Delta H_f^\circ = -393.5\ kJ\ mol^{-1}$ ...(i)

    $C + \dfrac{1}{2}O_2 \longrightarrow CO(g);\ \Delta H_f^\circ = -110.5\ kJ\ mol^{-1}$ ...(ii)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(g)$; $\Delta H_f^\circ = -241.8$ kJ mol^{-1} ...(iii)

Eq. (ii) + Eq. (iii) – Eq. (i)

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$; $\Delta H_r = 41.2$ kJ

21. $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -188$ kJ mol^{-1} ...(i)

$H_2 + O_2 \longrightarrow H_2O_2$; $\Delta H = -286$ kJ mol^{-1} ...(ii)

Multiply Eqs. (i) and (ii) by 2,

$2H_2 + O_2 \longrightarrow 2H_2O$; $\Delta H = -376$ kJ mol^{-1} ...(iii)

$2H_2 + 2O_2 \longrightarrow 2H_2O_2$; $\Delta H = -572$ kJ mol^{-1} ...(iv)

Eq. (iii) – Eq. (iv)

$2H_2O_2 \longrightarrow 2H_2O + O_2$; $\Delta H_r = +196$ kJ

22. ΔH_f°, standard heat of formation is the amount of heat evolved or absorbed when one gram mole of a substance is formed from its constituent elements.

For standard state temperature is 25°C or 298 K and pressure of gaseous substance is one atmosphere. Therefore, in given thermochemical equations, formation of HF represents the standard heat of formation of HF.

23. Calorific value is heat produced by 1 g of fuel.

Calorific value of ethane $= \frac{-341.1}{30} = -11.37$ kcal / g

Calorific value for ethyne $= \frac{-310.0}{26} = -11.92$ kcal / g

[Here 30 and 26 are molecular weight of ethane and ethyne respectively.]

∴Ratio of calorific values of ethane and ethyne

$= 11.37 : 11.92 = 0.95 : 1$

24. $BaCl_2(s) + aq \longrightarrow BaCl_2(aq)$; $\Delta H = -20.6$ kJ ...(i)

$BaCl_2 \cdot 2H_2O(s) + aq \longrightarrow BaCl_2(aq)$; $\Delta H = +8.8$ kJ ...(ii)

Eq. (i) can be split as

$BaCl_2(s) + 2H_2O(l) \longrightarrow BaCl_2 \cdot 2H_2O(s)$; $\Delta H = H_1$

$BaCl_2 \cdot 2H_2O(s) + aq \longrightarrow BaCl_2(aq)$; $\Delta H = H_2$

$\Delta H = H_1 + H_2 = -20.6$;

$H_1 = 8.8$ kJ

$H_2 = -20.6 - 8.8 = -29.4$ kJ

25. $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -241$ kJ ...(i)

$C_6H_{10} + \frac{17}{2}O_2 \longrightarrow 6CO_2 + 5H_2O$; $\Delta H = -3800$ kJ ...(ii)

$C_6H_{12} + 9O_2 \longrightarrow 6CO_2 + 6H_2O$; $\Delta H = -3920$ kJ ...(iii)

For the reaction, $C_6H_{10} + H_2 \longrightarrow C_6H_{12}$

Eq. (i) + Eq. (ii) – Eq. (iii)

$\Delta H = -241 - 3800 - (-3920) = -121$ kJ

26. $C + 2H_2 \rightarrow CH_4$

$\Delta_{ng} = 1 - 3 = -2$

$\Delta H^\circ = \Delta u^\circ + \Delta n_g RT = \Delta u^\circ - 2\Delta n_g RT$ (as $\Delta n_g = -$ve)

$\Delta H^\circ = \Delta u^\circ$

27. Energy absorbed $\propto \frac{1}{\text{stability of compound}}$

Energy released $\propto$ stability of compound

28. Metal identified by first student was W.

Heat lost by hot metal piece = Heat gained by water

$mC\Delta T = mC\Delta T$

$32.6 \times C \times 75.42 = 100 \times 4.184 \times 0.79$

$C = \frac{4.184 \times 100 \times 0.79}{32.6 \times 75.42}$

$= 0.1344$ J / g°C ≈ 0.135 of W

29. Metal identified by the student in the next laboratory was Mo.

Heat lost by hot metal piece

= Heat gained by water + calorimeter

$32.6 \times C \times 75.42 = 100 \times 4.184 \times 0.79 + 410 \times 0.79$

$32.6 \times C \times 75.42 = 330.536 + 323.9$

$32.6 \times C \times 75.42 = 654.436$

∴ $C = \frac{654.436}{32.6 \times 75.42} = 0.26$ J / g°C ≈ 0.25 of Mo

30. $\Delta H_f^\circ = \Delta H_{sub}^\circ$ Ca(s) + (IE$_1$ + IE$_2$) Ca(g) + 2 ΔH_{sub}° C (gr) – BE (C_2) + EA$_1$ + EA$_2$ + ΔU°

$-60 = 180 + 1750 + 1434 - 614 - 315 + 410 + \Delta U^\circ$

$\Delta U^\circ = -2905$ kJ mol^{-1}

31. $MgCl_2$ is most stable as it has highest lattice energy in the given species.

32. We use Born-Haber cycle to calculate unknown parameter which is electron affinity in this case

$Na(s) + \frac{1}{2}Br_2(g) \longrightarrow NaBr(s)$; $\Delta H_1^\circ = -376$ kJ mol^{-1}

(a) $Na(s) \longrightarrow Na(g)$; $\Delta H_{(sub)}^\circ = S = 109$ kJ mol^{-1}

(b) $Na(g) \longrightarrow Na^+(g) + e^-$; ΔH° (IE) $= I = 490$ kJ mol^{-1}

(c) $\frac{1}{2}Br_2(g) \longrightarrow Br(g)$; $\Delta H_{(diss.)}^\circ = \frac{D}{2} = 96$ kJ mol^{-1}

(d) $Br(g) + e^- \longrightarrow Br^-(g)$; ΔH° (EA) $= -E = ?$

(e) $Na^+(g) + Br^-(g) \longrightarrow NaBr(s)$; $\Delta U^\circ = -U$

$= -736$ kJ mol^{-1}

On adding (a) to (e)

$Na(s) + \frac{1}{2}Br_2(g) \longrightarrow NaBr(s)$; $\Delta H_2^\circ = S + I + \frac{D}{2} - E - U$

By Hess's law, $\Delta H^\circ = \Delta H_1^\circ$

∴ $S + I + \frac{D}{2} - E - U = \Delta H_1^\circ$

$109 + 490 + 96 - E - 736 = -376$

$E = 335$ kJ mol^{-1}

Hence, electron affinity of bromine $= -335$ kJ mol^{-1}

33. Both the statements I and II are correct and statement II is the correct explanation for statement I.

34. Both the statements I and II are false.

35. The dissociation of water to form H^+ and $OH^⊖$ is the reverse of heat of neutralisation with an opposite sign.

36. HF is a weak acid but the high value of heat of neutralisation is due to high hydration energy of F^- ion, being smallest anion.

37. $\because$ 58 g *iso*-butane provides energy = 2658 kJ

112×10^3 g *iso*-butane will provide energy

$$= \frac{2658 \times 112 \times 10^3}{58} = 513268.9 \text{ kJ}$$

The daily requirement of energy = 15000 kJ

$\because$ Loss of energy = 30%

$\therefore$ Total energy used for work $= \frac{513268.9 \times 70}{100}$

$\therefore$ Cylinder will last $= \frac{513268.9 \times 70}{100 \times 15000} = 24$ days

38. Heat generated $= C \times \Delta T = 1260 \times 0.667 = 840.4$ cal

$\therefore$ Moles of CH_4 in mixture $= \frac{840}{210.8 \times 10^3} = 3.98 \times 10^{-3}$

Total number of moles in the mixture,

$$n = \frac{74}{76 \times 0.0821 \times 298} = 3.98 \times 10^{-2}$$

$\therefore$ Mol % of $CH_4 = \frac{3.98 \times 10^{-3}}{3.98 \times 10^{-2}} \times 100 = 10\%$

39. $H_2C_2O_4(aq) \longrightarrow 2H^+(aq) + C_2O_4^{2-}(aq)$ $\quad \Delta_{ion}H = x$ kJ

$[H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \Delta_{neut}H = -57.3 \text{ kJ}] \times 2$

$H_2C_2O_4 + 2OH^- \longrightarrow 2H_2O(l) + C_2O_4^{2-}; \Delta H = x - 114.6$ kJ

But $\quad x - 114.6 = -106$ (given)

$\therefore \quad x = 8.6 \text{ kJ mol}^{-1}$

40. O_2 inhaled in one breathe $= \frac{200 \times 20}{100} = 40$ mL

O_2 exhaled in one breathe, $- = \frac{200 \times 10}{100} = 20$ mL

$\therefore$ O_2 used in one breathe = 40 − 20 = 20 mL

$\therefore$ Volume of O_2 used in 1200 breathe taken in one hour at $27°C = 1200 \times 20 = 24000$ mL

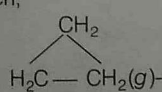
$\therefore$ Volume of O_2 used at $0°C = \frac{24000}{300} \times 273 = 21840$ mL

$\because 6 \times 22400$ mL O_2 is used during burning of 180 g glucose.

$\therefore$ 21840 mL O_2 is used during burning of

$$\left(\frac{180 \times 21840}{6 \times 22400}\right) \text{ g glucose} = 29.25 \text{ g}$$

41. Given,

 $(g) \longrightarrow CH_3CH = CH_2(g)$

$\Delta H = -33.0$ kJ ...(i)

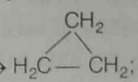
$C + O_2 \longrightarrow CO_2(g); \quad \Delta H = -393.5$ kJ ...(ii)

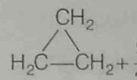
$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l); \Delta H = -285.8$ kJ ...(iii)

$3C + 3H_2 \longrightarrow CH_3 \cdot CH{=}CH_2(g)$

$\Delta H = 20.42$ kJ ...(iv)

Eq. (iv) − Eq. (i) yields

$3C + 3H_2 \longrightarrow$ ; $\quad \Delta H = 53.42$ kJ ...(v)

 $+ \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O$

$\Delta_r H = [3 \times (-393.5)] + (3 \times (-285.5)] - 53.42$

$= -2091.32$ kJ

42. $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O$

or $\quad N{\equiv}N + \frac{1}{2}O{=}O \longrightarrow N{=}N{=}O$

$\therefore \quad \Delta H = BE_{N\equiv N} + \frac{1}{2}BE_{O=O} - [BE_{N=N} + BE_{N=O}]$

$= 946 + \frac{1}{2} \times 498 - [418 + 607] = 1195 - 1025 = +170$

Resonance energy = Experimental value − calculated value

$= 82 - 170 = -88$ kJ

43. For isothermal process, $\Delta U = 0$

From first law of thermodynamics, $\Delta U = q + W$

At constant volume, $\quad \Delta V = 0$

$\therefore \quad W = 0$

So, $\quad \Delta U = q$

i.e., heat involved completely changes to internal energy.

If $\quad \Delta U = 0$

$$q = -W = -\left(-nRT \ln \frac{V_2}{V_1}\right) \qquad \left[\because W_{rev} = -nRT \ln \frac{V_2}{V_1}\right]$$

$$= nRT \ln \frac{V_2}{V_1}$$

44. Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the periodic table is as

2	16	18
Ca	S	Ar
Ba	Se	

Thus, the order of increasing ΔH_{IE_1} is

$$Ba < Ca < Se < S < Ar$$

45. For calculation of C≡C bond energy, we must first calculate dissociation energy of C_2H_2 as

$C_2H_2(g) \longrightarrow 2C(g) + 2H(g)$ ...(i)

By using the given bond energies and enthalpies,

$C_2H_2(g) \longrightarrow 2C(g) + H_2(g); \Delta H = -225$ kJ ...(ii)

$2C(s) \longrightarrow 2C(g);\ \Delta H = 1410$ kJ ...(iii)

$H_2(g) \longrightarrow 2H(g);\ \Delta H = 330$ kJ ...(iv)

On adding Eqs. (ii), (iii) and (iv) gives Eq. (i)

$C_2H_2(g) \longrightarrow 2C(g) + 2H(g);\ \Delta H = 1515$ kJ

$$1515 \text{ kJ} = 2 \times (\text{C—H}) \text{ BE} + (\text{C}\equiv\text{C}) \text{ BE}$$
$$= 2 \times 350 + (\text{C}\equiv\text{C}) \text{ BE}$$
$$(\text{C}\equiv\text{C}) \text{ BE} = 1515 - 700 = 815 \text{ kJ mol}$$

46. Given, $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

$$\Delta H_f^\circ = -46.0 \text{ kJ mol}^{-1}$$

$2H(g) \longrightarrow H_2(g);\ \Delta H_f^\circ = -436$ kJ mol^{-1}

$2N(g) \longrightarrow N_2(g);\ \Delta H_f^\circ = -712$ kJ mol^{-1}

Assuming X is the bond energy of N—H bond (in kJ mol^{-1})

$$\frac{1}{2} \times (-712) + \frac{3}{2} \times (-436) - 3X = -46.0$$
$$3X = 1056 \text{ kJ mol}^{-1}$$

So, $X = 352$ kJ mol^{-1}

47. Consider the heat of formation of H_2O

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -286.20 \text{ kJ}$$
$$\Delta H_r = \Delta_f(H_2O, l) - \Delta H_f(H_2, g)$$
$$-\frac{1}{2}\Delta H_f(O_2, g) - 286.20 = \Delta H_f(H_2O, l) - 0 - 0$$
$$\Delta H_f(H_2O, l) = -286.20$$

Now, consider the ionization of H_2O

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);\ \Delta H = 57.32 \text{ kJ}$$
$$\Delta H_r = \Delta H_f(H^+, aq) + \Delta H_f(OH^-, aq) - \Delta H_f(H_2O, l)$$
$$57.32 = 0 + \Delta H_f(OH^-, aq) - (-286.20)$$

Thus, $\Delta H_f(OH^-, aq) = 57.32 - 286.20 = -228.88$ kJ

48. For the process, $\frac{1}{2}Cl_2(g) \longrightarrow Cl^-(aq)$ using the given step

$$\Delta H = \frac{1}{2}\Delta_{disso}H_{Cl_2} + \Delta_{eg}H_{Cl} + \Delta_{hyd}H_{Cl^-}$$
$$= \frac{240}{2} - 349 - 381 \text{ kJ mol}^{-1}$$
$$= 120 - 349 - 381 \text{ kJ mol}^{-1}$$
$$= -610 \text{ kJ mol}^{-1}$$

49. $H_2O(l) \longrightarrow H_2O(g)$

$$\Delta n_g = 1 - 0 = 1$$
$$\Delta E = \Delta H - \Delta n_g RT = 41 - 1 \times 8.3 \times 373 \times 10^{-3}\ (\because R = 8.3 \times 10^{-3})$$
$$= 37.9 \text{ kJ mol}^{-1}$$

50. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3};\ K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3}$$

K_p or K_c remains constant for above reaction at constant temperature. Although in presence of catalyst the rate of forward as well as backward reaction is increased by same extent due to decreasing the activation energy of both reactions. So, the equilibrium is established in short time but equilibrium state is not affected in presence of catalyst. Hence, at equilibrium $\Delta G = 0$

$\because\ \Delta G = 2 \times G$ of $NH_3 - (3 \times G$ of $H_2 + G$ of $N_2)$

$\therefore\ G_{N_2} + 3G_{H_2} = 2G_{NH_3}$

51. $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl(g)$

$$\Delta H = \left[\frac{1}{2}\Delta H_{s\to g}(I_2) + \frac{1}{2}\Delta H_{diss}(Cl_2) + \frac{1}{2}\Delta H_{diss}(I_2)\right] - \Delta H_{ICl}$$
$$= \left(\frac{1}{2} \times 62.76 + \frac{1}{2} \times 242.3 + \frac{1}{2} \times 151.0\right) - 211.3$$
$$= 228.03 - 211.3 = 16.73$$

52. Carbon is found in solid state. The state of substance affects the enthalpy change.

$C(s) \longrightarrow C(g)$ sublimation

and $H_2(g) \longrightarrow 2H(g)$ dissociation

are required for C – H bond energy.

53. $\Delta H = \Delta E + \Delta n_g RT$

Δn_g = moles of gaseous products – moles of gaseous reactants

= negative

Thus, $\Delta H < \Delta E$

54. $X_2 + Y_2 \longrightarrow 2XY$

$$\Delta H = (BE)_{X-X} + (BE)_{Y-Y} - 2(BE)_{X-Y}$$

If BE of X—Y = a,

(BE) of (X—X) = a and (BE) of (Y—Y) = $a/2$

$$\Delta H_f(X\text{—}Y) = 200 \text{ kJ}$$
$$-400 \text{ (for 2 mol } XY) = a + \frac{a}{2} - 2a$$
$$-400 = -\frac{a}{2}$$
$$a = +800 \text{ kJ}$$

The bond dissociation energy of $X_2 = 800$ kJ mol^{-1}.

55. $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5$ kJ ...(i)

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);\ \Delta H = -283.0$ kJ ...(ii)

Eq. (i) – Eq. (ii) gives Eq. (iii)

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta H = -110.5$ kJ ...(iii)

56. $CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3$

$$\Delta H = (BE)_{reactants} - (BE)_{products}$$
$$= 4(BE)_{C-H} + (BE)_{C=C} + BE_{(H-H)} - [6(BE)_{C-H} + (BE)_{C-C}]$$
$$= -125 \text{ kJ}$$

Day 8

Solutions

Day 8
Outlines ...

- Solutions in Chemistry
- Vapour Pressure
- Raoult's Law
- Ideal Solutions
- Non-ideal Solutions
- Colligative Properties

Solutions in Chemistry

Solution is a homogeneous mixture of two or more substances on molecular level. A solution of two substances is called a binary solution. The substances forming the solution are called components of the solutions. As a generalisation, the component present in smaller amount is called solute and the other present in larger amount is called solvent.

Different Methods for Expressing Concentration of Solutions

1. $$\text{Molality }(m) = \frac{\text{Number of moles of solute}}{\text{Weight of solvent(in kg)}}$$
2. $$\text{Molarity }(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$$

Relation between molality (m) and molarity (M)

$$\text{Molarity }(M) = \frac{m \times d}{1 + \frac{m \times M_2}{1000}}$$

where, M_2 = molar mass of solute

d = density of the solution.

Relation between molarity and strength in g/L of the solution

$$\text{Molarity } (M) = \frac{\text{Strenght in g/L}}{\text{Molecular weight of the solute}}$$

3. Mole fraction of solute in the solution

$$x_{\text{solute}} = \frac{\text{Moles of solute } (n_{\text{solute}})}{\text{Total moles of solution } (n_{\text{solute}} + n_{\text{solvent}})}$$

Mole fraction of solvent in the solution

$$x_{\text{solvent}} = \frac{\text{Moles of solvent } (n_{\text{solvent}})}{\text{Total moles of solution } (n_{\text{solute}} + n_{\text{solvent}})}$$

Sum of mole fractions is always equal to 1

i.e., $x_{\text{solute}} + x_{\text{solvent}} = 1$

Relation between Molarity *and* Mole Fraction

Relation between molarity and mole fraction of the solute (X)

$$x = \frac{MM_1}{M(M_1 - M_2) + d}$$

Here, M_1 = molar mass of solvent

M_2 = molar mass of solute

4. Mass fraction of solute in solution

$$x_{\text{solute}} = \frac{\text{Mass of solute } (w_{\text{solute}})}{\text{Total mass } (w_{\text{solute}} + w_{\text{solvent}})}$$

Mass fraction of solvent in solution

$$x_{\text{solvent}} = \frac{\text{Mass of solvent } (w_{\text{solvent}})}{\text{Total mass } (w_{\text{solute}} + w_{\text{solvent}})}$$

Evidently,

$$x_{\text{solute}} + x_{\text{solvent}} = 1$$

5. $\text{Percentage by weight} = \dfrac{\text{Weight of solute} \times 100}{\text{Weight of solution}}$

6. Percentage by volume

(a) Weight of solute per 100 mL of solution (w/V)

(b) Volume of solute per 100 mL of solution (v/V)

7. ppm concentration

$$= \frac{10^6 \times \text{mass of solute}}{\text{Mass of (solute + solvent)}}$$

8. $\text{Normality} = \dfrac{\text{Moels of substance added to solution}}{\text{Volume of solution (in L)}}$

Vapour Pressure

The pressure exerted by the vapours of a liquid which are in equilibrium with it at a given temperature is called vapour pressure.

Vapour pressure variations with temperature is given as

$$2.303 \log_{10} \frac{p_2}{p_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

p_1 and p_2 are vapour pressures at T_1 and T_2 respectively. ΔH is heat of vaporisation.

Factors Affecting Vapour Pressure

Vapour pressure gets affected by following factors.

- **Purity of the Liquid**
  Pure liquid always has a vapour pressure higher than its solution.
- **Nature of the Liquid**
  Liquids which have weak intermolecular forces are volatile and have greater vapour pressure.
- **Temperature**
  The vapour pressure of a liquid increases with increase in temperature. This is because on increasing the temperature the kinetic energy of molecules increases that results into the fact that more molecules of the liquid can go into vapour phase.
- **Effect of Adding Solute**
  When a liquid contains a solute, some of the solvent molecules are replaced by the solute particles on the liquid surface and therefore, the available surface area for the escape of solvent molecule decreases.

  Due to the less available area on the surface of liquid for escape, rate of evaporation and hence, the rate of condensation both lowers.

  The vapour pressure of liquid in solution is known as its **partial vapour pressure** and is less than the vapour pressure of the pure liquid at the same temperature.

  If $p°$ be the vapour pressure of pure liquid and p_s be that of liquid in solution then lowering of vapour pressure of the liquid $= p° - p_s$

  $\therefore$ Relative lowering in pressure $= \dfrac{p° - p_s}{p°}$

Raoult's Law

Raoult's law for the solutions of liquids in liquids *"The equilibrium vapour pressure of a volatile solute is linearly proportional to the mole fraction of that component in liquid phase".*

$$p_A = X_A p_A^\circ \quad \text{and} \quad p_B = X_B p_B^\circ$$

where, A and B are volatile solute and solvent respectively.

p_A° and p_B° are the vapour pressures in pure state.

If Y_A and Y_B are the mole fraction of the components A and B respectively in the vapour phase then, $p_A = Y_A \cdot p_{\text{total}}$

$$p_B = Y_B \cdot p_{\text{total}}$$

Raoult's law for solutions of solids in liquids *i.e.*, for non-volatile solutes,

$$p_{\text{solution}} = X_{\text{solvent}} \, p_{\text{solvent}}^\circ$$

Limitations of Raoult's Law

1. It is applicable only to very dilute solutions.
2. It is applicable only to solutions containing non-volatile and non-electrolytic solutes which exist as a single molecule.
3. It is not applicable to solutes which dissociate or associate in the particular solution.

Raoult's Law as a Special Case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i \, p_i^\circ$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_H x$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial presssure of the volatile component or gas is directly proportional to its mole fraction in the solution. Only the proportionality constant K_H differs from p_i°, Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i°.

Ideal Solutions

The solutions, which obey Raoult's law are called ideal solutions.

For ideal solutions, $\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$

Solute-solute and solvent-solvent interactions $\approx$ solute-solvent interactions.

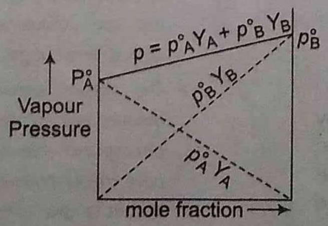
Non-ideal Solutions

The solution which shows deviation from Raoult's law is called non-ideal solution.

For such solutions,

$$\Delta H_{\text{mix}} \neq 0 \, , \, \Delta V_{\text{mix}} \neq 0$$

Practically no solution is ideal. *The graphical representation of ideal solutions is given below.*



Non-ideal Solutions Showing Positive Deviation

When the observed vapour pressure is more than that expected by Raoult's law, positive deviation is observed.

- For such a deviation, $p_A > p_A^\circ X_A$, $p_B > p_B^\circ X_B$
  $p_{\text{Total}} > p_A^\circ X_A + p_B^\circ X_B$

Due to the formation of weaker bonds.

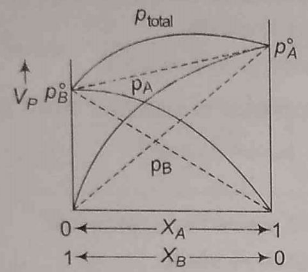


Fig. Graphical representation of the solution showing positive deviation

For such solutions, $\Delta H_{\text{mix}} > 0$ *i.e.*, energy is absorbed on mixing and $\Delta V_{\text{mix}} > 0$. These are usually obtained by mixing of polar liquids with non-polar ones.
e.g., cyclohexane and ethanol, H_2O and C_2H_5OH.

- **Minimum boiling azeotropes** are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components.
  e.g., C_2H_5OH (95.57%) + H_2O(4.43%) (by mass).

Non-ideal Solutions Showing Negative Deviation

When the observed vapour pressure is less than that expected by Raoult's law, this deviation is observed.

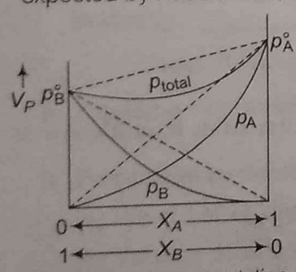


Fig. Graphical representation of the solution showing negative deviation

For such solutions, $\Delta H_{\text{mix}} < 0$, *i.e.*, energy is released on mixing and $\Delta V_{\text{mix}} < 0$, *i.e.*, attractive forces between unlike molecules are greater than the forces of attraction between like molecules.
e.g., chloroform and acetone.
For a solution showing negative deviation,

$$p_A < p_A^\circ \times X_A \text{ or } p_B < p_B^\circ \times X_B$$
$$p_{\text{Total}} < p_A^\circ X_A + p_B^\circ X_B$$

- **Maximum boiling azeotropes** are formed by those liquid pairs which show negative deviation from ideal behaviour. Such azeotropes have boiling points higher than either of the components. *e.g.*, H_2O (20.22% by mass) + HCl.

Colligative Properties

The properties which depend only on the number of moles of non-volatile solute are referred as ***colligative properties****. e.g., relative lowering of vapour pressure, depression in freezing point, elevation in boiling point, osmotic pressure etc.*

- *For different solutions of same molar concentration of different non-electrolyte solutes, the colligative properties have the same value for all.*
- *For different molar concentrations of the same solute, the colligative property has greater value for more concentrated solution.*
- *For solutions of different solutes having same % strength, the colligative property has greater value for the solute having least molecular weight.*

There are four types of colligative properties as given below

1. Relative Lowering of Vapour Pressure

Addition of non-volatile solute leads to the lowering of vapour pressure.

$$\frac{p^\circ - p}{p^\circ} = x_{\text{solute}}$$

or

$$\frac{p^\circ - p}{p^\circ} = \frac{n}{N}$$

where, $\frac{p^\circ - p}{p^\circ}$ = relative lowering of vapour pressure
n = moles of solute
N = moles of solvent
p° = vapour pressure of pure solvent.

$$M_B = \frac{w_B \cdot M_A}{w_A \cdot \left(\frac{p^\circ - p}{p^\circ}\right)}$$

where, w_B and w_A = mass of solute and solvent respectively
M_B and M_A = molecular weight of solute and solvent respectively.

- *Relative lowering in vapour pressure, $\frac{p^\circ - p}{p^\circ} = \frac{w_2}{w_1 + w_2}$ (from Ostwald and Walker method)*
  where, w_1 and w_2 are loss in mass of solution bulbs and solvent bulbs respectively.
- *Glycerol is a hygroscopic substance (absorbs moisture from atmosphere but does not change state after absorbing moisture). NaOH and $MgSO_4$ etc., are deliquescent substance, these also absorb moisture from atmosphere but get dissolve in it.*
- *The vapour pressure of saturated solutions of hygroscopic and deliquescent substances is lower than vapour pressure of water in atmosphere while in case of efflorescent substance, the hydrated crystals have vapour pressure greater than that of water vapours in atmosphere at that temperature.*

2. **Elevation in Boiling Point** (ΔT_b)

For dilute solutions,

$$\Delta T_b = K_b \times \text{molality}$$
$$\Delta T_b = T_b - T^\circ$$

where, T_b = boiling point of solution

T° = boiling point of pure solvent.

K_b is ebullioscopic constant or molal elevation constant (K_b depends only on solvent).

$$\therefore \quad M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

$$K_b = \frac{RT_0^2}{1000\ \Delta H_V}$$

where, R = gas constant and ΔH_V = latent heat of vaporisation.

3. **Depression in Freezing Point** (ΔT_f)

For dilute solutions

$$\Delta T_f = K_f \times \text{molality}$$
$$\Delta T_f = T^\circ - T_f$$

where T° = freezing point of pure solvent

T_f = freezing point of solution.

K_f = cryoscopic constant or molal depression constant

$$\therefore \quad M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$K_f = \dfrac{RT_0^2}{1000\ \Delta H_f}$ where, H_f = latent heat of fusion

4. **Osmosis and Osmotic Pressure**

Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to concentrated solution) is termed as osmosis.

Osmotic pressure $(\pi) = \dfrac{n}{V} RT = CRT$

where,

n = moles of solute, C = molar concentration

V = volume of solution (in litre), R = gas constant

T = temperature in kelvin (K).

$$\therefore \quad M_B = \frac{w_B RT}{\pi V}$$

Two solutions having same osmotic pressures at same temperature are termed as **isotonic solutions.**

When two solutions are being compared, the solution with higher osmotic pressure is termed as **hypertonic** and the solution with lower osmotic pressure is termed as **hypotonic.**

Osmotic pressure can be determined quite accurately, hence it is used in the determination of molecular weights of large proteins and similar substances.

van't Hoff Factor (i)

In 1880 van't Hoff introduced a factor i, known as the vant Hoff factor, to account for the extent of dissociation or association. This factor i is defined as

(i) $i = \dfrac{\text{number of particles after association or dissociation}}{\text{number of particles before association or dissociation}}$

(ii) $i = \dfrac{\text{normal molecular mass}}{\text{observed molecular mass}}$

(iii) $i = \dfrac{\text{observed value of colligative property}}{\text{calculated value of colligative property}}$

Degree of dissociation, $\alpha = \dfrac{i-1}{n-1}$

where, n = number of particles after dissociation.

Degree of association, $\alpha = \dfrac{i-1}{\dfrac{1}{n}-1}$

Here, n = number of particles after association

Modified Expressions of Colligative Properties

1. **Relative lowering of vapour pressure**

$$\frac{p^\circ - p}{p^\circ} = i\,\frac{n_B}{n_B + n_A}; \left(\begin{array}{c} n_B = n \\ n_B + n_A \approx N \end{array}\right)$$

2. **Elevation in boiling point**

$$\Delta T_b = i \cdot K_b \cdot m$$

Here, m = molality

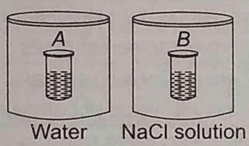
3. **Depression in freezing point**

$$\Delta T_f = i \cdot K_f \cdot m$$

4. **Osmotic pressure** $(\pi) = i \cdot CRT$

Practice Zone DAY 8

1. Two beakers of capacity 500 mL were taken. One of these beakers, labelled as A, was filled with 400 mL water whereas the beaker labelled B was filled with 400 mL of 2 M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in figure. **[NCERT Exemplar]**



At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution.
   (a) vapour pressure in container A is more than that in container B.
   (b) vapour pressure in container A is less than that in container B.
   (c) vapour pressure is equal in both the containers.
   (d) vapour pressure in container B is twice the vapour pressure in container A.

2. If two liquids A and B form minimum boiling azeotrope at some specific composition then .... **[NCERT Exemplar]**
   (a) $A-B$ interactions are stronger than those between $A-A$ or $B-B$.
   (b) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution.
   (c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution.
   (d) $A-B$ interactions are weaker than those between $A-B$ or $B-B$.

3. When mercuric iodide is added to the aqueous solution of potassium iodide, the
   (a) freezing point is raised
   (b) freezing point is lowered
   (c) freezing point does not change
   (d) boiling point does not change

4. Sea water is found to contain 5.85% NaCl and 9.5% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 70% ionisation for NaCl and 50% ionisation of $MgCl_2$ [K_b (H_2O) = 0.51 kg mol^{-1} K]
   (a) 101.4°C (b) 102.29°C
   (c) 103.27°C (d) 99.46°C

5. The molecular weight of benzoic acid in benzene is determined by depression in freezing point method corresponds to
   (a) ionisation of benzoic acid
   (b) dimerisation of benzoic acid
   (c) trimerisation of benzoic acid
   (d) solvation of benzoic acid

6. 1 g of MCO_3 was dissolved in 50 mL N.HCl. The remaining acid required 30 mL of N NaOH for complete neutralisation. The equivalent weight of MCO_3 is
   (a) 20 (b) 30
   (c) 40 (d) 50

7. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution having 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass, will be
   (a) 1.64 (b) 1.88 (c) 1.22 (d) 1.45

8. During depression in freezing point of a solution, the following are in equilibrium
   (a) liquid solvent, solid solvent (b) liquid solvent, solid solute
   (c) liquid solute, solid solute (d) liquid solute, solid solvent

9. An unknown compound is immiscible with water. It is steam distilled at 98.0°C. At 98.0°C, p and $p^{\circ}_{H_2O}$ are respectively 757 and 707 torr. This distillate was 75% by weight water. The molecular weight of the unknown will be
   (a) 318.15 gmol^{-1} (b) 300 gmol^{-1}
   (c) 306.76 gmol^{-1} (d) None of these

10. Which of the following aqueous solutions should have the highest boiling point? **[NCERT Exemplar]**
   (a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
   (c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3

11. 25 mL of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a litre value of 35 mL. The molarity of barium hydroxide solution was

(a) 0.14 (b) 0.28
(c) 0.35 (d) 0.07

12. The vapour pressure of benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solute weighing 2.175 g, is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance?

(a) 6.96 (b) 65.3
(c) 63.8 (d) None of these

13. If M is molecular weight of solvent, K_b is molal elevation constant, T_b is its boiling point, p° is its vapour pressure at temperature T and p_s is vapour pressure of its solution having a non-volatile solute at T K then

(a) $\dfrac{p^\circ - p_s}{p^\circ} = \dfrac{\Delta T_b}{K_b} \times M$

(b) $\dfrac{p^\circ - p_s}{p_s} = \dfrac{K_b}{T_b} \times M$

(c) $\dfrac{p^\circ - p_s}{p^\circ} = \dfrac{K_b}{T_b} \times \dfrac{M}{1000}$

(d) $\dfrac{p^\circ - p_s}{p^\circ} = \dfrac{\Delta T_b}{K_b} \times \dfrac{M}{1000}$

14. The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is

(a) 91.3% (b) 87%
(c) 100% (d) 74%

15. In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to

(a) −0.360°C
(b) −0.260°C
(c) +0.480°C
(d) −0.480°C

16. The depression in freezing point of 0.01 M aqueous solution of urea, sodium chloride and sodium sulphate is in the ratio of

(a) 1 : 1 : 1 (b) 1 : 2 : 3
(c) 1 : 2 : 4 (d) 2 : 2 : 3

17. The freezing point of 0.1M solution of glucose is −1.86° C. If an equal volume of 0.3M glucose solution is added, the freezing point of the mixture will be

(a) −7.44°C (b) −5.58°C
(c) −3.72°C (d) −2.79°C

18. A molal solution of sodium chloride has a density of 1.21 g mL^{-1}. The molarity of this solution is

(a) 4.15 (b) 1.143
(c) 2.95 (d) 3.15

19. Plot of $\dfrac{1}{x_A}$ vs $\dfrac{1}{y_A}$ (x_A = mole fraction of A in liquid and y_A in vapour) is linear whose slope and intercept respectively are given

(a) $\dfrac{p_B^\circ}{p_A^\circ}, \dfrac{p_B^\circ - p_A^\circ}{p_B^\circ}$ (b) $p_A^\circ - p_B^\circ, \dfrac{p_A^\circ - p_B^\circ}{p_B^\circ}$

(c) $\dfrac{p_A^\circ}{p_B^\circ}, \dfrac{p_B^\circ - p_A^\circ}{p_B^\circ}$ (d) $\dfrac{p_B^\circ}{p_A^\circ}, \dfrac{p_A^\circ - p_B^\circ}{p_B^\circ}$

20. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C. The osmotic pressure of dilute solution is 105.3 mm at 25°C. The extent of dilution can be shown as

(a) $V_{final} = 5\,V_{initial}$ (b) $V_{initial} > V_{final}$
(c) $V_{final} = 4\,V_{initial}$ (d) $V_{final} = 6\,V_{initial}$

21. An aqueous solution freezes at −0.186° C ($K_f = 1.86$, $K_b = 0.512$). What is the elevation in boiling point?

(a) 0.186 (b) 0.512
(c) 0.86 (d) 0.0512

22. A 0.001 molal solution of $[Pt(NH_3)_4Cl_4]$ in water had a freezing point depression of 0.0054° C. If K_f for water is 1.80, the correct formulation of the above molecule is

(a) $[Pt(NH_3)_4Cl_3]Cl$ (b) $[Pt(NH_3)_4Cl_2]Cl_2$
(c) $[Pt(NH_3)_4Cl]Cl_3$ (d) $[Pt(NH_3)_4Cl_4]$

23. Acetic acid exists in benzene solution in the dimeric form. In an actual experiment the van't Hoff factor was found to be 0.52. Then, the degree of dissociation of acetic acid is

(a) 0.48 (b) 0.88 (c) 0.96 (d) 0.52

24. The vapour pressure of a solvent decreases by 10 mm of mercury, when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent, if the decrease in vapour pressure is to be 20 mm of mercury?

(a) 0.8 (b) 0.6 (c) 0.4 (d) 0.7

25. The relative lowering of vapour pressure of an aqueous solution containing a non-volatile solute is 0.0125. The molality of the solution is

(a) 0.69 (b) 0.50
(c) 0.80 (d) 0.40

26. In comparison to a 0.01M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is .... **[NCERT Exemplar]**

(a) the same (b) about twice
(c) about three times (d) about six times

27. A compound X undergoes tetramerisation in a given organic solvent. The van't Hoff factor is

(a) 4.0 (b) 0.25
(c) 0.125 (d) 2.0

Directions *(Q. Nos. 28 to 30) Properties such as boiling point, freezing point and vapour pressure of a pure solvent change, when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day to day life. One of its examples is the use of ethylene glycol and water mixture as antifreezing liquid in the radiator of automobiles. 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}

Freezing point depression constant of ethanol ;
K_f (ethanol) = 2.0 K kg mol^{-1}

Boiling point elevation constant of ethanol;
K_b (ethanol) = 1.2 K kg mol^{-1}

Boiling point elevation constant of water;
K_b (water) = 0.52 K kg mol^{-1}

Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K
Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40.0 mm Hg
Molecular weight of water = 18 g mol^{-1}
Molecular weight 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.

28. The freezing point of the solution M is
(a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K

29. The vapour pressure of the solution M is
(a) 39.3 mm Hg (b) 36.0 mm Hg
(c) 29.5 mm Hg (d) 28.8 mm Hg

30. 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

Directions *(Q. Nos. 31 and 32) Vapour pressure of a solvent is the pressure exerted by the vapours when they are in equilibrium with its solvent at that temperature. The vapour pressure of solvent is dependent on nature of solvent, temperature, addition of non-volatile solute as well as nature of solute to dissociate or associate. After addition of a non-volatile solute, the vapour pressure of the solution is found to be lower than the vapour pressure of the pure solvent. According to French chemist Francois Marie Raoult, for a non-volatile solute-solvent system, $p_{solution}$ is directly proportional to the mole fraction of the solvent in the solution i.e., $p_{solution} = x_{solvent}\, p^\circ_{solvent}$*

31. The lowering of vapour pressure of the solvent takes place on dissolving a non-volatile solute because
(a) the density of the solution increases
(b) the surface tension of the solution decreases
(c) the molecules of the solvent on the surface are replaced by the molecules of the solute
(d) the mole fraction of solvent is less than 1

32. The amount of solute (mol. wt. 60) required to dissolve in 180 g of water to reduce the vapour pressure to 4/5 of the pure water is
(a) 120 g (b) 150 g
(c) 200 g (d) 60 g

Directions *(Q. Nos. 33 to 36) Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation of Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. Statement I 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.

Statement II Osmotic pressure is a colligative property but vapour pressure is not a colligative property, however lowering in vapour pressure is a colligative property.

34. Statement I Ebullioscopy or cryoscopy can not be used for the determination of molecular weight of polymers.

Statement II High molecular weight solute leads to very low value of ΔT_b or ΔT_f.

35. Statement I Evaporation and vapour pressure depend upon available surface area of solvent at any temperature.

Statement II Larger is the surface area of solvent for evaporation, more is evaporation.

36. Statement I Super heating means to heat a liquid just above its boiling point.

Statement II On direct heating, the layer in contact with flame has relatively higher temperature than the other layers of liquids.

37. At 100°C, benzene and toluene have vapour pressure of 1375 torr and 558 torr, respectively. Assuming these two form an ideal binary solution, calculate the mole fraction of benzene in vapour phase at 1 atm and 100°C?
(a) 0.247 (b) 0.753
(c) 0.447 (d) 0.553

38. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amount of these two?
(a) 157.8 mL (b) 0.1578 mL (c) 210.4 mL (d) 105.2 mL

39. An aqueous solution of 2% (wt/wt) non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute?
(a) 0.3655 (b) 36.55 (c) 41.34 (d) 40.16

40. Water boils at 95°C in Denver, the mile high city. What is the atmospheric pressure in Denver?
[ΔH_{vap} for H_2O = 40.67 kJ mol^{-1}]
(a) 0.738 atm (b) 0.837 atm (c) 1 atm (d) None of these

41. At 310 K, the vapour pressure of an ideal solution containing 2 moles of *A* and 3 moles of *B* is 550 mm of Hg. At the same pressure if one mole of *B* is added to this solution, the vapour pressure of solution increased by 10 mm of Hg. What is the vapour pressure of *A* in its pure state?
(a) 460 mm (b) 610 mm (c) 360 mm (d) 750 mm

42. 29.2% (wW) HCl Stock solution has density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of Stock solution required to prepare a 200 mL solution of 0.4 M HCl is
(a) 5.0 mL (b) 6.0 mL (c) 8.0 mL (d) 15.0 mL

43. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (mol. wt. 329) in 100 g of water (K_f = 1.86 K kg mol^{-1}) is
(a) -2.3×10^{-2} (b) -5.7×10^{-2}
(c) -5.7×10^{-3} (d) -1.2×10^{-2}

44. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (*i*) is
(a) 0.5 (b) 1 (c) 2 (d) 3

45. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K mol^{-1})
(a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2

46. 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. Degree of dissociation of Na_2SO_4 is
(a) 75% (b) 50% (c) 25% (d) 85%

AIEEE & JEE Main Archive

47. The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be **[JEE Main Online 2013]**
(a) 1.00 M (b) 1.75 M
(c) 0.975 M (d) 0.875 M

48. The density of 3M solution of sodium chloride is 1.252 g mL^{-1}. The molality of the solution will be
(molar mass, NaCl = 58.5 g mol^{-1}) **[JEE Main Online 2013]**
(a) 2.60 m (b) 2.18 m
(c) 2.79 m (d) 3.00 m

49. Vapour pressure of pure benzene is 119 torr and that of toluene is 37.0 torr at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50, will be **[JEE Main Online 2013]**
(a) 0.137 (b) 0.237 (c) 0.435 (d) 0.205

50. How many grams of methyl alcohol should be added to 10 L tank of water to prevent its freezing at 268 K?
(k_f for water is 1.86 K kg mol^{-1}) **[JEE Main Online 2013]**
(a) 880.07 g (b) 899.04 g
(c) 886.02 g (d) 868.06 g

51. 12 g of a non-volatile solute dissolved in 108 g of water produces the relative lowering of vapour pressure of 0.1. The molecular mass of the solute is **[JEE Main Online 2013]**
(a) 80 (b) 60 (c) 20 (d) 40

52. 10 mL of 2M NaOH solution is added to 200 mL of 0.5 L M of NaOH solution. What is the final concentration? **[JEE Main Online 2013]**
(a) 0.57 M (b) 5.7 M
(c) 11.4 M (d) 1.14 M

53. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity fo this solution is **[AIEEE 2012]**
(a) 0.50 M (b) 1.78 M (c) 1.02 M (d) 2.05 M

54. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to $-2.8°$ C? **[AIEEE 2012]**
(a) 72 g (b) 93 g (c) 39 g (d) 27 g

55. For a dilute solution containing 2.5 g of non volatile, nonelectrolyte 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 is much lower than the concentration of solvent, solution is (K_b = 0.76 K kg mol^{-1})
(a) 724 (b) 740 (c) 736 (d) 718

56. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution? **[AIEEE 2011]**
(a) 0.100 (b) 0.190 (c) 0.086 (d) 0.050

57. Ethylene glycol is used as an antifreeze in cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6°C will be (K_f for water = 1.86 K kg mol^{-1} and molar mass of ethylene glycol = 62 g mol^{-1}) **[AIEEE 2011]**

(a) 800.00 g (b) 204.30 g
(c) 400.00 g (d) 304.60 g

58. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression **[AIEEE 2011]**

(a) $\alpha = \dfrac{i-1}{(x+y-1)}$ (b) $\alpha = \dfrac{i-1}{x+y+1}$

(c) $\alpha = \dfrac{x+y-1}{i-1}$ (d) $\alpha = \dfrac{x+y+1}{i-1}$

59. A solution containing 2.675 g of $COCl_3 \cdot 6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is
(Atomic mass of Ag = 108 u) **[AIEEE 2010]**

(a) $[CO(NH_3)_6]Cl_3$ (b) $[COCl_2(NH_3)_4]Cl$
(c) $[COCl_3(NH_3)_3]$ (d) $[COCl(NH_3)_5]Cl_2$

60. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) **[AIEEE 2010]**

(a) 0.0372 K (b) 0.0558 K
(c) 0.0744 K (d) 0.0186 K

61. On mixing, heptane and octane form an ideal solution at 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}). **[AIEEE 2010]**

(a) 72.0 kPa (b) 36.1 kPa (c) 96.2 kPa (d) 144.5 kPa

62. Two liquids X and Y form an ideal solution at 300 K, vapour pressure of the solution containing 1 mol of X and 3 moles of Y is 550 mmHg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mmHg. Vapour pressure (in mmHg) of X and Y in their pure states will be, respectively **[AIEEE 2009]**

(a) 200 and 300 (b) 300 and 400
(c) 400 and 600 (d) 500 and 600

63. The vapour pressure of water at 20°C is 17.5 mm Hg.If 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be **[AIEEE 2008]**

(a) 16.500 mmHg (b) 17.325 mm Hg
(c) 17.675 mm Hg (d) 15.750 mm Hg

64. A 52.5% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be **[AIEEE 2007]**

(a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}
(c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}

65. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be **[AIEEE 2007]**

(a) 350 (b) 300 (c) 700 (d) 360

66. If α is the degree of dissociation of Na_2SO_4, the van't Hoff factor (i) used for calculating the molecular mass is **[AIEEE 2005]**

(a) $1-2\alpha$ (b) $1+2\alpha$ (c) $1-\alpha$ (d) $1+\alpha$

Answers

1. (a)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (b)	**6.** (d)	**7.** (c)	**8.** (a)	**9.** (a)	**10.** (b)
11. (d)	**12.** (b)	**13.** (d)	**14.** (b)	**15.** (d)	**16.** (b)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (a)
21. (d)	**22.** (b)	**23.** (c)	**24.** (b)	**25.** (a)	**26.** (b)	**27.** (b)	**28.** (d)	**29.** (b)	**30.** (b)
31. (d)	**32.** (a)	**33.** (a)	**34.** (a)	**35.** (d)	**36.** (b)	**37.** (c)	**38.** (a)	**39.** (c)	**40.** (b)
41. (a)	**42.** (c)	**43.** (a)	**44.** (c)	**45.** (a)	**46.** (a)	**47.** (d)	**48.** (c)	**49.** (b)	**50.** (c)
51. (c)	**52.** (a)	**53.** (d)	**54.** (b)	**55.** (a)	**56.** (c)	**57.** (a)	**58.** (a)	**59.** (a)	**60.** (b)
61. (a)	**62.** (c)	**63.** (b)	**64.** (a)	**65.** (a)	**66.** (b)				

Hints & Solutions

1. Due to the presence of non-volatile solute NaCl in the beaker B, the vapour pressure of beaker B decreases and becomes less than that of A.
2. Minimum boiling azeotrope shows positive deviations from Raoult's law due to the stronger solute interactions.
3. $2KI + HgI_2 \longrightarrow K_2HgI_4$.

   As a result of this reaction, number of ions decreases. So, the lowering in freezing point is less or the actual freezing point is raised.
4. 100 g solution contains = 5.85 g NaCl = 0.1 mol NaCl

   100 g solution contains = 9.50 g $MgCl_2$ = 0.1 mol $MgCl_2$

   Hence, weight of solvent (H_2O) = 100 −(5.85 + 9.50) = 84.65 g

   NaCl ionises 80%, $NaCl \rightleftharpoons Na^+ + Cl^-$

   $$i = 1 + (y-1)x = (1+x) = 1 + 0.8 = 1.8$$

   Here, y is the number of ions per mole of solute and x is the degree of ionisation.

   Hence, number of moles of NaCl from 0.1 mole due to ionisation = $1.8 \times 0.1 = 0.18$ mol

   $MgCl_2$ ionises 50%, $MgCl_2 \rightleftharpoons Mg^{2+} + 2\,Cl^-$

   $\therefore \quad i = 1 + (y-1)x = 1 + 2x = 1 + 2 \times 0.5 = 2$

   Hence, number of moles of $MgCl_2$ from 0.1 mole $= 2 \times 0.1 = 0.20$

   Total moles of NaCl and $MgCl_2$ in solution $= 0.18 + 0.20 = 0.38$

   $(n_1 + n_2)i = 0.38$

   $$\text{Elevation in boiling point } (\Delta T_b) = \frac{1000\,K_b\,(n_1+n_2)\,i}{w_2} = \frac{1000 \times 0.51 \times 0.38}{84.65} = 2.29°\text{ C}$$

   Hence, boiling point of solution = 100 + 2.29 = 102.29° C
5. Benzoic acid undergoes dimerisation in benzene.
6. Acid used in reaction = 50 − 30 = 20 mL (N)HCl

   $$\text{Equivalent weight} = \frac{\text{Heigh of substance (in g)}}{\text{Normality} \times \text{volume (in L)}} = \frac{1 \times 1000}{1 \times 20} = 50$$
7. $$\text{Molarity} = \frac{10 \times \text{density} \times \text{\% by wt. of solute}}{\text{mol. wt. of the solute}}$$

   $$\text{Density} = \frac{3.60 \times 98}{10 \times 29} = 1.21\text{ g/mL}$$
8. When freezing starts, liquid solvent is in equilibrium with the solid solvent (both have the same vapour pressure).
9. Since unknown compound is immiscible with water, hence vapour pressure ∝ moles.

   Given, $\quad p^\circ_{\text{total}} = 737$ torr

   $p^\circ_{H_2O} = 707$ torr,

   $\therefore \quad p^\circ_{\text{unknown}} = 737 - 707 = 30$ torr

   $W_{H_2O} = 100$ g

   $W_{\text{unknown}} = 75$ g

   $$\frac{p^\circ_{\text{unknown}}}{p^\circ_{\text{water}}} = \frac{n_{\text{unknown}}}{n_{H_2O}} = \frac{W_{\text{unknown}} \times m_{H_2O}}{W_{H_2O} \times m_{\text{unknown}}}$$

   or $$\frac{30}{707} = \frac{75.0 \times 18}{100 \times m_{\text{unknown}}}$$

   or $$m_{\text{unknown}} = 318.15\text{ g mol}^{-1}$$
10. Boiling point of the solution depends upon van't hoff factor (i). Na_2SO_3 possess larger value of i than other given solutions.
11. $Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

    $$\underset{Ba(OH)_2}{\frac{M_1 \times V_1}{1}} = \underset{(HCl)}{\frac{M_2 \times V_2}{2}}$$

    or $$\frac{M_1 \times 25}{1} = \frac{0.1 \times 35}{2}$$

    $\therefore \quad M_1 = 0.07$
12. $$\frac{640-600}{640} = \frac{2.175/M_2}{2.175/M_2 + 39/78}$$

    or $$0.0625\left[\frac{2.175}{M_2} + 0.5\right] = \frac{2.175}{M_2}$$

    or $$0.9375 \times \frac{2.175}{M_2} = 0.0625 \times 0.5$$

    or $$M_2 = 65.3$$
13. $$\frac{p^\circ - p_s}{p^\circ} = \frac{n}{N} = \frac{\text{molality} \times M}{1000}$$

    and $\quad \text{molality} = \dfrac{\Delta T_b}{K_b} \qquad (\because \Delta T_b = K_b \times m)$
14.

	$Ba(NO_3)_2$	$\rightleftharpoons$	Ba^{2+}	+	$2NO_3^-$
Initially	1 mol		0		0
After dissociation	$1-\alpha$		α		2α

    Total number of moles = $1 + 2\alpha$

    $\therefore \quad i = 1 + 2\alpha$

    or $$\alpha = \frac{i-1}{2} = \frac{2.74-1}{2} = 0.87 = 87\%$$
15.

	HX	$\rightleftharpoons$	H^+	+	X^-
Initially	1 mol		0		0
After dissociation	$1-0.3$		0.3		0.3

    Total moles = 1 − 0.3 + 0.3 + 0.3 = 1.3

    $$i = \frac{1.3}{1} = 1.3$$

    $$\Delta T_f = iK_f m = 1.3 \times 1.85 \times 0.2 = 0.481°\text{C}$$

    $\therefore \quad T_f = 0 - 0.481°\text{ C} = -0.481°\text{ C}$

16. Concentrations of particles of 0.01 M urea, NaCl and Na_2SO_4 are 0.01 M 0.02 M, 0.03 M respectively *i.e.*, they are in the ratio of 1:2:3. Hence, depression in freezing point will be in the same ratio.

17. $$K_f = \Delta T_f / M = 1.86 / 0.1 = 18.6$$

$$0.1 \times V + 0.3V = M_3 \times 2V$$

or $$M_3 = 0.2,$$

$$\Delta T_f = 18.6 \times 0.2 = 3.72°\text{C}$$

$\therefore$ $$T_f = -3.72°\text{ C}$$

18. 1 m NaCl solution = 1 mol NaCl in 1000 g water

= 58.5 + 1000 g solution

= 1058.5 g solution

= 1058.5/1.21 mL

= 875 mL.

$$\text{Molarity} = \frac{1}{875} \times 1000 = 1.143$$

19. $y_A = \dfrac{x_A p°_A}{p}$ and $y_B = \dfrac{x_B p°_B}{p}$

$\therefore$ $$\frac{x_B p°_B}{x_A p°_A} = \frac{y_B}{y_A}$$

or $$\frac{p°_B (1 - x_A)}{p°_A x_A} = \frac{1 - y_A}{y_A}$$

or $$\frac{p°_B}{p°_A}\left(\frac{1}{x_A} - 1\right) = \left(\frac{1}{y_A} - 1\right)$$

or $$\frac{1}{x_A} = \frac{p°_A}{p°_B} \times \frac{1}{y_A} + \left[1 - \frac{p°_A}{p°_B}\right]$$

or $$\frac{1}{x_A} = \frac{p°_A}{p°_B} \times \frac{1}{y_A} + \frac{p°_B - p°_A}{p°_B}$$

This is the equation of straight line, where $\dfrac{p°_A}{p°_B}$ is slope and $\dfrac{p°_B - p°_A}{p°_B}$ is intercept.

20. For initial solution,

$\because$ $$\pi = \frac{500}{760}\text{ atm},$$

$$T = 283\text{ K}$$

$\therefore$ $$\frac{500}{760} \times V_{\text{initial}} = n \times R \times 283 \quad \ldots\text{(i)}$$

After dilution

$$\pi = \frac{105.3}{760}\text{ atm}, T = 298\text{ K}$$

$\therefore$ $$\frac{105}{760} \times V_{\text{final}} = n \times R \times 298 \quad \ldots\text{(ii)}$$

From Eqs. (i) and (ii), we get

$\dfrac{V_{\text{initial}}}{V_{\text{final}}} = \dfrac{1}{5}$ *i.e.*, solution was diluted to 5 times.

21. $0.186 = 1.86 \times m$ or $m = 0.1$,

$$\Delta T_b = 0.512 \times 0.1 = 0.0512°\text{C}$$

22. Suppose,

$$[Pt(NH_3)_4Cl_4] \xrightarrow{\text{Dissociation}} n \text{ moles of product ions}$$

$\therefore$ $$i = n.$$

But from the given data

$$\Delta T_f = iK_f m$$

$\Rightarrow$ $$0.0054 = n \times 1.80 \times 0.001$$

$\therefore$ $$n = 3$$

Hence, the formula must be the one which gives 3 ions of products.

23.
$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

	$2CH_3COOH$	$(CH_3COOH)_2$
Initially	1	0
After dissociation	$1 - \alpha$	$\alpha / 2$

$$i = 1 - \frac{\alpha}{2}$$

or $$\alpha = 2(1 - i) = 2(1 - 0.52) = 0.96$$

24. $$\frac{\Delta p}{p°} = x_2$$

$\therefore$ $$\frac{10}{p°} = 0.2$$

or $$p° = 50\text{ mm}$$

Again, $$\frac{20}{p°} = x_2$$

or $$\frac{20}{50} = x_2 \text{ i.e., } x_2 = 0.4$$

$\therefore$ $$x_1 = 1 - 0.4 = 0.6$$

25. $$\frac{p° - p_s}{p°} = \frac{m \times M}{1000}$$

$$0.0125 = \frac{m \times 18}{1000} \quad \text{(mol. wt. of } H_2O = 18\text{)}$$

$$m = \frac{0.0125 \times 1000}{18} = 0.69$$

26. Glucose does not undergo ionisation when dissolved in water whereas $MgCl_2$ releases 3 ions $[Mg^{+} + 2Cl^{-}]$ when dissolved in water. Thus, i for $MgCl_2$ is 3 while that of glucose is 0. Thus, depression of freezing point of 0.01 M, $MgCl_2$ solution is about three times than 0.01 M glucose solution.

27.
$$\begin{array}{ccc} 4A & \rightleftharpoons & (A)_4 \\ 1 - \alpha & & \dfrac{\alpha}{4} \end{array}$$

$$i = \frac{1 - \alpha + \dfrac{\alpha}{4}}{1} = 1 - \frac{3}{4}\alpha$$

α = degree of dissociation = 1 = 100%

$\therefore$ $$i = 1 - \frac{3}{4} = 0.25$$

28. Solution M is the mixture of ethanol and water.
Mole fraction of ethanol is 0.9 $\Rightarrow$ solvent is C_2H_5OH
Mole fraction of water is 0.1 $\Rightarrow H_2O$ is solute

$$\text{Molality of } H_2O = \frac{n_2}{n_1M_1}$$

$$= \frac{0.1}{0.9 \times 46} \times 1000 = 2.415$$

$$\Delta T_f = K_f m = 2 \times 2.415 = 4.83$$

and freezing point of solution = 155.7 − 4.83
= 150.87 K

29. Total vapour pressure, $p = p_A^\circ x_A$

$$p = 40 \times 0.9 = 36 \text{ mm Hg}$$

In the paragraph, it has been directed to take solute as non-volatile, thus H_2O do not contribute in the total vapour pressure.

30. $x_{H_2O} = 0.9$ (solvent), $x_{C_2H_5OH} = 0.1$ (solute)

$$\Delta T_b = K_b m$$

$$= 0.52 \times \frac{0.1 \times 1000}{0.9 \times 18}$$

$$= 3.2 \text{ K}$$

Boiling point, $T_b = 373 + 3.2 = 376.2$ K

31. Vapour pressure does not depend upon surface area of a volatile liquid.

$$\frac{p}{p^\circ} = x_{\text{solvent}}$$

In case of solution, $x_{\text{solvent}} < 1$

$\therefore \quad p < p^\circ$

32.
$$\frac{p^\circ - p_s}{p^\circ} = \frac{n}{N}$$

or
$$\frac{p^\circ - \frac{4}{5}p^\circ}{p^\circ} = \frac{w_{\text{solute}} \times 18}{60 \times 180}$$

or $w_{\text{solute}} = 120$ g

33. Statement II is the correct explanation of Statement I.

34. The changes observed in these properties are very small, (*e.g.*, 0.00001 K for substances having molar masses of the order of 10^6 g mol^{-1}). A little error in measurement of ΔT_b or ΔT_f will cause abnormal values of molecular weight.

35. Vapour pressure is independent of surface area.

36. These are facts about superheating.

37. Let x_1 be the mole fraction of benzene in solution

Applying Raoult's law

$$p = x_1p^\circ_1 + (1 - x_1)p^\circ_2$$

or
$$760 = x_1(1375) + (1 - x_1)(558)$$

or
$$x_1 = \frac{760 - 558}{1375 - 558} = 0.247 \text{ torr}$$

Mole fraction of benzene in vapour phase

$$y_1 = \frac{x_1p^\circ_1}{p}$$

$$= \frac{0.247 \times 1375}{760} = 0.447$$

38. Let amount of Na_2CO_3 be 'x' g and $NaHCO_3$ will be $(1 - x)$ g.

$\because \quad n_{Na_2CO_3} = n_{NaHCO_3}$

$\therefore \quad \frac{x}{106} = \frac{1 - x}{84}$

$\Rightarrow \quad x = \frac{106}{190} = 0.5578 \text{ g}, 1 - x = 0.4422 \text{ g}$

$$n_{Na_2CO_3} = n_{NaHCO_3}$$

$$= \frac{0.5578}{106} = 0.00526 \text{ mol}$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

and
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$\underset{(HCl)}{M_1V_1} = \underset{(Na_2CO_3)}{M_2V_2} + \underset{(NaHCO_3)}{M_3V_3}$$

$$0.1 \times V_1 = 2 \times 0.00526 + 0.00526$$

$$V_1 = 157.8 \text{ mL}$$

39. $p^\circ = 1.013$ bar = 1 atm (at boiling point)

$$w_{\text{solvent}} = 100 - 2 = 98 \text{ g},$$

According to Raoult's law

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w_{\text{solute}}}{M_{\text{solute}}} \times \frac{M_{\text{solvent}}}{w_{\text{solvent}}}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{M_{\text{solute}} \times 98}$$

$\therefore \quad M_{\text{solute}} = 41.34 \text{ g mol}^{-1}$

40.
$$2.303 \log \frac{p_2}{p_1} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1T_2}$$

or
$$2.303 \log \frac{p_2}{p_1} = \frac{40.67 \times 10^3}{8.314} \times \frac{[373 - 368]}{373 \times 368}$$

(At $p_2 = 76$ cm, $T_b = 100°$ C)

($p_1 = ?, T_b = 95°$ C)

$$\log \frac{p_2}{p_1} = 0.077$$

$$p_1 = 63.65 = 0.837 \text{ atm}$$

41. $p = x_Ap^\circ_A + x_Bp^\circ_B$

or
$$550 = p^\circ_A \left(\frac{2}{5}\right) + p^\circ_B \left(\frac{3}{5}\right)$$

or
$$2p^\circ_A + 3p^\circ_B = 2750 \quad \ldots(i)$$

$\Rightarrow$ When 1 mole of B is added to it,

$$560 = p^\circ_A \left(\frac{2}{6}\right) + p^\circ_B \left(\frac{4}{6}\right)$$

or

$$2p^\circ_A + 4p^\circ_B = 3360 \quad \ldots\text{(ii)}$$

From Eqs. (i) and (ii), we get

$$p^\circ_A = 460 \text{ mm}$$

42. Mass of HCl in 1.0 mL Stock solution

$$= 1.25 \times \frac{29.2}{100} = 0.365 \text{ g}$$

Mass of HCl required for 200 mL = 0.4 M HCl

$$= \frac{200}{1000} \times 0.4 \times 36.5$$

$$= 0.08 \times 36.5 \text{ g}$$

$\because$ 0.365 g of HCl is present in 1.0 mL Stock solution

$\therefore$ 0.08 × 36.5 g HCl will be present in

$$\frac{0.08 \times 36.5}{0.365} = 8 \text{ mL stock solution}$$

43. van't Hoff factor (i) = 4 $\{3K^+ + [Fe(CN)_6]^{3-}\}$

$$\text{Molality} = \frac{0.1 \times 1000}{329 \times 100} = \frac{1}{329}$$

$$-\Delta T_f = iK_f m$$

$$= 4 \times 1.86 \times \frac{1}{329}$$

$$= 2.3 \times 10^{-2}$$

(As freezing point of water is 0°C.)

44. Actual molecular weight of naphthoic acid, $(C_{11}H_8O_2) = 172$

$$\text{Molecular mass (calculated)} = \frac{1000 \times K_f \times w_{\text{solute}}}{w_{\text{solvent}} \times \Delta T_f}$$

$$= \frac{1000 \times 1.72 \times 20}{50 \times 2} = 344$$

$$\text{van't Hoff factor } (i) = \frac{\text{actual mol. wt.}}{\text{calculated mol. wt.}}$$

$$= \frac{172}{344} = 0.5$$

45.

	$CuCl_2$	$\rightleftharpoons Cu^{2+}$	$+ \; 2Cl^-$
Initially	1 mol	0	0
After ionisation	$(1-\alpha)$ mol	α mol	2α mol

Thus, number of particles after ionisation

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

van't Hoff factor (i)

$$= \frac{\text{Number of particles after ionisation}}{\text{Number of particles before ionisation}}$$

$$i = \frac{1 + 2\alpha}{1} \text{ (on 100\% ionisation, } \alpha = 1)$$

$$= \frac{1 + 2 \times 1}{1} = 3$$

$\because \quad \Delta T_b = iK_b m$

$$\therefore \quad \Delta T_b = \frac{3 \times 0.52 \times 13.44}{134.4 \times 1}$$

$$= 0.156$$

$$\approx 0.16°\text{C}$$

46. 0.004 M Na_2SO_4 solution is isotonic with 0.01 M solution of glucose, so their osmotic pressure are equal to each other. Osmotic pressure of 0.01 M glucose,

$$\pi_{\text{glucose}} = CRT = 0.01 \times 0.0821 \times T$$

$$= (\pi_{\text{obs}})Na_2SO_4 = \pi_{\text{glucose}}$$

$$= 0.01 \times 0.0823 \times T$$

	$Na_2SO_4 \rightleftharpoons$	$2Na^+$	$+ \; SO_4^{2-}$
Initially	1	0	0
After dissociation	$1-\alpha$	2α	α

$$(\pi_{\text{cal}})\, Na_2SO_4 = CRT$$

$$= 0.004 \times 0.0821 \times T$$

By van't Hoff factor;

$$i = \frac{(\pi_{\text{obs}})Na_2SO_4}{(\pi_{\text{cal}})Na_2SO_4}$$

$$= \frac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}}$$

$$= \frac{1 - \alpha + 2\alpha + \alpha}{1}$$

$$\frac{0.01 \times 0.0821 \times T}{0.004 \times 0.0821 \times T} = \frac{1 + 2\alpha}{1}$$

$$\frac{10}{4} = \frac{1 + 2\alpha}{1}$$

$$\alpha = \frac{10 - 4}{8} = 0.75$$

$\therefore$ Percentage of α = 75%

47. $M_1V_1 + M_2V_2 = MV$ (Total Moles)

$$M = \frac{M_1V_1 + M_2V_2}{V}$$

$$M = \frac{0.5 \times 750 + 2 \times 250}{1000}$$

$$M = 0.875$$

48. 3M solution means 3 moles of solute (NaCl) are present in 1000 L of solution.

Mass of solution = volume of solution × density

$$= 1000 \times 1.252$$

$$= 1252 \text{ g}$$

Mass of solute = No. of moles × molar mass of NaCl

$$= 3 \times 58.5 \text{ g}$$

$$= 175.5 \text{ g}$$

Mass of solvent $= (1252 - 175.5)$ g
$= 1076.5$ g
$= 1.076$ kg

$$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent (in kg)}} = \frac{3}{1.076} = 2.79\,\text{m}$$

49. From Raoult's law, for ideal solution,

$$p = p_B^0 x_B + p_T^0 x_T$$

[B = Benzene, T = Toluene]

$$= 119 \times 0.5 + 37 \times 0.5 \qquad (\because x_B = 1 - x_T)$$
$$= 59.5 + 18.5$$
$$= 78 \text{ torr}$$

Mole fraction of toluene in vapour phase

$$(x_T)_v = \frac{p_T^0 x_T}{p} = \frac{18.5}{78} = 0.237$$

50. Normal freezing point of water $= 273.15$ K. In order to prevent freezing at 268 K, let the amount of methanol added be x g.

$\therefore$ Molality, $\quad m = \dfrac{x}{32 \times 10} = \dfrac{x}{320}$

[$\because$ Molar mass of $CH_3OH = 32$ g mol^{-1} and mass of $H_2O = V$ of H_2O because density of water $\simeq 1$ gm L^{-1}]

Lowering in freezing point $= K_f \cdot m$

$$273.15 - 268 = 1.86 \times \frac{x}{320}$$
$$5.15 = \frac{1.86x}{320}$$

or $\quad x = \dfrac{5.15 \times 320}{1.86} = 886.02$ g

51. From Raoult's law

Relative lowering in vapour pressure

$$\Delta p = \frac{p^\circ - p}{p^\circ} = \frac{n}{N} = \frac{w}{m} \times \frac{M}{W}$$

$w = 12$ g; $W = 108$ g, $m = ?$

$M = 18$ g, $\Delta p = 0.1$

$$\Delta p = \frac{w}{m} \times \frac{M}{W}$$
$$0.1 = \frac{12}{m} \times \frac{18}{108}$$
$$m = \frac{12 \times 18}{10.8} = 20$$

52. Final Concentration, $M = \dfrac{M_1V_1 + M_2V_2}{V_1 + V_2}$

$$= \frac{10 \times 2 + 200 \times 0.5}{200 + 10} = \frac{20 + 100}{210} = \frac{120}{210} = 0.57\ \text{M}$$

53. Total mass of solution $= 10000$ g water $+ 120$ g urea.
$= 1120$ g

Density of solution $= 1.15$ g/ml

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{120\,\text{g}}{1.15\,\text{g/ml}}$$
$$= 973.91\,\text{ml} = 0.974\ \text{L}$$

$$\text{Mass of solute} = \frac{120}{60} = 2$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume (L) of solution}} = \frac{2}{0.974} = 2.05\ \text{mol/L}$$

54. Coolant is glycol ($C_2H_6O_2$) which is non-electrolyte.

$$\Delta T_f = 2.8^\circ\ \text{C}$$
$$\Delta T_f = \frac{1000\, K_f\, w_1}{m_1 w_2}$$
$$2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$\therefore \quad w_1 = 93.33$ g

55. The elevation in boiling point is

$$\Delta T_b = K_b \cdot m \left(m = \frac{n_2 \times 1000}{w_1} \right)$$
$$\Delta T_b = 2 = \frac{0.76 \times n_2 \times 1000}{100}$$

or $\quad n_2 = \dfrac{5}{19}$

From Raoult's law of lowering of vapour pressure

$$\frac{-\Delta p}{p^\circ} = x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \qquad (\because n_1 >> n_2)$$
$$-\Delta p = 760 \times \frac{5 \times 18}{19 \times 100} = 36 \text{ mm of Hg}$$
$$p = 760 - 36 = 724 \text{ mm of Hg}$$

56. Molality $= \dfrac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$

$$= \frac{5.2 \text{ mol } CH_3OH}{1 \text{ kg } (= 1000 \text{ g}) \ H_2O}$$

$$n_1\ (CH_3OH) = 5.2$$
$$n_2\ (H_2O) = \frac{1000}{18} = 55.56$$

$\therefore$ $$n_1 + n_2 = 5.20 + 55.56 = 60.76 \text{ mol}$$

$\therefore$ Mole fraction of CH_3OH, x_{CH_3OH}

$$= \frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086$$

57. ΔT_f = freezing point of H_2O – freezing point of ethylene glycol solution $= 0 - (-6^\circ) = 6^\circ$

$K_f = 1.86^\circ$ kg mol^{-1} kg mol^{-1}

w_1 = Mass of ethylene glycol in grams

w_2 = Mass of solvent (H_2O) in grams = 4000 g

m_1 = Molar mass of ethylene glycol = 62 g mol^{-1}

i = van't Hoff factor = 1

($\because$ ethylene glycol is non-electrolyte)

From, $$\Delta T_f = \frac{1000\, K_f\, w_1(i)}{m_1\, w_2}$$

$\therefore$ $$6 = \frac{1000 \times 1.86 \times w_1 \times 1}{62 \times 4000}$$

$$w_1 = 800 \text{ g}$$

58. $$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

	A_xB_y	xA^{y+}	yB^{x-}
Initially	1	0	0
After dissociation	$(1-\alpha)$	$x\alpha$	$y\alpha$

$$i = n(A_xB_y) + n(A^{y+}) + n(B^{x-})$$

$$= 1 - \alpha + x\alpha + y\alpha = 1 + \alpha(x + y - 1)$$

$\therefore$ $$\alpha = \frac{i-1}{(x+y-1)}$$

59. Mole of $CoCl_3 \cdot 6NH_3 = \frac{2.675}{267.5} = 0.01$

$$AgNO_3(aq) + Cl^-(aq) \longrightarrow \underset{\text{(white)}}{AgCl\downarrow}$$

$$\text{Moles of AgCl} = \frac{4.78}{143.5} = 0.03$$

0.01 mol $CoCl_3 \cdot 6NH_3$ gives = 0.03 mol AgCl

$\therefore$ 1 mol $CoCl_3 \cdot 6NH_3$ ionises to give = 3 mol Cl^-

Hence, the formula of compound is $[Co(NH_3)_6]Cl_3$.

60. $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

$\therefore$ van't Hoff factor (i) for $Na_2SO_4 = 3$

From $$\Delta T_f = i \times K_f \times m$$

$$= 3 \times 1.86 \times 0.01 \qquad \left[\because m = \frac{0.01}{1} = 0.01\right]$$

$$= 0.0558 \text{ K}$$

61. $p_T = X_H \cdot p_H^\circ + X_O \cdot p_O^\circ$

$$X_H = \frac{\frac{25}{100}}{\frac{25}{100} + \frac{35}{114}} = 0.45$$

$\therefore$ $$X_O = 1 - 0.45 = 0.55$$

$$p_T = 0.45 \times 105 + 0.55 \times 45 = 72 \text{ kPa}$$

62. $p_T = p^\circ_A\, X_A + p^\circ_B\, X_B$

$$550 = p^\circ_A \times \frac{1}{4} + p^\circ_B \times \frac{3}{4}$$

Thus, $$p^\circ_A + 3p^\circ_B = 2200 \quad \text{...(i)}$$

When, 1 mole of y is further added to the solution

$$560 = p^\circ_A + \frac{1}{5} + p^\circ_B \times \frac{4}{5}$$

Thus, $$p^\circ_A + 4p^\circ_B = 2800 \quad \text{...(ii)}$$

On subtracting, Eq. (ii) – Eq (i)

$$p^\circ_B = 2800 - 2200$$

$$= 600 \text{ mm Hg}$$

Putting the value of p°_B in Eq. (i)

$$p^\circ_A + 3 \times 600 = 2200$$

$$p^\circ_A = 2200 - 1800$$

$$= 400 \text{ mm Hg}$$

63. $$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

or $$\frac{17.5 - p_s}{p^\circ} = \frac{18/180}{1782/18 + 18/180}$$

or $$\frac{17.5 - p_s}{17.5} = \frac{1/10}{9.9 + 0.1}$$

or $$p_s = 17.325 \text{ mm Hg.}$$

64. Molar concentration of the substance

= Molar concentration of urea

$$\frac{52.5\text{g L}^{-1}}{M} = \frac{15\text{gL}^{-1}}{60 \text{ g mol}^{-1}}$$

($\therefore$ 100 g solution = 100 mL as d = 1gmL^{-1})

$\therefore$ $$M = 210 \text{ g mol}^{-1}$$

65. According to Raoult's law

$$p = p^\circ_A\, x_A + p^\circ_B\, x_B$$

$$290 = 200 \times 0.4 + p^\circ_B \times 0.6$$

$$p^\circ_B = 350$$

66. $Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

van't Hoff factor, $i = [1 + (y-1)\alpha]$

Where, y is the number of ions obtained from one mole solute, (in this case = 3), α is the degree of dissociation.

$\therefore$ $$i = 1 + 2\alpha$$

Day 9

Physical and Chemical Equilibrium

Day 9

Outlines ...

- Equilibrium State
- Physical Processes
- Chemical Equilibrium
- Reaction Quotient (Q)
- Le-Chatelier's Principle

Equilibrium State

In a reversible reaction, the point at which there is no further change in concentration of reactants and products, is called equilibrium state.

Some important features of equilibrium state are

(i) Equilibrium is attained in a closed container.

(ii) At equilibrium,
Rate of forward reaction = Rate of backward reaction.

(iii) At equilibrium, concentration of reactants and products becomes constant.

(iv) **Dyanamic Nature** Equilibrium is always dynamic in nature *i.e.*, the reaction does not stop but goes on forward and backward directions with equal speed.

Example solid $\rightleftharpoons$ liquid (physical equilibria)

$$H_2O(s) \rightleftharpoons H_2O(l) \quad (273 \text{ K}, 1 \text{ atm})$$

It indicates that at equilibrium, rate of conversion of ice into water = rate of conversion of water into ice

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \text{(Chemical equilibria)}$$

(v) Catalyst helps in attaining the state of equilibrium quickly without changing the state of equilibrium.

Types of Equilibrium

On the basis of physical state of reactants and products, equilibrium may be of following two types

(i) **Homogeneous equilibria,** in which reactants and products are in same phase e.g.,

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(ii) **Heterogeneous equilibria,** in which reactants and products are in different phase e.g.,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

On the basis of processes involved equilibrium may be of following types

(i) Physical equilibrium
(ii) Chemical equilibrium
(iii) Ionic equilibrium

Physical Equilibrium

A physical equilibrium is a state at which two phases of a compound can co-exist and an equilibrium is established between these two states.

This may be attained by the following ways.

- **Solid-liquid Equilibrium**

  $$\text{Ice} \rightleftharpoons \text{Water}$$

  at equilibrium, rate of melting of ice = rate of freezing of water
- **Liquid-gas Equilibrium**

  $$\text{Water} \rightleftharpoons \text{Water vapours}$$

  at equilibrium, rate of evaporation of water = rate of condensation of water vapours
- **Solid-gas Equilibrium**

  Certain solids on heating directly change from solid into vapour state (sublimation).

  $$\underset{\text{(solid)}}{\text{Naphthalene}} \rightleftharpoons \underset{\text{(vapour)}}{\text{Naphthalene}}$$

Law of Chemical Equilibrium

The rate of reversible reactions at which the concentration of the reactants and products do not change with time is known as chemical equilibrium.

Active mass = molar concentration (mol/L)

Law of mass action states

"Rate of reaction is directly proportional to the concentration of reactants with each concentration term raised to the power equal to the respective stoichiometric coefficient".

$$aA + bB \rightleftharpoons cC + dD$$

Rate of forward reaction $\propto [A]^a [B]^b$

Rate of forward reaction $= k_f [A]^a [B]^b$

Rate of backward reaction $\propto [C]^c [D]^d$

Rate of backward reaction $= k_b [C]^c [D]^d$

At equilibrium- $k_f [A]^a [B]^b = k_b [C]^c [D]^d$

$$\frac{k_f}{k_b} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where,

K_c = equilibrium constant
k_f = rate constant for forward reaction
k_b = rate constant for backward reaction

This expression is also known as law of chemical equilibrium

For a gaseous reaction, $K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$

where, K_p = equilibrium constant in terms of partial pressure

Units of K_c and K_p

- If $\Delta n_g = 0$, $K_p = K_c$, no units for both K_c and K_p.
- If $\Delta n_g > 0$, unit of K_c is $(\text{mol L}^{-1})^{\Delta n_g}$ and that of K_p is $(\text{atm})^{\Delta n_g}$
- If $\Delta n_g < 0$, unit of K_c is $(\text{L mol}^{-1})^{\Delta n_g}$ and that of K_p is $(\text{atm})^{\Delta n_g}$

Significance of K_c and K_p

- If $K_c > 10^3$, products predominate over reactants. In other words, if K_c is very large, the reaction proceeds almost in all the ways to completion.
- If $K_c < 10^{-3}$, reactants predominate over products. In other words, if K_c is very small, the reaction proceeds hardly at all.
- If K_c is in the range 10^{-3} to 10^3, appreciable concentration of both reactants and products are present.
- Relation between K_p and K_c

$$K_p = K_c (RT)^{\Delta n_g}$$

R = gas constant, T = temperature in kelvin
Δn_g = gaseous moles of products–gaseous moles of reactants

Hence, (i) If $\Delta n_g = 0, K_p = K_c$
(ii) If $\Delta n_g = +\text{ve}, K_p > K_c$
(iii) If $\Delta n_g = -\text{ve}, K_p < K_c$

» *Equilibrium constant in terms of mole fractions,* K_x

$$aA + bB \rightleftharpoons cC + dD$$

$$K_x = \frac{[x_C]^c [x_D]^d}{[x_A]^a [x_B]^b}$$

Similarly, $K_p = K_x (p)^{\Delta n_g}$

» *Equilibrium constant in terms of activities,* K_a

$$K_a = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Activity = activity coefficient × molality (or molarity)

i.e., $a = \gamma \times m$

Some Facts Related to Equilibrium Constant

(i) Equilibrium constant (K_p or K_c) does not depend on pressure, volume, concentration and catalyst but depends only upon temperature.

(ii) Equilibrium constant for a given reaction is independent of the reaction mechanism.

(iii) Equilibrium constant depends on stoichiometric coefficient *e.g.,*

$$H_2(g) + I_2(g) \xrightleftharpoons{K_{c_1}} 2HI(g)$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \xrightleftharpoons{K_{c_2}} HI(g)$$

$$K_{c_2} = \sqrt{K_{c_1}}$$

$$HI(g) \xrightleftharpoons{K_{c_3}} \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$$

$$K_{c_3} = \frac{1}{K_{c_2}} = \frac{1}{\sqrt{K_{c_1}}}$$

(iv) If a reaction is multiplied by n, the rate constant, K_c becomes $(K_c)^n$. n can be fraction also (+ve only).

(v) If K_1 be equilibrium constant for $P \rightleftharpoons Q$ and K_2 be equilibrium constant for $R \rightleftharpoons S$, equilibrium constant for $P + R \rightleftharpoons Q + S$ is K_1K_2.

Effect of Temperature on Equilibrium Constant (K_C)

For exothermic reactions, K_c decreases with increase in temperature.
For endothermic reactions, K_c increases with increase in temperature.
For reactions having zero heat energy, temperature has no effect.

Relation between K and $\Delta G°$

Gibbs free energy change and reaction quotient are related as $\Delta G° = -2.303\, RT \log K_c$

or $\quad \Delta G° = -2.303\, RT \log K_p$

Significance of are $\Delta G°$ *given below*

- If $\Delta G° < 0, \log K < 0 \Rightarrow K < 1$
  Therefore, forward reaction is spontaneous
- If $\Delta G° > 0, \log K < 0 \Rightarrow K < 1$
  Therefore, backward reaction is spontaneous
- If $\Delta G° = 0, \log K = 0, \Rightarrow K = 1$
  Therefore, reaction is at equilibrium

Reaction Quotient (Q)

Reaction quotient is the ratio of the molar concentration or partial pressure of the product species to that of reactant species at any stage in the reaction.

For a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{and} \quad Q_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

At any stage of the reaction

(i) if $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

(ii) if $Q_c < K_c$, the reaction will move in the direction of the products.

(iii) if $Q_c = K_c$, reaction mixture is already at equilibrium.

Relation between Degree of Dissociation and Density

Degree of dissociation (α) of a gaseous compound is related to its vapour density by

$$\alpha = \frac{D-d}{d(y-1)}$$

Here, D = molardensity before dissociation/initial density

d = density after dissociation/density of the gaseous mixture

y = number of moles of products

$$\text{Density of gas} = \frac{\text{molecular weight}}{2}$$

$$\text{Molecular weight} = \text{Density of gas} \times 2$$

$$M_O = D \times 2$$

or

$$M_C = d \times 2$$

Here, M_O = Observed molecular weight [Abnormal]

M_C = Calculated molecular weight [Theoritical]

Formulae Used for Calculation

- Pressure $\propto$ moles (V, T constant)
- Volume $\propto$ moles (p, T constant)
- Mole percentage = volume percentage

$$\frac{\text{initial moles}}{\text{total moles at equilibrium}} = \frac{\text{initial volume}}{\text{total volume at equilibrium}} = \frac{\text{total density at equilibrium}}{\text{initial density}}$$

- Partial pressure = Total pressure $\times$ mole fraction

Illustration

If 1 mole of PCl_5 is kept in a container of volume V litre and at equilibrium, pressure is p atm,

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+ Cl_2(g)$
Initial	1	0	0
At equilibrium	$1-\alpha$	α	α

Total moles $= 1-\alpha+2\alpha = 1+\alpha$

$$p_{PCl_5} = \frac{1-\alpha}{1+\alpha} \cdot p$$

$$p_{PCl_3} = p_{Cl_2} = \frac{\alpha}{1+\alpha} \cdot p$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha} \cdot p\right)\left(\frac{\alpha}{1+\alpha} \cdot p\right)}{\left(\frac{1-\alpha}{1+\alpha} \cdot p\right)}$$

$$\therefore \quad K_p = \frac{\alpha^2 . p}{1-\alpha^2}$$

where, α = degree of dissociation

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

$$[PCl_5] = \frac{1-\alpha}{V},$$

$$[PCl_3] = \frac{\alpha}{V} = [Cl_2]$$

$$K_c = \frac{\alpha^2}{(1-\alpha) \times V}$$

Le-Chatelier's Principle

It states that change in any of the factors that determine the equilibrium conditions of a system, will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

Different factors affecting equilibrium are discussed below.

1. Effect of Concentration Change

The concentration stress of an added reactant or product is relieved by net reaction in the direction that consumes the added substance. *e.g.*,

$$A + B \rightleftharpoons C$$

(i) If we increase the concentration of either A or B (reactants), the equilibrium goes in the direction that consumes A or B, i.e., forward side.

(ii) If we increase the concentration of C (product), the equilibrium goes in the direction that consumes C, i.e., backward side.

(iii) If we remove C (product), the equilibrium goes in the direction in which its concentration increases, i.e., forward side.

(iv) If any of the species is in solid or liquid state, its addition does not alter the original equilibrium.

» *Sweet substances cause tooth decay because on fermentation these produce H^+ ions which combine with OH^- ions and shift the equilibrium in forward direction*

$$Ca_5(PO_4)_3OH(s) \underset{\text{Remineralisation}}{\overset{\text{Demineralisation}}{\rightleftharpoons}} 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

2. Effect of Pressure

At high pressure, reaction goes from higher moles to lower moles or from higher volume to lower volume and *vice-versa*.

(i) If $\Delta n_g = 0$, no effect on equilibrium due to pressure change.

(ii) If $\Delta n_g > 0$, the increase in pressure favours backward reaction.

(iii) If $\Delta n_g < 0$, the increase in pressure favours forward reaction.
(Δn_g = number of moles of gaseous products − number of moles of gaseous reactants).

Flash evaporation technique is used for concentrating some aqueous solutions which cannot be concentrated by normal boiling. Concentration of this type of solution is carried out under reduced pressure below 100°C.

3. Effect of Temperature

At high temperature, reaction goes to endothermic direction while at low temperature reaction goes to exothermic direction. The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

$$K \propto T; \text{ if } \Delta H^\circ = +\text{ ve (endothermic)}$$

$$K \propto \frac{1}{T}; \text{ if } \Delta H^\circ = -\text{ ve (exothermic)}$$

Freeze drying technique is used for drying heat sensitive substances. In this technique, water is made to sublime off at a temperature below 0°C.

4. Effect of Catalyst

A catalyst increases the rate of forward reaction as well as the rate of backward reaction, so it does not affect the equilibrium and equilibrium constant.

5. Effect of Inert Gas

At constant volume, there is no effect of addition of inert gas. At constant pressure, when inert gas is added, reaction goes from lower moles to higher moles.

Applications of Le-Chatelier's Principle

The Le-Chatelier's principle is applicable to physical as well as chemical equilibria. *Some of its aplications are mentioned below*

1. To Chemical Equilibrium

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \Delta H = -\text{ve}$$

To get better yield of ammonia, required conditions are

High pressure as $n_g = -\text{ve}$

Low temperature as reaction is exothermic

High concentration of reactants

Removal of NH_3

2. To Physical Equilibria

(i) Effect of pressure on melting point

(ii) Ice-water equilibrium

$$\text{Ice } (s) \rightleftharpoons \text{water } (l)$$

An increase in pressure favours the melting of ice into water because $V_{ice} > V_{water}$. Therefore, on increasing pressure more and more ice will melt. (melting point of ice decreases with increase in pressure).

(iii) Solid- liquid equilibrium

$$\text{Solid} \rightleftharpoons \text{liquid}$$

An increase in pressure favours the backward reaction because $V_{solid} < V_{liquid}$. Therefore, melting point of solid increases with increase in pressure.

(iv) Effect of pressure on solubility of gases

$$e.g., \text{Gas} + \text{Solvent} \rightleftharpoons \text{Solution}$$

An increase in pressure always favours the dissolution of gas in the solvent. Therefore, solubility of gas increases with increase in pressure.

The amount of gas dissolved per unit volume of solvent is directly proportional to its pressure **(Henry's law).** *i.e.*, $m \propto p$

(v) Effect of temperature on solubility of solids

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}; \Delta H = +\text{ve}$$

An increase in temperature always favours endothermic reaction, therefore solutes having endothermic dissolution show an increase in their solubility with temperature and solutes having exothermic dissolution (dissolution of lime in water) show a decrease in their solubility with temperature.

Practice Zone DAY 9

1. A reversible chemical reaction is having two reactants in equilibrium. If the concentration of the reactants are doubled then the equilibrium constant will
(a) be doubled (b) become one fourth
(c) be halved (d) remain the same

2. The ratio of K_p/K_c for the reaction,
$$CO\,(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)\text{, is}$$
(a) 1 (b) RT
(c) $(RT)^{1/2}$ (d) $(RT)^{-1/2}$

3. Consider the equilibrium reactions,
$$H_3PO_4 \xrightleftharpoons{K_1} H^+ + H_2PO_4^-$$
$$H_2PO_4^- \xrightleftharpoons{K_2} H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \xrightleftharpoons{K_3} H^+ + PO_4^{3-}$$
The equilibrium constant, K for the following dissociation
$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}\text{, is}$$
(a) $K_1/K_2 \cdot K_3$ (b) $K_1 \cdot K_2 \cdot K_3$
(c) $K_2/K_1 \cdot K_3$ (d) $K_1 + K_2 + K_3$

4. If K_1 and K_2 are the equilibrium constants of the equilibria (i) and (ii) respectively, what is the relationship between the two constants ?
(i) $SO_2(g) + \frac{1}{2}O_2(g) \xrightleftharpoons{K_1} SO_3(g)$
(ii) $2\,SO_3(g) \xrightleftharpoons{K_2} 2\,SO_2(g) + O_2(g)$
(a) $(K_1)^2 = \frac{1}{K_2}$ (b) $K_2 = (K_1)^2$
(c) $K_1 = \frac{1}{K_2}$ (d) $K_1 = K_2$

5. The equilibrium constant for the reaction, $H_2(g) + I_2\,(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to half of the original volume, the value of the equilibrium constant will be
(a) 16 (b) 32
(c) 64 (d) 128

6. Starting with one mole of O_2 and two moles of SO_2, the equilibrium for the formation of SO_3 was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present, the equilibrium constant will be
(a) $\frac{x^2V}{(1-x)^3}$ (b) $\frac{4x^2}{(2-x)(1-x)}$
(c) $\frac{(1-x)^3}{2V}$ (d) $\frac{x^2}{(2-x)(1-x)}$

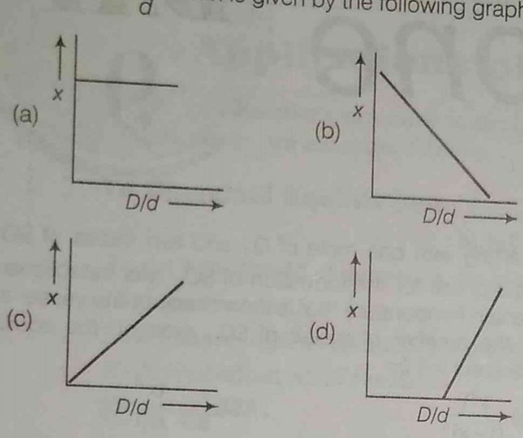
7. The equilibrium constant, K_p for the reaction,
$$A \rightleftharpoons 2B$$
is related to degree of dissociation α of A and total pressure p as
(a) $\frac{4\alpha^2 p}{1-\alpha^2}$ (b) $\frac{4\alpha^2 p^2}{1-\alpha^2}$
(c) $\frac{4\alpha^2 p^2}{1-\alpha}$ (d) $\frac{4\alpha^2 p}{1-\alpha}$

8. Given the reaction,
$$2X\,(g) + Y\,(g) \rightleftharpoons Z\,(g) + 80\text{ kcal}$$
which combination of pressure and temperature gives the highest yield of Z at equilibrium?
(a) 1000 atm and 500°C
(b) 500 atm and 500°C
(c) 1000 atm and 100°C
(d) 500 atm and 100°C

9. For the following equilibrium, $N_2O_4 \rightleftharpoons 2\,NO_2$ in gaseous phase, NO_2 is 50% of the total volume when equilibrium is set up. Hence, per cent of dissociation of N_2O_4 is
(a) 50% (b) 25%
(c) 66.66% (d) 33.33%

10. The following reactions are known to occur in the body
$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
If CO_2 escapes from the system
(a) pH will decreases
(b) hydrogen ion concentration will diminish
(c) H_2CO_3 concentration will be altered
(d) the forward reaction will be promoted

11. For the dissociation of PCl_5 into PCl_3 and Cl_2 in gaseous phase reaction, d is the observed vapour density and D the theoretical vapour density with x as degree of dissociation. Variation of $\frac{D}{d}$ with x is given by the following graph



12. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$\underset{\text{pink}}{[Co(H_2O)_6]^{3+}}(aq) + 4Cl^-(aq) \rightleftharpoons [C_oCl_4]^{2-}(aq) + 6H_2O(l)$$

[NCERT Exemplar]

(a) $\Delta H > 0$ for the reaction
(b) $\Delta H < 0$ for the reaction
(c) $\Delta H = 0$ for the reaction
(d) The sign of ΔH cannot be predicted on the basis of this information.

13. 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) ?

(a) Neither K_p nor α changes
(b) Both K_p and α changes
(c) K_p changes but α does not
(d) K_p does not change but α changes

14. In a chemical reaction, the rate constant for the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. The rate constant for the forward reaction is

(a) 5×10^{-4} (b) 2×10^{-3}
(c) 1.125×10^{-3} (d) 9.0×10^{-4}

15. 56 g of N_2 and 6 g of H_2 were kept at 400°C in 1 L vessel. The equilibrium mixture contained 27.54 g of NH_3. The approximate value for K_c for the above reaction in mol^2L^{-2} is

(a) 10 (b) 20
(c) 30 (d) 40

16. XY_2 dissociates as

$$XY_2(g) \rightleftharpoons XY(g) + Y(g)$$

When the initial pressure of XY_2 is 600 mm Hg, the total equilibrium pressure is 800 mm Hg. Calculate K for the reaction assuming that the volume of the system remains unchanged.

(a) 50 (b) 100 (c) 166.6 (d) 400.0

17. 1.1 moles of A are mixed with 2.2 moles of B and the mixture is kept in a 1 L flask till the equilibrium, $A + 2B \rightleftharpoons 2C + D$ is reached. At equilibrium, 0.2 mole of C is formed. The equilibrium constant of the above reaction is

(a) 0.0002 (b) 0.004 (c) 0.001 (d) 0.003

18. The concentration of CO_2 which will be in equilibrium with 2.5×10^{-2} mol L^{-1} of CO at 100°C for the reaction

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g); K_c = 5.0 \text{ will be}$$

(a) 0.5×10^{-1} mol L^{-1} (b) 1.25×10^{-1} mol L^{-1}
(c) 2×10^{-2} mol L^{-1} (d) None of these

19. At certain temperature and a total pressure of 10^5 Pa, iodine vapours contains 40% by volume of iodine atoms. K_p for the equilibrium $I_2(g) \rightleftharpoons 2I(g)$ will be

(a) 0.67 (b) 1.5
(c) 2.67×10^4 (d) 9.0×10^4

20. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the degree of dissociation at equilibrium is 0.2 at 1 atm pressure. The equilibrium constant, K_p will be

(a) 1/2 (b) 1/4 (c) 1/6 (d) 1/8

21. One mole of N_2 and 3 moles of H_2 are mixed in a litre flask. If 50% N_2 is converted into ammonia by the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the total number of moles of gas at equilibrium is

(a) 1.5 (b) 3.0 (c) 4.5 (d) 6.0

22. For $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$; at equilibrium $p_{Br_2} = \frac{p}{9}$ and p is the total pressure, the ratio $\frac{K_p}{p}$ will be

(a) $\frac{1}{3}$ (b) $\frac{1}{9}$ (c) $\frac{1}{81}$ (d) $\frac{1}{27}$

23. At 30°C, K_p for the dissociation reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2$$

is 2.9×10^{-2} atm. If the total pressure is 1 atm, the degree of dissociation of SO_2Cl_2 is (assume, $1 - \alpha^2 = 1$)

(a) 87% (b) 13% (c) 17% (d) 29%

24. The equilibrium constant K_p for the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \text{ is 1.6 at 200°C.}$$

The pressure at which PCl_5 will be 50% dissociated at 200°C is

(a) 3.2 atm (b) 4.8 atm (c) 2.4 atm (d) 6.4 atm

25. Ammonium carbamate decomposes as

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

For this reaction, $K_p = 2.9 \times 10^{-5} atm^3$. If we start with 1 mole of the compound, the total pressure at equilibrium would be

(a) 0.0766 atm (b) 0.0582 atm
(c) 0.0388 atm (d) 0.0194 atm

26. On decomposition of NH_4HS, the following equilibrium is established

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

If the total pressure is p atm, the equilibrium constant K_p is equal to

(a) p atm (b) $p^2 atm^2$ (c) $p^2 / 4\ atm^2$ (d) $2p$ atm

27. Formaldehyde polymerises to form glucose according to the reaction, $6HCHO \rightleftharpoons C_6H_{12}O_6$

The theoretically computed equilibrium constant for this reaction is found to be 6×10^{22}. If 1M solution of glucose dissociates according to the above equilibrium, the concentration of formaldehyde in the solution will be

(a) 1.6×10^{-2} M (b) 1.6×10^{-4} M
(c) 1.6×10^{-6} M (d) 1.6×10^{-8} M

Directions (Q. Nos. 28 to 30) *Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists of calcium silicates, calcium aluminates formed by heating and grinding of clay and lime stone. In the later steps of cement production a small amount of gypsum, $CaSO_4 \cdot 2H_2O$ is added to improve subsequent hardening of the concrete.*

The use of elevated temperatures during final production may lead to the formation of unwanted hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$.

Consider the following reaction,

$$CaSO_4 \cdot 2H_2O(s) \longrightarrow CaSO_4 \cdot \frac{1}{2}H_2O(s) + 1\frac{1}{2}H_2O(g)$$

The following thermodynamic data apply at 25°C, standard pressure is bar.

Compound	$H°/(kJmol^{-1})(\Delta H_f^\circ)$	$S°/(JK^{-1}mol^{-1})$
$CaSO_4 \cdot 2H_2O(s)$	−2021.0	194.0
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	−1575.0	130.5
$H_2O(g)$	−241.8	188.6

Gas constant; $R = 8.314\ J\ mol^{-1} K^{-1}$.

28. $\Delta H°$ for the transformation of 1.00 kg of $CaSO_4 \cdot 2H_2O$ (s) to $CaSO_4 \cdot \frac{1}{2}H_2O$ (s) is

(a) +446 kJ (b) +484 kJ
(c) −446 kJ (d) −484 kJ

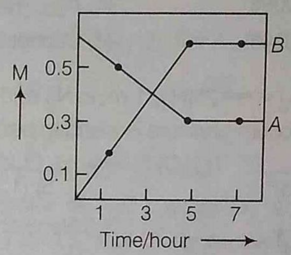
29. Equilibrium pressure (in bar) of water vapours in a closed vessel containing $CaSO_4 \cdot 2H_2O$ (s), $CaSO_4 \cdot \frac{1}{2}H_2O$ (s) and H_2O (g) at 25°C is

(a) 7.35×10^{-4} bar (b) 8.10×10^{-3} bar
(c) 2.15×10^{-4} bar (d) 7.00×10^{-4} bar

30. Temperature at which the equilibrium water vapour pressure is 1.00 bar, is

(a) 107°C (b) 38°C (c) 215°C (d) 240°C

Directions (Q. Nos. 31 and 32) *The progress of the reaction, $A \rightleftharpoons nB$ with time is shown below in the graph.*



31. Stoichiometric coefficient of the product B is

(a) 1 (b) 2 (c) 3 (d) 4

32. Equilibrium constant, K_c of the above graphical study is

(a) 2 (b) 0.83 (c) 0.5 (d) 1.2

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. Statement I In the dissociation of PCl_5 at constant pressure and temperature, addition of helium at equilibrium increases the dissociation of PCl_5.

Statement II Helium removes Cl_2 from the field of action.

34. Statement I The reaction,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

is favoured in the forward direction with increase of pressure.

Statement II The reaction is exothermic.

35. Statement I The equilibrium constant for a reaction having positive $\Delta H°$ increases with increase of temperature.

Statement II The temperature dependence of the equilibrium constant is related to $\Delta S°$ and $\Delta H°$ for the reaction.

36. **Statement I** Haber's synthesis of NH_3 is carried out in the presence of a catalyst.

Statement II The catalyst shifts the position of the equilibrium of reaction, $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ to the product side.

37. 1% CO_2 in air is 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 much would the partial pressure of CO_2 have to be to promote this reaction at 120°C?

(a) $p'_{CO_2} < 0.0095$ (b) $p'_{CO_2} = 0.0095$
(c) $p'_{CO_2} > 0.0095$ (d) Cannot be predicted

38. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, 1 mole N_2 and 3 moles H_2 are at 4 atm. Equilibrium pressure is found to be 3 atm. Hence, K_p is

(a) $\dfrac{1}{(0.5)\,(0.15)^3}$ (b) $\dfrac{1}{(0.5)\,(1.5)^3}$
(c) $\dfrac{3\times 3}{(0.5)\,(0.5)^3}$ (d) None of these

39. N_2O_4 is 25% dissociated at 37°C and 1 atm pressure. The percentage dissociation at 0.1 atm and 37°C will be

(a) 55.3% (b) 50% (c) 63.2% (d) 65.2%

40. When alcohol and acetic acid are mixed together in equimolar proportions, 66.5% are converted into ester. How much ester will be formed if 1 mole acetic acid is heated with 0.5 mole of alcohol?

(a) 1.57 (b) 0.423
(c) 0.525 (d) 1.50

41. Reaction between nitrogen and oxygen takes place as following

$$2\,N_2(g) + O_2(g) \rightleftharpoons 2\,N_2O\,(g)$$

If a mixture of 0.482 mole N_2 and 0.933 mole of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_c = 2.0\times 10^{-37}$, the equilibrium concentration of $[N_2O]$ will be

(a) 7.06×10^{-20} mol L^{-1} (b) 6.58×10^{-21} mol L^{-1}
(c) 4.82×10^{-4} mol L^{-1} (d) 9.36×10^{-7} mol L^{-1}

AIEEE & JEE Main Archive

42. In reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of B was 1.5 times of $[A]$, but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is **[JEE Main Online 2013]**

(a) 8 (b) 4
(c) 12 (d) 6

43. A molecule M associates in a given solvent according to the equation $M \rightleftharpoons (M)_n$. For a certain concentration of M, the van't Hoff factor was found to be 0.9 and the fraction of associated molecules was 0.2. The value of n is **[JEE Main Online 2013]**

(a) 3 (b) 5 (c) 2 (d) 4

44. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),\ K_1$ ...(i)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g),\ K_2$ ...(ii)

$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g),\ K_3$ ...(iii)

The equation for the equilibrium constant of the reaction $2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g),\ (K_4)$ in terms of K_1, K_2 and K_3 is **[JEE Main Online 2013]**

(a) $\dfrac{K_1K_2}{K_3}$ (b) $\dfrac{K_1K_3^2}{K_2}$
(c) $K_1K_2K_3$ (d) $\dfrac{K_2K_3^3}{K_1}$

45. The ratio $\dfrac{K_p}{K_c}$ for the reaction,

$$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g) \text{ is}$$

[JEE Main Online 2013]

(a) $\dfrac{1}{\sqrt{RT}}$ (b) $(RT)^{1/2}$ (c) RT (d) 1

46. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \longrightarrow 2\,NO\,(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction. $NO\,(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2\,(g)$ at the same temperature is **[AIEEE 2012]**

(a) 0.02 (b) 2.5×10^2 (c) 4×10^{-4} (d) 50.0

47. 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 the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is **[AIEEE 2011]**

(a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm

48. In aqueous solution, the ionisation constants for carbonic acid are $K_1 = 4.2\times 10^{-7}$ and $K_2 = 4.8\times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **[AIEEE 2010]**

(a) The concentration of CO_3^{2-} is 0.034 M
(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(c) The concentration of H^+ and HCO_3^- are approximately equal
(d) The concentration of H^+ is double that of CO_3^{2-}

49. The values of K_{p_1} and K_{p_2} for the reaction

$$X \rightleftharpoons Y + Z \quad \ldots(i)$$

and

$$A \rightleftharpoons 2B \quad \ldots(ii)$$

are in the ratio of 9 : 1. If the degree of dissociation of X and A are equal, then total pressure at equilibrium (i) and (ii) are in the ratio **[AIEEE 2008]**

(a) 3 : 1 (b) 1 : 9 (c) 36 : 1 (d) 1 : 1

50. For the following three reactions (1), (2) and (3), equilibrium constants are given **[AIEEE 2008]**

(1) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$

(2) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$

(3) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

Which of the following relation is correct?

(a) $K_3 = K_1K_2$ (b) $K_3K_2^3 = K_1^2$ (c) $K_1\sqrt{K_2} = K_3$ (d) $K_2K_3 = K_1$

51. The equilibrium constant, K_c for the reaction,

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

is 4.9×10^{-2}. The value of K_c for the reaction,

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

will be **[AIEEE 2006]**

(a) 416 (b) 2.40×10^{-3} (c) 9.8×10^{-2} (d) 4.9×10^{-2}

52. Phosphorus pentachloride dissociates as follows in a closed reaction vessel,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If total pressure at equilibrium, of the reaction mixture is p and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be **[AIEEE 2006]**

(a) $\left(\frac{x}{x+1}\right)p$ (b) $\left(\frac{2x}{1-x}\right)p$ (c) $\left(\frac{x}{x-1}\right)p$ (d) $\left(\frac{x}{2-x}\right)p$

53. The exothermic formation of $ClF_3(g)$ is represented by the equation, $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$; $\Delta H_r = -329$ kJ

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3? **[AIEEE 2005]**

(a) Adding F_2
(b) Increasing the volume of the container
(c) Removing Cl_2
(d) Increasing the temperature

54. For the reaction, $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$[K_c = 1.8 \times 10^{-6}$ at 184°C, $R = 0.00831$ kJ/(mol K)]

When K_p and K_c are compared at 184°C it is found that **[AIEEE 2005]**

(a) whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
(b) $K_p = K_c$
(c) K_p is less than K_c
(d) K_p is greater than K_c

55. What is the equilibrium expression for the reaction,

$$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)?$$ **[AIEEE 2004]**

(a) $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$ (b) $K_c = \frac{[P_4O_{10}]}{5\,[P_4][O_2]}$

(c) $K_c = [O_2]^5$ (d) $K_c = \frac{1}{[O_2]^5}$

56. For the reaction,
$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the K_p/K_c is equal to **[AIEEE 2004]**

(a) $1/RT$ (b) RT (c) $\sqrt{RT}$ (d) 1.0

57. For the reaction equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_c for the reaction is **[AIEEE 2003]**

(a) 3.3×10^{-2} mol L^{-1} (b) 3×10^{-1} mol L^{-1}
(c) 3×10^{-3} mol L^{-1} (d) 3×10^{3} mol L^{-1}

58. Consider the reaction equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H° = -198\text{kJ}$$

On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is **[AIEEE 2003]**

(a) lowering of temperature as well as pressure
(b) increasing of temperature as well as pressure
(c) lowering the temperature and increasing the pressure
(d) any value of temperature and pressure

59. One of the following equilibria is not affected by change in volume of the flask. **[AIEEE 2002]**

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(c) $N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g)$
(d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

60. For the following reaction in gaseous phase
$CO + \frac{1}{2}O_2 \longrightarrow CO_2$. K_c/K_p is **[AIEEE 2002]**

(a) $(RT)^{1/2}$ (b) $(RT)^{-1/2}$ (c) (RT) (d) $(RT)^{-1}$

Answers

1. (d)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (c)	**9.** (d)	**10.** (b)
11. (d)	**12.** (d)	**13.** (d)	**14.** (c)	**15.** (a)	**16.** (b)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (c)
21. (b)	**22.** (c)	**23.** (c)	**24.** (b)	**25.** (b)	**26.** (c)	**27.** (b)	**28.** (b)	**29.** (b)	**30.** (a)
31. (b)	**32.** (d)	**33.** (d)	**34.** (b)	**35.** (b)	**36.** (c)	**37.** (a)	**38.** (b)	**39.** (c)	**40.** (b)
41. (b)	**42.** (b)	**43.** (c)	**44.** (d)	**45.** (a)	**46.** (d)	**47.** (c)	**48.** (c)	**49.** (c)	**50.** (a)
51. (a)	**52.** (a)	**53.** (a)	**54.** (a)	**55.** (d)	**56.** (a)	**57.** (c)	**58.** (c)	**59.** (c)	**60.** (a)

Hints & Solutions

1. Equilibrium constant depends only upon the temperature, not upon the concentration of reactant. Thus, on doubling concentration, equilibrium constant remains the same.

2. $$\Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = \frac{-1}{2}$$

$$\therefore \quad K_p = K_c (RT)^{-\frac{1}{2}}$$

or $$\frac{K_p}{K_c} = (RT)^{-\frac{1}{2}}$$

3. $K = K_1 \cdot K_2 \cdot K_3$

4. Reaction (ii) is double and reverse of (i).

Hence, $$K_2 = \frac{1}{K_1^2} \text{ or } K_1^2 = \frac{1}{K_2}$$

5. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

For this reaction, $\Delta n_g = 0$

$\therefore$ The reaction and its equilibrium constant is not affected by change in volume. Moreover, equilibrium constant depends only on temperature.

6.

	$2SO_2$ +	O_2 $\rightleftharpoons$	$2SO_3$
Initial	2 mol	1 mol	0 mol
At eq.	$(2-2x)$ $=2(1-x)$	$(1-x)$	$(2x)$
Molar conc.	$2(1-x)/V$	$(1-x)/V$	$2x/V$

$$K_c = \frac{(2x/V)^2}{[2(1-x)/V]^2 (1-x)/V} = \frac{x^2 V}{(1-x)^3}$$

7.

	$A \rightleftharpoons$	$2B$
Initial	1	0
At eq.	$1-\alpha$	2α

Total moles = $1+\alpha$

$$p_A = \frac{(1-\alpha)\cdot p}{1+\alpha},$$

$$p_B = \frac{2\alpha}{1+\alpha} p$$

$$K_p = \frac{p_B^2}{p_A} = \frac{\left(\frac{2\alpha}{1+\alpha}\cdot p\right)^2}{\left[\frac{1-\alpha}{1+\alpha} p\right]} = \frac{4\alpha^2 p}{(1+\alpha)(1-\alpha)} = \frac{4\alpha^2 p}{1-\alpha^2}$$

8. Since, $n_P < n_r$ and the reaction is exothermic. So, high pressure and low temperature favour forward reaction.

9.

N_2O_4 $\rightleftharpoons$	$2NO_2$
1	0
$(1-x)$	$2x$

Total moles = $(1+x)$

$$\therefore \text{ \% of } NO_2 \text{ by volume} = \frac{2x}{1+x} \times 100 = 50$$

or $$x = \frac{1}{3} = 0.33$$

Hence, per cent of dissociation 33.33%

10. If CO_2 escapes, equilibrium will shift in the backward direction so, that (H^+) will diminish.

11. $1 + x = \frac{D}{d}$

when $x = 0$, $\frac{D}{d} = 1$

When, x increases, $(1+x)$ increases hence, $\frac{D}{d}$ also increases.

12. $\Delta H > 0$ because on cooling the reaction mixture, the reaction mixture becomes less coloured (pink) which suggests the reaction is endothermic.

13. K_p is constant at constant temperature. As volume is halved, pressure will be doubled. Hence, equilibrium will shift in the backward direction *i.e.*, degree of dissociation (α) decreases.

14. $$K = k_f / k_b, \; 1.5 = k_f / (7.5 \times 10^{-4})$$

or $$k_f = 1.125 \times 10^{-3}$$

15. $$56\text{g } N_2 = \frac{56}{28} = 2 \text{ mol},$$

$$6\text{g } H_2 = \frac{6}{2} = 3 \text{ mol}$$

$$27.54\text{g } NH_3 = \frac{27.54}{17} = 1.62 \text{ mol}$$

	N_2	$+ 3H_2 \rightleftharpoons$	$2NH_3$
Initial moles	2	3	0
At eq.	$2-0.81$ $=1.19$	$3-2.43$ $=0.57$	1.62

$$K_c = \frac{(1.62)^2}{(1.19)(0.57)^3} = 11.9 \approx 10$$

16.

	XY_2 $\rightleftharpoons$	XY +	Y
Initial	600 mm	0	0
At eq.	$600-p$	p	p

Total pressure $= 600 - p + p + p = 600 + p$

or $600 + p = 800$ mm $\Rightarrow$ $p = 200$ mm

and, p due to $XY_2 = 400$ mm

$$K = \frac{200 \times 200}{400} = 100$$

17.

	A +	$2B \rightleftharpoons$	$2C$ +	D
Initial moles	1.1	2.2	0	0
moles at eq.	1.0	2.0	0.2	0.1

$$\therefore \quad K = \frac{(0.2/V)^2 (0.1/V)}{(1/V)(2/V)^2} = 0.001$$

18. $K_c = \dfrac{[CO_2]}{[CO]}$ or $5 = \dfrac{[CO_2]}{2.5\times10^{-2}}$

or $[CO_2] = 1.25\times10^{-1}\ \text{mol L}^{-1}$

$$I_2(g) \rightleftharpoons 2I\ (g)$$

19. Partial pressure of iodine atoms $(p_I) = \dfrac{40}{100}\times10^5$
$= 0.40\times10^5$ Pa

Partial pressure of $I_2 (p_{I_2})$

$$= \frac{60}{100}\times10^5\ \text{Pa} = 0.60\times10^5\ \text{Pa}$$

$$\therefore \quad K_p = \frac{p_I^2}{p_{I_2}} = \frac{(0.40\times10^5)^2}{0.60\times10^5} = 2.67\times10^4.$$

20. $N_2O_4 \rightleftharpoons 2\,NO_2$

	N_2O_4	$2NO_2$
Initial moles	a	0
At eq.	$a-0.2a$ $=0.8a$	$0.4a$

Total moles $= 1.2\,a$

$$p_{N_2O_4} = \frac{0.8a}{1.2a}\times1\ \text{atm} = 2/3\,\text{atm},$$

$$p_{NO_2} = \frac{0.4a}{1.2a}\times1\ \text{atm} = 1/3\,\text{atm}$$

$$K_p = \frac{(1/3)^2}{(2/3)} = 1/6$$

21. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

	N_2	$3H_2$	$2NH_3$
Initial moles	1	3	0
At eq.	$1-0.5$ $=0.5$	$3-1.5$	2×0.5 $=1.5=1$

Total moles $= 0.5 + 1.5 + 1 = 3$

22. $2\,NOBr\ (g) \rightleftharpoons 2\,NO\ (g) + Br_2\ (g)$

$$p - \left(\frac{2p}{9} + \frac{p}{9}\right) = \frac{6p}{9} \qquad \frac{2p}{9} \qquad \frac{p}{9}$$

$$\text{From } K_p = \frac{(p_{NO})^2\times(p_{Br_2})}{(p_{NOBr})^2} = \frac{\left(\frac{2p}{9}\right)^2\left(\frac{p}{9}\right)}{\left(\frac{6p}{9}\right)^2} = \frac{p}{81}$$

$$\therefore \quad \frac{K_p}{p} = \frac{1}{81}$$

23. $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$

	SO_2Cl_2	SO_2	Cl_2
Initial	1	0	0
At eq.	$1-\alpha$	α	α

Total moles $= 1+\alpha$

$$p_{SO_2Cl_2} = \frac{1-\alpha}{1+\alpha},\ p_{SO_2} = \frac{\alpha}{1+\alpha},\ p_{Cl_2} = \frac{\alpha}{1+\alpha}$$

$$K_p = \left(\frac{\alpha}{1+\alpha}\right)^2 \Big/ \left(\frac{1-\alpha}{1+\alpha}\right) = \frac{\alpha^2}{1-\alpha^2}$$

$$= \alpha^2;\ (1-\alpha^2 = 1)$$

$$\alpha = \sqrt{K_p}$$
$$= \sqrt{2.9\times10^{-2}}$$
$$= 0.17$$

$\therefore$ Degree of dissociation $= 17\%$

24. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial moles	1	0	0
Moles at eq.	0.5	0.5	0.5

Total moles $= 1.5$

Partial pressure $= \dfrac{0.5}{1.5}p;\quad \dfrac{0.5}{1.5}p;\quad \dfrac{0.5}{1.5}p$

(where, p is the total pressure)

$$K_p = \left(\frac{0.5}{1.5}p\right)^2 \Big/ \left(\frac{0.5}{1.5}p\right)$$

$$= \frac{1}{3}p = 1.6\ \text{(Given)}$$

or $\quad p = 4.8$ atm

25. At equilibrium, if partial pressure of $CO_2 = p$, that of $NH_3 = 2p$

$$K_p = p^2_{NH_3}\times p_{CO_2} = (2p)^2\times p = 4p^3$$

$$K_p = 2.9\times10^{-5} = 4p^3$$

$$p^3 = 0.725\times10^{-5}$$

$$p^3 = 7.25\times10^{-6}$$

$$p = 1.935\times10^{-2}$$

Hence, total pressure $= 3p$
$= 3\times1.935\times10^{-2}$
$= 5.81\times10^{-2}$
$= 0.0581$ atm

26. $p_{NH_3} = p_{H_2S} = \dfrac{p}{2}$

Hence, $K_p = p_{NH_3}\times p_{H_2S} = \dfrac{p}{2}\times\dfrac{p}{2} = \dfrac{p^2}{4}$

27. A very high value of K for the given equilibrium shows that dissociation of glucose to form HCHO is very very small. Hence, at equilibrium, we can take $C_6H_{12}O_6 = 1M$

$$K = \frac{C_6H_{12}O_6}{[HCHO]^6}$$

i.e., $\quad 6\times10^{22} = \dfrac{1}{[HCHO]^6}$

or $\quad [HCHO] = \left(\dfrac{1}{6\times10^{22}}\right)^{\frac{1}{6}} = 1.6\times10^{-4}M$

28. $CaSO_4\cdot2H_2O(s) \rightarrow CaSO_4\cdot\frac{1}{2}H_2O(s) + 1\frac{1}{2}\,H_2O(g)$

$$\Delta H^\circ = H\left[CaSO_4\cdot\tfrac{1}{2}H_2O(s)\right] + H\ [1.5\ H_2O(g)]$$

$$-H\ [CaSO_4\cdot2H_2O\ (s)]$$

$= (-1575 - 1.5 \times 241.8) - (-2021.0)$
$= 83.3 \text{ kJ mol}^{-1}$
$= +484 \text{ kJ for 1 kg}$

29. $\Delta S° = 219.4 \text{ JK}^{-1} \text{ mol}^{-1}$

($\Delta S°$ is also calculated as $\Delta H°$)

From, $\Delta G° = \Delta H - T\Delta S$

$\Delta G° = 17920 \text{ J mol}^{-1}$

Again from, $\Delta G° = -2.303 RT \log K_p$

$$\log K_p = \frac{\Delta G°}{2.303 RT}$$

$$K_p = 7.22 \times 10^{-4} = (p_{H_2O})^{3/2}$$

$$(p_{H_2O}) = 8.1 \times 10^{-3} \text{atm}$$

30. $p_{H_2O} = 1,\ K_p = 1,\ \Delta G° = 0,$

At equilibrium,

$$\Delta H° = T\ \Delta S°$$

$$T = \Delta H°/\Delta S° = \frac{83.3 \times 1000}{219.4}$$

$$\approx 380 \text{ K} = 107°\text{C}$$

31. Concentration of A changes from 0.5 M to 0.3 M and that of B from 0.2 M to 0.6 M in the time interval 1 h to 5 h.

$$-\Delta[A] = 0.2 \text{ M}$$
$$\Delta[B] = 0.4 \text{ M}$$

Thus, $n = 2$

32. At equilibrium, $[A] = 0.3$ M

$[B] = 0.6$ M

$$K_c = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{(0.3)} = 1.2$$

33. Both the statements, I and II are incorrect.

34. With increase of pressure, equilibrium shifts in that direction in which lesser number of gaseous moles are produced.

35. Increased temperature always shifts the equilibrium towards endothermic reaction.

36. Catalyst does not affect equilibrium. It increases the rate of chemical reactions by providing a new low energy pathway for the forward and reverse reactions by exactly the same amount.

37. $M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$

$\therefore \quad K_p = p'_{CO_2} = 0.0095 \text{ atm} \quad \ldots\text{(i)}$

$\because$ CO_2 is 1% in air,

$$\therefore \quad p'_{CO_2} = \frac{1}{100} \times p_{air} = \frac{1}{100} \times 1 = 0.01 \text{atm}$$

The decomposition of M_2CO_3 is carried out in the presence of p'_{CO_2} of 0.01 atm and thus, practically there is no decomposition of M_2CO_3. Thus, 1% CO_2 is sufficient to prevent any loss in weight. If at all decomposition is desired, $p'_{CO_2} < 0.0095$.

38.

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initial	1		3		0
Equili.	$(1-x)$		$(3-3x)$		$2x$

Initial moles, $n_1 = 4$

Pressure, $p_1 = 4$ atm

At equilibrium moles, $n_2 = 4 - 2x$

At equilibrium pressure, $p_2 = 3$ atm

$$\frac{n_2}{n_1} = \frac{p_2}{p_1}$$

$$\frac{4-2x}{4} = \frac{3}{4}$$

$$4 - 2x = 3 \text{ or } x = 0.5$$

$$x_{N_2} = \frac{1-x}{4-2x} = \left(\frac{0.5}{3}\right)$$

$$x_{H_2} = \frac{3-3x}{4-2x} = \frac{1.5}{3}$$

$$x_{NH_3} = \frac{2x}{4-2x} = \frac{1}{3}$$

$$p_{N_2} = 3 \times \frac{0.5}{3} = 0.5 \text{ atm}$$

$$p_{H_2} = 1.5 \text{ atm}$$

and $p_{NH_3} = 1$ atm

$$k_p = \frac{(p_{NH_3})^2}{p_{N_2}\ (p_{H_2})^3} = \frac{1}{(0.5)\ (1.5)^3}$$

39.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial	1		0
At eq.	$(1-x)$		$2x$

Total moles $= (1-x) + 2x = (1+x)$

$$p_{N_2O_4} = \left(\frac{1-x}{1+x}\right)p,\ p_{NO_2} = \left(\frac{2x}{1+x}\right)p$$

Since, N_2O_4 is 25% dissociated

$\therefore \quad x = 0.25$ and $p = 1$ atm

$$p_{N_2O_4} = \left(\frac{1-0.25}{1+0.25}\right) \times 1 = 0.6 \text{ atm}$$

$$p_{NO_2} = \left(\frac{2 \times 0.25}{1+0.25}\right) \times 1 = 0.4 \text{ atm}$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{0.4 \times 0.4}{0.6} = 0.\ 267 \text{ atm}$$

Suppose the degree of dissociation of N_2O_4 at 0.1 atm is α, then

$$p_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right) \times 0.1$$

and

$$p_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right) \times 0.1$$

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 \times (0.1)^2}{\left(\frac{1-\alpha}{1+\alpha}\right) \times 0.1}$$

$$= \frac{4\alpha^2 \times 0.1}{(1-\alpha)(1+\alpha)} = \frac{0.4\alpha^2}{(1-\alpha^2)}$$

$$0.267 = \frac{0.4\alpha^2}{1-\alpha^2}$$

$$0.267 - 0.267\alpha^2 = 0.4\alpha^2$$

$$0.267 = 0.667\alpha^2$$

$\therefore$ Percentage dissociation $\alpha = 63.2\%$

40. $CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$

100   100   66.5   66.5

Applying law of mass action

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{66.5 \times 66.5}{(100-66.5)\times(100-66.5)} \approx 4$$

For 0.5 moles of alcohol and 1 mole of acetic acid, we have

$$K_c = 4 = \frac{x^2}{(0.5-x)(1-x)}$$

or $\quad x^2 = (0.5 - 1.5x + x^2) \times 4$

On solving we get :

$x = 0.423$ or 1.57. The later value is not acceptable because 0.5 mole of alcohol can never produce 1.57 mole of ester. Hence, the number of moles of ester formed = 0.423.

41.

	$2N_2(g)$	+ $O_2(g)$ $\rightleftharpoons$	$2N_2O(g)$
Initial	0.482	0.933	0
At equili.	$(0.482-2x)$	$0.933-x$	$2x$
Active mass	$\left(\frac{0.482-2x}{10}\right)$	$\left(\frac{0.933x}{10}\right)$	$\left(\frac{2x}{10}\right)$

$$K_c = 2.0 \times 10^{-37}$$

Magnitude of K_C is very very small such that at equilibrium

$$\frac{0.482-2x}{10} \approx \frac{0.482}{10} = 0.0482$$

$\therefore$ $\quad [N_2]_{eq} = 0.0482 \text{ mol L}^{-1}$

$$[O_2]_{eq} = 0.0933 \text{ mol L}^{-1}$$

$$K_C = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$2.0 \times 10^{-37} = \frac{\frac{4x^2}{100}}{(0.0482)^2\,(0.0933)}$$

$$x = 3.29 \times 10^{-20}$$

$\therefore$ $\quad [N_2O] = \frac{2x}{10} \quad \therefore \quad [N_2O] = \frac{2 \times 3.292 \times 10^{-20}}{10}$

$$= 6.58 \times 10^{-21} \text{ mol L}^{-1}$$

42. Let the degree of dissociation = x

	A +	$2B$ $\rightleftharpoons$	$2C$ +	D
Initial concentration	1	1.5	0	0
At equilibrium	$(1-x)$	$(1.5-2x)$	$2x$	x

Given, $\quad (1-x) = (1.5-2x)$

$$1 = 1.5 - 2x + x$$

$$1 = 1.5 - x$$

$$x = 1.5 - 1 = 0.5$$

Equilibrium constant for the reaction

$$K_C = \frac{[C]^2[D]}{[A][B]^2} = \frac{(2x)^2(x)}{(1-x)(1.5-2x)^2}$$

$\because$ $\quad x = 0.5$

$$K_C = \frac{(2\times 0.5)^2\,(0.5)}{(1-0.5)\,(1.5-2\times 0.5)^2}$$

$$= \frac{(1)\times(0.5)}{(0.5)\,(0.5)^2} = \frac{0.5}{0.5\times 0.25} = \frac{0.5}{0.125} = 4$$

43. Let the degree of association be α.

M $\rightleftharpoons$	$(M)_n$	
1	0	Initially
$1-\alpha$	$\frac{\alpha}{n}$	At time t

Total moles after association $= 1 - \alpha + \frac{\alpha}{n} = 1 + \left(\frac{1}{n} - 1\right)\alpha$

$$i = \frac{\text{moles after association}}{\text{initial moles}}$$

$$i = \frac{1 + \left(\frac{1}{n}-1\right)\alpha}{1}$$

or $\quad (i-1) = \left(\frac{1}{n} - 1\right)\alpha$

We have, $\quad i = 0.9$ and $\alpha = 0.2$

On putting values,

$$0.9 - 1 = \left(\frac{1}{n} - 1\right)0.2$$

$$-0.1 = -0.2 + \frac{0.2}{n}$$

$$-0.1 + 0.2 = \frac{0.2}{n}$$

$$n = \frac{0.2}{0.1} = 2$$

44. In the required equation NH_3 is on LHS, so invert the equation (i)

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g); K_5 = \frac{1}{K_1} \quad \ldots(iv)$$

Moreover, there are three moles of H_2O, so multiply Eq. (iii) by 3

$$3H_2(g) + \frac{3}{2}O_2(g) \rightleftharpoons 3H_2O(g); K_6 = K_3^3 \quad \ldots(v)$$

(because when a reaction is multiplied by n, K becomes K^n).

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2$$

On adding Eqs. (iv), (ii) and (v) we get

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

$$K_4 = K_2 \times K_5 \times K_6$$

[because equilibrium constants are multiplied, when two or more reactions are added.]

On putting the values of K_5 and K_6, we get

$$K_4 = K_2 \cdot \frac{1}{K_1} \cdot K_3^3 = \frac{K_2K_3^3}{K_1}$$

45. We know that,

$$K_p = K_c(RT)^{\Delta n_g}$$

where, Δn_g = No. of moles of gaseous products – No. of moles of gaseous reactants

For the given reaction,

$$\Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = -0.5$$

On putting the value of Δn_g,

$$K_p = K_c(RT)^{-0.5}$$

$$K_p = \frac{K_c}{\sqrt{RT}}$$

$$\frac{K_p}{K_c} = \frac{1}{\sqrt{RT}}$$

46. $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$$

$$2NO(g) \longrightarrow N_2(g) + O_2(g)$$

$$K_c' = \frac{1}{K_c} = \frac{[N_2][O_2]}{[NO]^2} = \frac{1}{4 \times 10^{-4}} = \frac{10^4}{4}$$

$$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

$$K_c'' = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \sqrt{K_c'} = \sqrt{\frac{10^4}{4}} = \frac{100}{2} = 50$$

47. $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

	$CO_2(g)$	$2CO(g)$
Initial	0.5 atm	
At equal.	$(0.5 - p)$	$2p$ atm

This is a case of heterogeneous equilibrium.

C(s) being solid is not considered

Total pressure of CO_2 and CO gases.

$$p_{CO_2} + p_{CO} = p_{total}$$

$$0.5 - p + 2p = 0.8$$

$$p = 0.3 \text{ atm2}$$

$$\therefore \quad p_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$

$$p_{CO} = 2p = 0.6 \text{ atm}$$

$$K_p = \frac{p_{CO}^2}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8 \text{ atm}$$

48. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \quad K_1 = 4.2 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}; \quad K_2 = 4.8 \times 10^{-11}$

$$K_1 >> K_2$$

$$\therefore \quad [H^+] = [HCO_3^-]$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

So, $\quad [CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

49. Suppose total pressure at equilibrium for reactions (i) and (ii) are p_1 and p_2 respectively, then

$$X \rightleftharpoons Y + Z$$

	X	Y	Z
Initial	1 mol	0	0
At eq.	$1-\alpha$	α	α,

(Total moles = $1 + \alpha$)

$$p_X = \frac{1-\alpha}{1+\alpha} \times p_1,$$

$$p_Y = \frac{\alpha}{1+\alpha} \times p_1,$$

$$p_Z = \frac{\alpha}{1+\alpha} \times p_1$$

$$K_{p_1} = \frac{\left(\frac{\alpha}{1+\alpha}p_1\right)^2}{\frac{1-\alpha}{1+\alpha} \times p_1} = \frac{\alpha^2 p_1}{1-\alpha^2} \approx \alpha^2 p_1$$

$$A \rightleftharpoons 2B$$

	A	$2B$
Initially	1 mol	0
At eq.	$1-\alpha$	2α

Total moles $= 1 + \alpha$

$$p_A = \frac{1-\alpha}{1+\alpha} \times p_2, \quad p_B = \frac{2\alpha}{1+\alpha}p_2$$

$$K_{p_2} = \frac{\left(\frac{2\alpha}{1+\alpha}p_2\right)^2}{\frac{1-\alpha}{1+\alpha}p_2} = \frac{4\alpha^2}{1-\alpha^2}p_2 = 4\alpha^2 p_2$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{\alpha^2 p_1}{4\alpha^2 p_2} = \frac{p_1}{4p_2} = \frac{9}{1} \text{ (given)}$$

or $\frac{p_1}{p_2} = \frac{36}{1} = 36:1$

50. $$K_1 = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$K_2 = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$$

Obviously, $K_1 \times K_2 = K_3$

51. Equilibrium constant for the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$K_c = \frac{1}{4.9 \times 10^{-2}}$$

and for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2 = \frac{10^4}{(4.9)^2} = 416.490$$

52.

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$	$+Cl_2(g)$
Initial conc.	1	0	0
Eq. conc.	$1-x$	x	x

Total number of moles at equilibrium $= (1-x) + x + x = 1 + x$

$$p_{PCl_3} = \left[\frac{x}{1+x}\right] \cdot p$$

53. Reaction is exothermic. By Le-Chatelier's principle, a reaction is spontaneous in forward side (in the direction of formation of more ClF_3, if F_2 is added, temperature is lowered and ClF_3 is removed.

54. $$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$K_c = 1.8 \times 10^{-6}$ at 184°C (= 457 K)

$R = 0.00831 \text{ kJ mol}^{-1}\text{K}^{-1}$

$K_p = K_c (RT)^{\Delta n_g}$

where,

Δn_g = (gaseous products − gaseous reactants)

$= 3 - 2 = 1$

$\therefore \quad K_p = 1.8 \times 10^{-6} \times 0.00831 \times 457$

$= 6.836 \times 10^{-6} > 1.8 \times 10^{-6}$

Thus, $K_p > K_c$

55. $P_4(s) + 5\,O_2(g) \rightleftharpoons P_4O_{10}(s)$

$$K_c = \frac{1}{[O_2]^5};$$

(For solid state, molar concentrations are taken as 1.]

56. $K_p = K_c (RT)^{\Delta n_g}$

Δn_g = sum of coefficients of gaseous products − sum of coefficients of gaseous reactants.

57. $$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{(1.2 \times 10^{-2})^2}{4.8 \times 10^{-2}}$$

$= 3 \times 10^{-3} \text{mol L}^{-1}$

58. $\Delta n_g = -$ ve ; Reaction takes place with decrease in number of moles or pressure; hence increase in pressure shifts the equilibrium in forward side.

$\Delta H° = -$ ve ; Reaction takes place with evolution of heat or increase in temperature, hence decrease in temperature shifts the equilibrium in forward side.

59. $N_2(g) + O_2(g) \rightleftharpoons 2NO\,(g)$

Change in volume of the flask does not affect the equilibria because number of moles of gaseous reactants are equal to the number of moles of gaseous products.

60. $K_p = K_c (RT)^{\Delta n_g}$

$\Delta n_g = 1 - 1.5 = -0.5$

$K_p = K_c (RT)^{-1/2}$

$$= \frac{K_c}{(RT)^{1/2}}$$

$$\therefore \quad \frac{K_c}{K_p} = (RT)^{1/2}$$

Day 10

Ionic Equilibrium

Day 10 Outlines ...

- Concept of Equilibrium
- Degree of Ionisation
- Acids and Bases
- pH Scale
- Salt Hydrolysis
- Buffer Solution

Concept of Ionic Equilibrium

The weak electrolytes are only partially ionized and a dynamic equilibrium is maintained after sometime between the ions and unionized molecules. This is known as ionic equilibrium. Hence, ionic equilibrium can be defined as equilibrium which is established between the unionized molecules and the ions in the solution of weak electrolytes.

Weak and Strong Electrolytes and their Ionisation

Weak electrolytes dissociate partially in the solutions and such solutions are poor conductor of electricity. *e.g.*, CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, HCN etc.

Strong electrolytes dissociate completely into their ions in solution and such solutions are very good conductor of electricity. e.g., HCl, H_2SO_4, NaOH, KOH, NaCl, KCl etc.

Separation of an electrolyte into their ions either on fusion or dissolution is called **ionisation or dissociation.**

$$NaCl + aq \longrightarrow Na^+(aq) + Cl^-(aq)$$

(Usually the term dissociation is used for weak electrolyte and ionization for strong electrolyte).
The solution of weak electrolytes contain ions, which are in equilibrium with unionised molecules.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

This equilibrium is known as **ionic equilibrium** and is dynamic in nature.

Degree of Ionisation

The fraction of total number of moles undergoing ionisation is called degree of ionisation or dissociation (α). *Alternately, the fraction of the amount of an electrolyte present in the solution as free ions is called degree of ionisation* (α).

$$\alpha = \frac{\text{number of moles of electrolyte dissociated as ions}}{\text{total number of moles of electrolyte dissolved}}$$

or

$$\alpha = \frac{\text{amount of electrolyte dissociated}}{\text{initial amount}}$$

Ostwald's Dilution Law

It states that degree of dissociation of weak electrolyte is inversely proportional to the square root of concentration.

$$\alpha \propto \frac{1}{\sqrt{c}}, \quad \alpha = \sqrt{\frac{k}{c}} = \sqrt{kV}$$

where, α = degree of dissociation
V = volume containing 1 mole of weak electrolyte
k = dissociation constant.

Ostwald's dilution law is used to calculate the degree of dissociation, α for weak acids & bases from the known value of K.

- *The value of k can be calculated for only weak electrolytes.*
- *Ostwald's dilution law is applicable only to weak electrolytes because for strong electrolytes,*

$$\alpha \approx 1, \text{ i.e., } K_a \to \infty$$

Applications of Ostwald's Dilution Law

This law is used

1. To calculate the value of dissociation constant (K) of the weak acids and weak bases, by determining the degree of dissociation (α) from conductance measurement $\left(\frac{\lambda_V}{\lambda_\infty}\right)$ at any concentration C.
2. To calculate the degree of dissociation, α of weak acids and bases by knowing the value of K.
   For weak acid, put $[A^+] = [H^+]$ and $K = K_a$
   Similarly for weak bases,
   $$[B^-] = [OH^-] \quad \text{and} \quad K = K_b$$

Limitations of Ostwald's Law

- This law holds good only in case of weak electrolytes. Even weak electrolytes do not obey this law in concentrated solutions.
- The value of K can be calculated only in dilute solutions of weak electrolytes.

Factors Influencing Degree of Ionisation/Dissociation

- For strong electrolyte, $\alpha = 1$ at normal dilution while for most of the polar covalent compounds *i.e.,* weak electrolytes, $\alpha <<< 1$.
- Degree of ionisation of an electrolyte increases with polarity of the solvent.
- The degree of ionisation of an electrolyte decreases with increase in concentration of the electrolyte.
- The degree of ionisation rises with raise in temperature of the solution.
- The addition of species possessing a common ion to that of weak electrolyte causes a decrease in the degree of dissociation of weak electrolyte.

Acids and Bases

*An **acid** is that whose aqueous solution tastes sour, turns blue litmus red, neutralises bases and so on. On the other hand, the aqueous solution of a **base** tastes bitter, turns red litmus blue, neutralises acid and so on.*

Arrhenius Theory

When dissolved in water, the substances which release H^+ ions are called acids and which release OH^- ions are called bases.

Limitations of Arrhenius Theory

1. Free H^+ and OH^- ions do not exist in water.
2. The concept is limited to aqueous solutions only.
3. It cannot explain the acidic character of certain salts like, $AlCl_3$, BF_3 and basic character of NH_3, PH_3.
4. It cannot be applied to compounds which do not contain free H^+ or OH^- ions.

Bronsted-Lowry Concept

Acids are proton donors while bases are proton acceptors.

Conjugate base

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow H_3O^+ + Cl^-$$

Conjugate acid

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \longrightarrow NH_4^+ + OH^-$$

The substances which behave like both as an acid and a base are called **amphiprotic**. *e.g.*, H_2O, HSO_3^-, HS^- etc.

Conjugate base of weak acid is strong or *vice-versa*.

- *The strength of acid depends upon the nature of solvent. e.g., H_2SO_4, $HClO_4$, HNO_3 and HCL, all have same strength in water due to levelling effect of water.*
- *In acetic acid solvent, the order of their acidic strength is $HClO_4 > H_2SO_4 > HCl > HNO_3$.*

Limitations of Bronsted-Lowry Concept

1. The protonic definition cannot be used to explain the reactions occurring in the non-protonic solvents such as $COCl_2, SO_2, N_2O_4$ etc.
2. This concept cannot explain the reactions between some acidic oxides (such as CO_2, SO_2, SO_3) and basic oxides (such as CaO, BaO, MgO) which take place even in the absence of the solvent, *e.g.*,

$$CaO + SO_3 \longrightarrow CaSO_4$$

3. BF_3, $AlCl_3$ etc., do not have any hydrogen and hence, cannot give a proton but are known to behave as acids.

Lewis Concept

Acids are the substances which accept a pair of electrons to form a coordinate bond and bases are the substances which donate a pair of electrons to form coordinate bond.

Following species can act as Lewis acids

(i) Molecules in which central atom has incomplete octet *e.g.*, BF_3, $AlCl_3$, $FeCl_3$ etc.

(ii) Molecules in which the central atom is either non-metal cation or metal cation with empty *d*-orbital (*d*-block elements)
e.g., SiX_4, GeX_4, PX_3, $TiCl_4$, H^+, Ag^+ etc.

Lewis bases should satisfy following conditions

(i) Octet should be complete and central atom should be more electronegative.

(ii) Lone pair/pairs should be present *e.g.*, NH_3, H_2O, $R—OH$, $R—OR$ etc.

(iii) Negatively charged species *e.g.*, CN^-, OH^-, Cl^- etc.

Limitations of Lewis Concept

1. The strength of Lewis acids and bases is found to depend on the type of reaction, *it is not possible to arrange them in any order of their relative strength.*
2. It does not explain the behaviour of protonic acids such as HNO_3, HCl, H_2SO_4 etc.
3. Catalytic activity of Lewis acid can't be explained because the catalytic activity of many acids is due to their tendency to furnish H^+. Lewis acid does not do so.

Relative Strength of Mono Acidic Bases

Relative strength of mono acidic bases (or mono basic acids) of equimolar concentrations

$$\frac{\text{Strength of base (BOH)}_1}{\text{Strength of base (BOH)}_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \frac{\alpha_1}{\alpha_2}$$

$$\frac{\text{Strength of acid (HA)}_1}{\text{Strength of acid (HA)}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\alpha_1}{\alpha_2}$$

Ionic Product of Water (K_w)

Pure water is a weak electrolyte and is ionised according to following equation.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

At 25°C, for pure water $[H_3O^+] = [OH^-] = 10^{-7}$ mol/L

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

$$K = \frac{K_w}{55.55}$$

where, K = ionisation constant.

Value of K_w depends upon temperature. If temperature increases, value of K_w also increases.

pH Scale

It is used to express and compare the acidic and basic strength of a solution. It is defined as the negative logarithm of H_3O^+ *ion concentration (in moles per litre) present in it.*

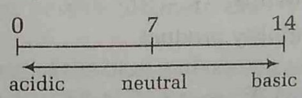
Thus, $$pH = -\log [H_3O^+]$$

Similarly, $$pOH = -\log [OH^-]$$

$$pH + pOH = 14$$

pH Scale Range

pH scale range is 0 to 14 and it depends upon the value of K_w. As temperature increases, value of pH decreases at 25°C. pH scale range will be



(i) pH of very dilute ($\sim 10^{-8}$ M or lower) acids or bases is nearly 7 but not 7 (*i.e.*, not simply – log [acid or base]) due to ionisation of water.

(ii) pH of strong acids with concentration > 1 M is never negative, it is zero only.

pH of Mixtures of Acids and Bases

The rules for determining the pH *of mixtures of acids and bases are as follows*

(i) If strong acid or strong base remains unused, calculate the concentration or molarity of $H^{\oplus}$ ions and $\overset{\ominus}{O}H$ ions left in the solution and then calculate the pH or pOH accordingly.

(ii) If weak acid or weak base is left behind or remains unused, a buffer (acidic or basic) is formed. Calculate the concentration of salt formed (mmoles of salt formed/volume of solution) and the concentration of weak acid or weak base left behind. Use the buffer equation to calculate the pH of the solution.

(iii) If acids or bases are completely neutralised, then salt is formed. Calculate the concentration of the salt formed and use the hydrolysis equation to calcualte the pH of the solution.

- *pH value of a solution decreases on heating because ionisation of water is an endothermic process. pH of boiling water is 6.5625, although it is neutral.*
- *When pH decreases by one unit, H^+ ion concentration increases by a factor of 10. Similarly, when pH decreases by two units, H^+ ion concentration increases by a factor of 100.*

Common Ion Effect

It states that if to the solution of a weak electrolyte, a solution of strong electrolyte is added which furnishes an ion common to that furnished by the weak electrolyte, the ionisation of the weak electrolyte is suppressed.

e.g., $$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

If NH_4Cl or NaOH is added to NH_4OH solution, the above equilibrium will shift to the left due to high concentration of common ion and therefore, the ionisation of NH_4OH is further suppressed.

In II[nd] group of qualitative analysis, H_2S is passed in the presence of HCl. This is due to the fact that HCl suppresses the ionisation of weakly dissociated H_2S. Due to this only sulphides of II group radicals are precipitated. Sulphides of III, IV etc., groups are not precipitated because of their high solubility product.

Salt Hydrolysis

The process of salt hydrolysis is actually the reverse process of neutralisation. The reaction of an anion or cation with water accompanied by cleavage of O—H bond, is called ***hydrolysis****.*

Salt hydrolysis affects the pH of the solution.

Neutral Salts

Salts of strong acids and strong bases (*i.e.*, neutral salts) do not undergo hydrolysis *e.g.*, NaCl, $CaSO_4$ etc.

If such salt is dissolved in water, pH of the solution remains 7.

Acidic Salts

Salt of a strong acid and weak base *e.g.*, NH_4Cl are called **acidic salts**.

Such salts undergo cationic hydrolysis.

pH of acidic salt solution will be less than 7.

For such salts, $[H_3O^+] = \sqrt{K_h \times C}$

$$K_h = \frac{K_w}{K_b} \text{ or } pH = 7 - \frac{1}{2}[pK_b + \log C]$$

where, K_h = hydrolysis constant

K_b = ionisation constant for weak base

C = molar concentration of salt.

Basic Salts

Salt of strong base and weak acid *e.g.*, $NaNO_2$, NaCN, CH_3COONa are termed as basic salts.

Such salts undergo anionic hydrolysis.

pH of basic salt solution will be more than 7.

For basic salts, $[OH^-] = \sqrt{K_h \times C}$ or $K_h = \frac{K_w}{K_a}$

$$pH = 7 + \frac{1}{2}[pK_a + \log C]$$

Salts of Weak Acid and Weak Base

The salts other than halides, sulphates, nitrates of metals fall into this cotegory, *e.g.*, CH_3COONH_4 etc.

For such salts, $K_h = \frac{K_w}{K_a \times K_b}$, $pH = 7 + \frac{1}{2}[pK_a - pK_b]$

$$BaSO_4(s) \xrightleftharpoons[\text{in water}]{\text{Saturated solution}} \underset{s}{Ba^{2+}}(aq) + \underset{s}{SO_4^-}(aq)$$

There is no effect of dilution on the hydrolysis of salts of weak acid and weak base because h, pH and K_h are all independent of concentration, C.

Solubility Product

It is defined as the product of molar concentration of its ions in a concentrated solution, each concentration terms raised to the power equal to the number of ions produced on dissociation of one molecule of electrolyte.

$$A_xB_y \rightleftharpoons xA^+ + yB^-$$

$\therefore$ $K_{sp} = [A^+]^x\,[B^-]^y$

e.g.,

$$BaSO_4 \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{s}{SO_4^{2-}}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$\therefore$ $K_{sp} = S^2$

or $S = \sqrt{K_{sp}}$

where,

S = solubility,

K_{sp} = solubility product

e.g.,

$$A_2X_3 \longrightarrow \underset{2S}{2A^{3+}} + \underset{3S}{3X^{2-}}$$

$$K_{sp} = [A^{3+}]^2[X^{2-}]^3$$

$$K_{sp} = (2S)^2(3S)^3$$

$\therefore$ $K_{sp} = 108S^5$

Ionic Product (Q)

(at any stage of reaction)

It is the product of ions and give the direction of reaction.

If $Q > K_{sp}$, precipitateate will be formed.

If $Q < K_{sp}$, precipitateate does not form.

If $Q = K_{sp}$, reaction is at equilibrium.

Buffer Solution

The solution, which maintains its pH constant or reserve acidic or basic nature even upon addition of small amounts of acid or base, is called ***buffer solution.*** *The ability of buffer solution to resist changes in pH on addition of acid or base is called* ***buffer action.***

Types of buffer solutions
- Acidic buffer [pH < 7]
- Basic buffer [pH > 7]

Characteristics of a Buffer Solution

A buffer solution should exhibit following characteristics

(i) Buffer solutions posses a definite pH value.

(ii) Their pH value remains constant on keeping long or dilution.

(iii) The pH value is not changed on the addition of a strong acid in acidic buffer and a strong base in basic buffer.

1. Acidic Buffer

A buffer solution pH of which is less than 7 is called acidic buffer.

Weak acid + salt of the acid with strong base

e.g., $CH_3COOH + CH_3COONa$;

$HCN + NaCN$

2. Basic Buffer

A buffer solution having pH more than 7 is called basic buffer.

Weak base + salt of the base with strong acid.

e.g., $NH_4OH + NH_4Cl$, $C_6H_5NH_2 + C_6H_5NH_3^+Cl^-$

Henderson's Equation for Buffer Solution

For acidic buffer; $pH = pK_a + \log\frac{[salt]}{[acid]}$

For basic buffer; $pOH = pK_b + \log\frac{[salt]}{[base]}$

$pH + pOH = 14$

Buffer Capacity

Buffer capacity is quantitatively defined as the number of moles of acid or base added in 1L of solution to change the pH by unity.

Buffer capacity

$$= \frac{\text{number of moles of acid / base added to 1 L of buffer}}{\text{change in pH}}$$

Buffer capacity is maximum when

(a) $[salt] = [acid]$, $pH = pK_a$ for acidic buffer

(b) $[salt] = [base]$, $pH = pKb$ for basic buffer

Greater the buffer capacity, larger is its capacity to resist the change in pH value.

Acid-Base Indicators

An acid-base indicator is a substance which possess one colour in acid solution and altogether different colour in alkaline medium. *i.e.,* its colour changes with pH.

Ostwald's Theory

According to this theory

- Indicators are either weak acid or weak base.
- Their unionised molecules possess different colour from those of the ions which they give in the solution.
- An acidic indicator yields a coloured anion while a basic indicator yields a coloured cation in solution.
- Since they are weak electrolytes, they are not sufficiently ionised in solution. But in presence of strong acid or alkali, their degree of ionisation is considerably increased and they produce a large number of coloured ions.
- An indicator changes colour when the concentration of hydrogen ion (in mol per litre) solution is equal to the ionisation constant of the indicator, *i.e.*, indicator is 50% dissociated.

Practice Zone

DAY 10

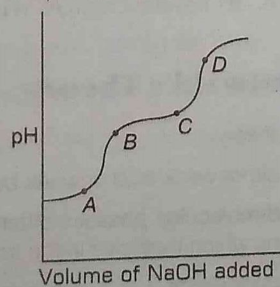
1. The ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature? **[NCERT Exemplar]**
(a) 7.0 (b) 5.98 (c) 6.78 (d) 4.58

2. Of the given anions, the strongest Bronsted base is
(a) ClO^- (b) ClO_3^- (c) ClO_2^- (d) ClO_4^-

3. Which of the following salts undergoes anionic hydrolysis?
(a) $CuSO_4$ (b) NH_4Cl (c) $FeCl_3$ (d) Na_2CO_3

4. The best indicator for the detection of end point in the titration of a weak acid and a strong base is (bracket value = pH range of indicator)
(a) methyl orange (3 to 4)
(b) bromo thymol blue (6 to 7.5)
(c) methyl red (5 to 6)
(d) phenolphthalein (8 to 9.6)

5. For the titration of a dibasic weak acid H_2A ($pK_{a(2)} - pK_{a(1)} \geq 2$) with a strong base, pH *vs* volume of the base graph is as shown in the figure $pK_{a(1)}$ and $pK_{a(2)}$ are equal to the pH values corresponding to the points



(a) *B* and *D* respectively (b) *A* and *B* respectively
(c) *C* and *D* respectively (d) *A* and *C* respectively

6. The pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is
(a) 8 (b) 6 (c) 7 (d) 9

7. The solubility of $AgBrO_3$ in an aqueous solution of $NaBrO_3$ (as compared to that in water) is
(a) the same
(b) more
(c) less
(d) unpredictable due to a new chemical reaction

8. The acid having the highest pK_a value among the following is
(a) HCOOH (b) CH_3COOH
(c) $ClCH_2COOH$ (d) FCH_2COOH

9. Species acting both as Bronsted acid and base is
(a) HSO_4^- (b) Na_2CO_3
(c) NH_3 (d) OH^-

10. How do we differentiate between Fe^{3+} and Cr^{3+} in group III?
(a) By taking excess of NH_4OH
(b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration
(d) Both (b) and (c)

11. The solubility of a sparingly soluble salt, AB_2 in water is 1.0×10^{-5} mol L^{-1}. Its solubility product will be
(a) 4×10^{-10} (b) 1×10^{-15}
(c) 1×10^{-10} (d) 4×10^{-15}

12. The pH of 0.1 M solution of a weak acid is 3. What is the value of the ionisation constant for the acid?
(a) 0.1 (b) 10^{-3}
(c) 10^{-5} (d) 10^{-7}

13. 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^{-54} respectively, which one will precipitate first?
(a) FeS (b) MgS
(c) HgS (d) ZnS

14. 1 M NH_4OH and 1M HCl are mixed to make total volume of 300 mL. If pH of the mixture is 9.26 and pK_a $[NH_4^+] = 9.26$ then volume ratio of NH_4OH and HCl will be
(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) 3 : 1

15. At the equilibrium of the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the observed molar mass of N_2O_4 is 77.70 g. The percentage of ionisation of N_2O_4 is
(a) 28.4 (b) 46.7
(c) 22.4 (d) 18.4

16. What will be the pH at which an acid indicator with $K_a = 1 \times 10^{-5}$ changes colour when the indicator concentration is 1×10^{-3}M?
(a) 5 (b) 7 (c) 3 (d) 6.5

17. The solubility product of a sparingly soluble salt *AB* at room temperature is 1.21×10^{-6}. Its molar solubility is
(a) 1.21×10^{-6} (b) 1.21×10^{-3}
(c) 1.1×10^{-4} (d) 1.1×10^{-3}

18. The solubility of AgI in NaI solution is less than that in pure water because
(a) AgI forms complex with NaI
(b) of common ion effect
(c) solubility product of AgI is less
(d) the temperature of the solution decreases

19. For the reaction, $Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2$; $k = 1.65 \times 10^{13}$ concentration of Hg^{2+} at the equivalence point in the titration of 2.0 m mol of Hg^{2+} with Cl^- when final volume is 100 mL, is
(a) 8.25×10^{14} M (b) 1.65×10^{13} M
(c) 2.87×10^{6} M (d) 6.72×10^{-6} M

20. A 50.00 mL sample of acetic acid was titrated with 0.1200 M KOH and 38.62 mL of base were required to reach the equivalent point. What was the pH of the titration mixture when 19.31 mL of base has been added? [pK_a (acetic acid) = 4.74]
(a) 2.94 (b) 3.54 (c) 4.74 (d) 5.74

21. The pK_w of a neutral solution at 50°C is 13.36, that would be the pH of the solution at this temperature? **[NCERT Exemplar]**
(a) 7.63 (b) 7.00 (c) 6.68 (d) 7.96

22. The pH of a 10^{-9} M solution of HCl in water is
(a) 8 (b) –8
(c) between 7 and 8 (d) between 6 and 7

23. What will be the degree of ionisation of 0.05 M acetic acid if its pK_a value is 4.74 ?
(a) 0.019% (b) 1.9% (c) 3.0% (d) 4.74%

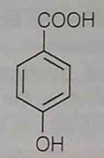
24. The molar solubility (mol L^{-1}) of a sparingly soluble salt MX_4 is '*S*'. The corresponding solubility product is K_{sp}. '*S*' is given in terms of K_{sp} by the relation
(a) $S = 256\,(K_{sp})^{1/5}$ (b) $S = (128\,K_{sp})^{1/4}$
(c) $S = (K_{sp}\ 1128)^{1/4}$ (d) $S = (K_{sp}/256)^{1/5}$

25. Dissociation constant of a weak acid is 1×10^{-4}. Equilibrium constant of its reaction with strong base is
(a) 1×10^{-4} (b) 1×10^{10} (c) 1×10^{-10} (d) 1×10^{4}

26. The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} solution will start on adding H_2SO_4 of concentration
(a) 10^{-9} M (b) 10^{-8} M (c) 10^{-7} M (d) 10^{-6} M

27. 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) Both (a) and (b) (d) None of these

Directions (Q. Nos. 28 to 30) *Following titration method is taken to compute stepwise ionisation constant of a weak dibasic acid.*

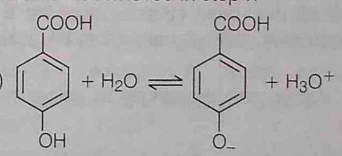
A :

p-hydroxy benzoic acid

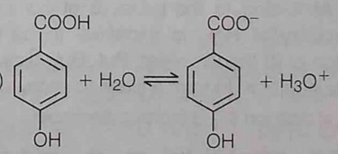
A has two ionisable proton and there can be stepwise neutralisation by NaOH.

25 mL of a dilute aqueous solution of A is titrated with 0.02 M NaOH (aq) and pH is measured.

Step	Volume of NaOH added	pH
I	8.12 mL	4.57
II	16.24 mL	7.02 (at equivalence point)

28. Which H^+ is removed in step I?

(a)


(b)


(c) Both (a) and (b) 50% in each part
(d) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ (autoprotolysis of H_2O)

29. pK_{a_1} ($= -\log K_{a_1}$) of *p*-hydroxy benzoic acid is
(a) 4.57 (b) 9.47 (c) 4.90 (d) 7.00

30. pK_{a_2} ($= -\log K_{a_2}$) of *p*-hydroxy benzoic acid is
(a) 4.57 (b) 7.00
(c) 9.47 (d) 4.90

Directions (Q. Nos. 31 and 32) *Acid rain is an environmental concern all over the world. In assessing the acidity of rainfall, it is important to have an idea of the acidity of natural rain water. Assuming that natural rain water (that is, rain water uncontaminated with nitric acid or sulphuric acid) is in equilibrium with* 3.6×10^{-4} atm CO_2 *(the Henry's law constant is* 1.25×10^6 *torr).*

$[K_{a_1}(H_2CO_3) = 4.3 \times 10^{-7}]$

31. What is the pH of natural rain water?
(a) 5.64 (b) 5.70 (c) 7.00 (d) 7.40

32. If SO_2 content in the atmosphere is 0.12 ppm by volume, pH of rain water (assume 100% ionisation of acid rain as monobasic acid)
(a) 5.7 (b) 5.6 (c) 5.4 (d) 2.0

Directions (Q. Nos. 33 to 36) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true, Statement II is false.
(d) Statement I is false, Statement II is true.

33. Statement I When HCl gas passes through saturated solution of NaCl, a solid NaCl separates out from the solution.

Statement II HCl decreases the solubility product of NaCl. **[NCERT Exemplar]**

34. Statement I In an acid-base titration, involving a strong base and a weak acid, methyl orange can be used as an indicator.

Statement II Methyl orange changes its colour in the pH range 3 to 5.

35. Statement I According to the principle of common ion effect, the solubility of HgI_2 is expected to be less in aqueous solution of KI than in water. But HgI_2 dissolves in an aqueous solution of KI to form a clear solution.

Statement II Iodide ion (I^-) is highly polarisable.

36. Statement I The addition of Ag^+ ions to a mixture of an aqueous solution of NaCl and NaBr causes precipitation of AgBr, instead of AgCl.

Statement II Solubility product of AgCl is less than that of AgBr. **[NCERT Exemplar]**

37. A solution of monoprotic weak acid has ionisation constant K_a. What is the minimum concentration C in terms of K_a, such that the concentration of the undissociated acid can be equated to C within a 10% limit of error.
[Assume that activity coefficient correction are negligible.]
(a) $45K_a$ (b) $10K_a$
(c) $90K_a$ (d) $80K_a$

38. In a excess of $NH_3(aq)$, Cu^{2+} ions form a deep blue complex ion, $[Cu(NH_3)_4]^{2+}$ having formation constant $K_f = 5.6 \times 10^{11}$. If a solution is prepared by adding 5.0×10^{-3} moles of $CuSO_4$ to 0.50 L of 0.40 M NH_3, what will be the concentration of Cu^{2+} in this solution?
(a) 5.32×10^{13} (b) 6.26×10^{-10}
(c) 53.2×10^{-6} (d) 5.32×10^{-13}

39. The degree of ionisation of 1.0 M weak acid, HA is 0.5%. If 2 mL of 1.0 M HA solution is diluted to 32 mL, the degree of ionisation of the acid and H_3O^+ ion concentration in the resulting solution will be respectively
(a) 0.02 and 3.125×10^{-4} (b) 0.02 and 1.25×10^{-3}
(c) 1.25×10^{-3} and 0.02 (d) 0.02 and 8.0×10^{-12}

40. What will be 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 $HCO_3^- = 5.63 \times 10^{-11}$]
(a) 10.197 (b) 8.089 (c) 9.858 (d) 6.400

41. What is the minimum concentration of NH_3 required to prevent AgCl (s) from precipitating from 1.00 L of a solution containing 0.10 mole of $AgNO_3$ and 0.010 mole NaCl?
[$K_{sp}(AgCl) = 1.8 \times 10^{-10}$, K_f $[Ag(NH_3)_2^+] = 1.6 \times 10^7$]
(a) 0.936 M (b) 0.789 M (c) 0.538 M (d) 0.347 M

42. 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
(a) 3.7×10^{-13}M (b) 3.2×10^{-7}M
(c) 3.2×10^{-2}M (d) 2.7×10^{-2}M

43. Solubility product constant (K_{sp}) of salts of types 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 (mol dm^{-3}) of the salts at temperature 'T' are in the order
(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$
(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

44. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$, $k_1 = 3.5 \times 10^{-3}$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.7 \times 10^{-3}$
then the formation constant of $[Ag(NH_3)_2]^+$ is
(a) 6.08×10^{-6} (b) 6.08×10^{6}
(c) 6.08×10^{-9} (d) None of these

45. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution?
(a) 8×10^{-2} M (b) 8×10^{-11} M
(c) 1.6×10^{-11} M (d) 8×10^{-5} M

46. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is
(a) 0.01% (b) 0.0001% (c) 0.1% (d) 0.5%

JEE Main & AIEEE *Archive*

47. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), K_1$ ...(i)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2$ ...(ii)

$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g), K_3$ ...(iii)

The equation for the equilibrium constant of the reaction $2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g), (K_4)$ in terms of K_1, K_2 and K_3 is **[JEE Main Online 2013]**

(a) $\frac{K_1K_2}{K_3}$ (b) $\frac{K_1K_3^2}{K_2}$

(c) $K_1K_2K_3$ (d) $\frac{K_2K_3^3}{K_1}$

48. What is the pH of a 10^{-4}MOH^- solution at 330K, if K_w at 330 K is $10^{-13.6}$? **[JEE Main Online 2013]**

(a) 4 (b) 9.0 (c) 10 (d) 9.6

49. Bond distance in HF is 9.17×10^{-11} m. Dipole moment of HF is 6.104×10^{-30} Cm. The per cent ionic character in HF will be (electron charge $= 1.60 \times 10^{-19}$ C) **[JEE Main Online 2013]**

(a) 61.0% (b) 38.0%

(c) 35.5% (d) 41.5%

50. How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **[JEE Main Online 2013]**

(a) 0.1 L (b) 0.9 L

(c) 2.0 L (d) 9.0 L

51. What would be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL?

($K_a = 1.75 \times 10^{-5}, pK_a = 4.76$) **[JEE Main Online 2013]**

(a) pH = 4.70

(b) pH < 4.70

(c) pH of solution will be equal to pH of acetic acid

(d) 4.76 < pH < 5.0

52. Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts $Hg_2Cl_2, Cr_2(SO_4)_3, BaSO_4$ and $CrCl_3$ respectively? **[JEE Main Online 2013]**

(a) $\left(\frac{K_{sp}}{108}\right)^{1/5}, \left(\frac{K_{sp}}{27}\right)^{1/4}, (K_{sp})^{1/2}, \left(\frac{K_{sp}}{4}\right)^{1/3}$

(b) $(K_{sp})^{1/2}, \left(\frac{K_{sp}}{4}\right)^{1/3}, \left(\frac{K_{sp}}{27}\right)^{1/4}, \left(\frac{K_{sp}}{108}\right)^{1/5}$

(c) $(K_{sp})^{1/2}, \left(\frac{K_{sp}}{108}\right)^{1/5}, \left(\frac{K_{sp}}{27}\right)^{1/4}, \left(\frac{K_{sp}}{4}\right)^{1/3}$

(d) $\left(\frac{K_{sp}}{4}\right)^{1/3}, \left(\frac{K_{sp}}{108}\right)^{1/5}, (K_{sp})^{1/2}, \left(\frac{K_{sp}}{27}\right)^{1/4}$

53. NaOH is a strong base. What will be pH of 5.0×10^{-2}M NaOH solution? (log 2 = 0.3) **[JEE Main Online 2013]**

(a) 14.00 (b) 13.70

(c) 13.00 (d) 12.70

54. Values of dissociation constant, K_a are given as follows

Acid	K_a
HCN	6.2×10^{-10}
HF	7.2×10^{-4}
HNO_2	4.0×10^{-4}

Correct order of increasing base strength of the base CN^-, F^- and NO_2^- will be **[JEE Main Online 2013]**

(a) $F^- < CN^- < NO_2^-$ (b) $NO_2^- < CN^- < F^-$

(c) $F^- < NO_2^- < CN^-$ (d) $NO_2^- < F^- < CN^-$

55. In reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of B was 1.5 times of [A], but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is **[JEE Main Online 2013]**

(a) 8 (b) 4

(c) 12 (d) 6

56. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At which concentration of Ba^{2+}, precipitate of $BaCO_3$ begins to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

(a) 5.1×10^{-5} M (b) 7.1×10^{-5} M

(c) 4.1×10^{-5} M (d) 8.1×10^{-2} M

57. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of the acid is **[AIEEE 2012]**

(a) 3×10^{-1} (b) 1×10^{-3} (c) 1×10^{-5} (d) 1×10^{-7}

58. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is **[AIEEE 2011]**

(a) $\sqrt[2]{1.6 \times 10^{-30}}$ (b) $\sqrt[4]{1.6 \times 10^{-30}}$

(c) $\sqrt[4]{1.6 \times 10^{-30}/27}$ (d) $1.6 \times 10^{-30}/27$

59. An acid HA ionizes as

$$HA \rightleftharpoons H^+ + A^-$$

The pH of 1.0 M solution is 5. Its dissociation constant would be **[AIEEE 2012]**

(a) 1×10^{-10} (b) 5.0 (c) 5×10^{-8} (d) 1×10^{-5}

60. Three reactions involving $H_2PO_4^-$ are given below

(i) $H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$

(ii) $H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$

(iii) $H_2PO_4^- + OH^- \longrightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid?
(a) (ii) only
(b) (i) and (ii) [AIEEE 2010]
(c) (iii) only
(d) (i) only

61. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is [AIEEE 2010]
(a) 1.2×10^{-10} g
(b) 1.2×10^{-9} g
(c) 6.2×10^{-5} g
(d) 5.0×10^{-8} g

62. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions? [AIEEE 2010]
(a) 9 (b) 10 (c) 11 (d) 8

63. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) [ALEE 2009]
(a) 4.1×10^{-5} M
(b) 5.1×10^{-5} M
(c) 8.1×10^{-8} M
(d) 8.1×10^{-7} M

64. The pK_a of a weak acid, HA is 4.80. The pK_b of a weak base BOH is 4.78. The pH of an aqueous solution of the corresponding salt BA, will be [AIEEE 2008]
(a) 7.01 (b) 9.22 (c) 9.58 (d) 4.79

65. Four species are listed below
I. HCO^{-3}
II. H_3O^+
III. HSO_4^-
IV. $HSOF_3$

Which one of the following is the correct sequence of their acidic strength? [AIEEE 2008]
(a) IV<II<III<I
(b) II<III<I<IV
(c) I<III< II<IV
(d) III<I<IV<II

66. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid ionised is [AIEEE 2007]
(a) 4.5 (b) 2.5 (c) 9.5 (d) 7.0

67. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283), the equilibrium sets as $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$

If the solubility product constant, K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution? [AIEEE 2007]
(a) 28.3×10^{-2} g
(b) 2.83×10^{-3} g
(c) 1.0×10^{-7} g
(d) 1.0×10^{-4} g

68. The solubility product of a salt having general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is [AIEEE 2007]
(a) 4.0×10^{-10} M
(b) 1.6×10^{-4} M
(c) 1.0×10^{-4} M
(d) 2.0×10^{-6} M

69. What is the conjugate base of OH^-? [AIEEE 2005]
(a) O^{2-}
(b) O
(c) H_2O
(d) O_2

70. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be [AIEEE 2005]
(a) 3.98×10^{-6}
(b) 3.68×10^{-6}
(c) 3.88×10^{6}
(d) 3.88×10^{8}

71. The conjugate base of $H_2PO_4^-$ is [AIEEE 2004]
(a) PO_4^{3-}
(b) P_2O_5
(c) H_3PO_4
(d) HPO_4^{2-}

72. The molar solubility (in mol L^{-1}) of a sparingly soluble salt Mx_4 is S. The corresponding solubility product is K_{sp}.S is given in terms of K_{sp}. by the relation [AIEEE 2004]
(a) $S = (K_{sp}/128)^{1/4}$
(b) $S = (128K_{sp})^{1/4}$
(c) $S = (256K_{sp})^{1/5}$
(d) $S = (K_{sp}/256)^{1/5}$

73. Which one of the following statements is not true? [AIEEE 2003]
(a) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.
(b) pH + pOH = 14 for all aqueous solutions.
(c) The pH of 1×10^{-8} M HCl is 8.
(d) 96,500 C of electricity when passed through a solution of $CuSO_4(aq)$ deposits 1 g equivalent of Cu at cathode.

74. Which one of the following substances has the highest proton affinity? [AIEEE 2003]
(a) H_2O (b) H_2S (c) NH_3 (d) PH_3

75. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be [AIEEE 2003]
(a) 4×10^{-15}
(b) 4×10^{-10}
(c) 1×10^{-15}
(d) 1×10^{-10}

76. pH of 0.005 M calcium acetate (pK_a of $CH_3COOH = 4.7$) is [AIEEE 2002]
(a) 7.04
(b) 9.37
(c) 9.26
(d) 8.37

77. Which one of the following species act as both Bronsted acid and base? [AIEEE 2002]
(a) $H_2PO_2^-$
(b) HPO_3^{2-}
(c) HPO_4^{2}
(d) All of the above

78. Solubility of $Ca(OH)_2$ is S mol L^{-1}. The solubility product (K_{sp}) under the same condition is [AIEEE 2002]
(a) $4S^3$
(b) $3S^4$
(c) $4S^2$
(d) S^3

79. An aqueous solution of 1 M NaCl and 1 M HCl is [AIEEE 2002]
(a) not a buffer but pH < 7
(b) not a buffer but pH > 7
(c) a buffer with pH < 7
(d) a buffer with pH > 7

Answers

1. (c)	2. (a)	3. (d)	4. (d)	5. (d)	6. (b)	7. (c)	8. (b)	9. (a)	10. (d)
11. (d)	12. (c)	13. (c)	14. (c)	15. (d)	16. (a)	17. (d)	18. (b)	19. (d)	20. (c)
21. (c)	22. (d)	23. (b)	24. (d)	25. (b)	26. (d)	27. (b)	28. (b)	29. (a)	30. (c)
31. (a)	32. (a)	33. (b)	34. (d)	35. (b)	36. (c)	37. (c)	38. (d)	39. (b)	40. (a)
41. (b)	42. (c)	43. (d)	44. (a)	45. (b)	46. (a)	47. (d)	48. (d)	49. (d)	50. (d)
51. (d)	52. (d)	53. (d)	54. (c)	55. (b)	56. (a)	57. (c)	58. (c)	59. (a)	60. (a)
61. (b)	62. (b)	63. (b)	64. (a)	65. (a)	66. (c)	67. (b)	68. (c)	69. (a)	70. (a)
71. (d)	72. (d)	73. (c)	74. (c)	75. (a)	76. (d)	77. (c)	78. (a)	79. (a)	

Hints & Solutions

1. $k_w = [H^+][OH^-]$

But $[H^+] = [OH^-]$, therefore,

$$K_w = [H^+]^2$$

$$[H^+] = \sqrt{K_w} = \sqrt{2.7 \times 10^{-14}} = 1.643 \times 10^{-7} \text{ M}$$

$$pH = -\log[H^+] = -\log[1.643 \times 10^{-7}] = 6.78$$

2. HClO is the weakest acid, hence its conjugate base *i.e.*, ClO^- is the strongest Bronsted base.

3. Anionic hydrolysis means anion reacts with water.

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$$

or $2Na^+ + CO_3^{2-} + 2H_2O \rightleftharpoons 2Na^+ + 2OH^- + H_2CO_3$

or $CO_3^{2-} + 2H_2O \rightleftharpoons 2OH^- + H_2CO_3$

4. The best indicator for the titration of weak acid with strong base is phenolphthalein.

5. $pH = pK_{a(1)}$ when $[HA^-] = [H_2A]$

$pH = pK_{a(2)}$ when $[A^{2-}] = [HA^-]$

The points *A* and *C* represent half stages of the reactions

(i) $H_2A + OH^- \rightarrow HA^- + H_2O$

(ii) $HA^- + OH^- \rightarrow A^{2-} + H_2O$

6. $NH_4OH + HCl$ forms NH_4Cl, which gives acidic solution with $pH < 7$.

7. $NaBrO_3$ gives BrO_3^- ions. Hence, $[BrO_3^-]$ increases. To keep K_{sp} constant, $[Ag^+]$ decreases.

8. Weak acids consist of highest pK_a value and strong acids consist of less pK_a value.

9. HSO_4^- can accept proton to form H_2SO_4 and also give a proton to form SO_4^{2-} therefore, it acts both as Bronsted acid is well as base.

10. In group III of analysis, addition of NH_4Cl increases NH_4^+ ion concentration and decreases OH^- ion concentration produced from NH_4OH due to common ion effect.

11. $AB_2 \longrightarrow A^{2+} + 2B^-$

$$K_{sp} = [A^{2+}][B^-]^2 = (1.0 \times 10^{-5})(2 \times 1.0 \times 10^{-5})^2 = 4 \times 10^{-15}$$

12. $HA \rightleftharpoons H^+ + A^-$

$[H^+] = 10^{-3}$ M

$\therefore$ $[A^-] = 10^{-3}$ M

Hence, $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{10^{-3} \times 10^{-3}}{0.1} = 10^{-5}$

13. The one with lowest value of K_{sp} *i.e.*, HgS will precipitate out first.

14. $pH = 9.26$ indicates $[NH_4OH] > [HCl]$ and thus mixture is a buffer since HCl will react with equivalent amount of NH_4OH forming NH_4Cl.

Let $HCl = x$ mL $= x$ millimol

$NH_4OH = (300 - x)$ mL $= (300 - x)$ millimol

NH_4Cl formed $= x$ millimol

NH_4OH unreacted $= 300 - x - x = (300 - 2x)$ millimol

$$POH = 14 - 9.26 = 4.74$$

$$pK_b = 14 - 9.26 = 4.74$$

$$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]]}$$

or $$4.74 = 4.74 + \log\frac{x}{300 - 2x}$$

$$\frac{x}{300 - 2x} = 1$$

$x = 100$ mL = volume of HCl

$(300 - x) = 200$ mL = volume of NH_4OH

Hence, volume ratio of NH_4OH and HCl = 2 : 1.

15. $\alpha = \dfrac{M_{Th} - M_{Obs}}{M_{Obs}(n - 1)}$

Molar mass of $N_2O_4 = 92 \text{ g mol}^{-1}$

Here,
$$n = 2$$
$$\alpha = \frac{92.00 - 77.70}{77.70\,(2-1)} = 0.184$$

Hence, percentage dissociation = 18.4%

16. An acid indicator dissociates at equilibrium as

$$HIn \rightleftharpoons H^+ + In^-$$
$$\therefore \quad K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

At the mid point, $[In^-] = [HIn]$

$$\therefore \quad K_{In} = [H^+] = 1 \times 10^{-5}$$
$$\therefore \quad [H^+] = 1 \times 10^{-5} \text{ or } pH = 5$$

17. $\because$ AB is a binary electrolyte,

$$S = \sqrt{K_{sp}} = \sqrt{1.21 \times 10^{-6}} = 1.1 \times 10^{-3}\ M$$

18. Solubility is decreased due to common ion effect.

$$AgI \rightleftharpoons Ag^+ + I^-$$
$$NaI \rightleftharpoons Na^+ + I^-$$

I^- is common ion in both the reactions.

19. $[Hg^{2+}] = 2.0$ millimol in 100 mL solution

$$= \frac{2 \times 10^{-3}\ mol}{0.1\ L} = 2 \times 10^{-2}\ M = 0.02\ M$$

Since, stability constant of $HgCl_2$ is large (1.65×10^{13}), the value of $[Hg^{2+}]$ should be small.

At the end point, $[Cl^-] = 2\,[Hg^{2+}]$

$$[HgCl_2] = 0.020 - [Hg^{2+}]$$
$$\approx 0.02\ M$$
$$\frac{[HgCl_2]}{[Hg^{2+}]\,[Cl^-]^2} = 1.65 \times 10^{13}$$
$$\frac{0.02}{[Hg^{2+}]\,(2\,[Hg^{2+}])^2} = 1.65 \times 10^{13}$$
$$4\,[Hg^{2+}]^3 = \frac{0.02}{1.65 \times 10^{13}}$$
$$[Hg^{2+}] = 6.72 \times 10^{-6}\ M$$

20. For equivalent point KOH required = 38.62 mL when half of this volume (19.31 mL) has been added 50% acid is neutralised and at this stage

$$[CH_3COOK] = [CH_3COOH]$$
$$pH = pK_a = 4.74$$

21. $pK_w = pH + pOH$

But $\quad [H^+] = [OH^-] \Rightarrow pH = pOH,$

$$\therefore \quad pK_w = 2\,pH$$
$$pH = \frac{pK_w}{2} = \frac{13.36}{2} = 6.68$$

22. As the solution is acidic, pH < 7. This is because $[H^+]$ from H_2O $[10^{-7}\ M]$ cannot be neglected in comparison to 10^{-9} M.

23.
$$\begin{array}{lccc} & CH_3COOH \rightleftharpoons & CH_3COO^- & + H^+ \\ & 1 & 0 & 0 \\ & 1-\alpha & \alpha & \alpha \end{array}$$
$$pK_a = -\log K_a = 4.74$$
$$\therefore \quad K_a = 1.82 \times 10^{-5}$$

From, $\quad K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad (1-\alpha \approx 1)$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = 0.019 \text{ or } 1.9\%$$

24. $MX_4 \longrightarrow \underset{S}{M^{4+}} + \underset{4S}{4X^-}$;

$$K_{sp} = (4S)^4 S \text{ or } K_{sp} = 256 S^5$$
$$\therefore \quad S = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

25. $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{...(i)}$$
$$HA + NaOH \rightleftharpoons ANa + H_2O$$

or
$$HA + OH^- \rightleftharpoons A^- + H_2O$$
$$K_c = \frac{[A^-]}{[HA][OH^-]}$$

or
$$K_c = \frac{[A^-][H^+]}{[HA][H^+][OH^-]} \quad \text{...(ii)}$$

From Eqs. (i) and (ii)

$$K_c = \frac{K_a}{[H^+][OH^-]} = \frac{K_a}{K_w} = \frac{1 \times 10^{-4}}{1 \times 10^{-14}} = 1 \times 10^{10}$$

26. K_{sp} of $BaSO_4 = 1.5 \times 10^{-9}$

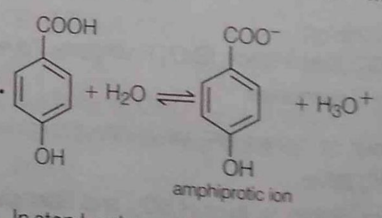
$$Ba^{2+} = 0.01\ M$$
$$SO_4^{2-} > \frac{1.5 \times 10^{-9}}{0.01} > 1.5 \times 10^{-7}$$

i.e., $\quad SO_4^{2-} > 10^{-6}$ M

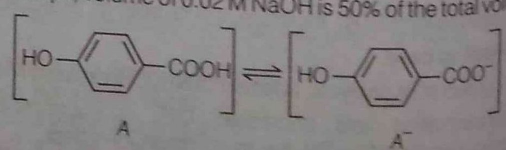
27. When ionic product is greater than K_{sp}, then precipitation occurs.

$$K_{sp} < 10^{-2}\ M\ Ca^{2+} + 10^{-3}\ MF^-$$

28.



29. In step I, volume of 0.02 M NaOH is 50% of the total volume.



Thus, 50% of acid A is neutralised. At this point,

$$pH = pK_{a_1} + \log \frac{[A^-]}{[A]}$$

$$\therefore \quad pK_{a_1} = 4.57$$

30. For amphiprotic ion,

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$$

$$pK_{a_2} = 2pH - pK_{a_1}$$

$$pK_{a_2} = (2 \times 7.02) - 4.57 = 9.47$$

31. By Henry's Law,

$$p_{CO_2} = X_{CO_2} K_h$$

$$X_{CO_2} = \frac{p_{CO_2}}{K_h} = \frac{(3.6 \times 10^{-4} \text{ atm}) \times 760 \text{ torr atm}}{1.25 \times 10^6 \text{ torr}}$$

$$= 2.2 \times 10^{-7} = \frac{n_{CO_2}}{n_{total}}$$

$$X_{H_2O} = (1 - 2.2 \times 10^{-7}) = \frac{n_{H_2O}}{n_{total}}$$

$$\frac{n_{CO_2}}{n_{H_2O}} = \frac{2.2 \times 10^{-7}}{1 - 2.2 \times 10^{-7}} = 2.2 \times 10^{-7}$$

Molarity of CO_2 solution

$$= \frac{2.2 \times 10^{-7} \times 1000}{18} = 1.2 \times 10^{-5} \text{ M}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{[H^+]^2}{[H_2CO_3]}$$

$$H^+ = \sqrt{K_a \cdot [H_2CO_3]}$$

$$= \sqrt{4.3 \times 10^{-7} \times 1.2 \times 10^{-5}}$$

$$= 2.3 \times 10^{-6} \text{ M}$$

$$\therefore \quad pH = 5.64$$

32. 0.12 ppm $= 0.12$ g in 10^6 mL

$$[H^+] = [SO_2]$$

$$[H_2SO_3] = \frac{0.12}{64} \times 10^{-3} \text{ M}$$

$$pH = 5.7$$

33. The ionization of NaCl is suppressed due to the common ion effect of Cl^- which results in the precipitation of NaCl.

34. In case of titration of a weak acid with a strong base, there is an inflection point near the equivalence point only from 7.46 to 10, so we can use only phenolphthalein as a suitable indicator.

35. HgI_2 combines with KI to form the soluble complex K_2HgI_4.

36. The value of solubility product of AgCl is greater than that of AgBr. Since, compounds with lower value of solubility product is precipitated first, therefore AgBr precipitates out more easily than AgCl.

37. $\underset{C}{HA} + H_2O \longrightarrow \underset{0}{H_3^+O} + \underset{0}{A^-}$

$$C(1-\alpha) \qquad C\alpha \qquad C\alpha$$

$$K_a = \frac{[H_3^+O][A^-]}{[HA]} = \frac{C^2\alpha^2}{C(1-\alpha)}$$

Within an error of 10%,

$$C(1-\alpha) \text{ or } C - C\alpha = 0.90\,C$$

or $\quad C\alpha = 0.10C$

$$\because \quad K_a = \frac{(0.10C)^2}{0.90C} = \frac{C}{90} \text{ or } C = 90K_a$$

38.

	Cu^{2+}	+ $4NH_3(l)$	$\rightleftharpoons$ $[Cu(NH_3)_4]^{2+}$;
Initial moles	0.005	$0.5 \times 0.4 = 0.2$	0

$$K_f = 5.6 \times 10^{11}$$

K_f is large and thus, most of the Cu^{2+} will give $[Cu(NH_3)_4]^{+2}$.

Let the Cu^{2+} left is a, then

$$[Cu(NH_3)_4]^{2+} = 0.005 - a = 0.005 \text{ mole}$$

$$= \frac{0.005}{0.5} \text{M} \qquad (\because 0.005 >> a)$$

$$[Cu^{2+}] = \frac{a}{0.5} \text{M}$$

Let NH_3 left is b, then

$$[NH_3] = 0.2 - 4 \times 0.005 + b$$

$$= 0.2 - 0.02 + b \, (0.18 >> b)$$

$$= 0.18 \text{ mol} = \frac{0.18}{0.5} \text{M}$$

$$\therefore \quad K_f = 5.6 \times 10^{11} = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4} = \frac{\frac{0.005}{0.5}}{\frac{a}{0.5} \times \left[\frac{0.18}{0.5}\right]^4}$$

$$a = \frac{0.005 \times (0.5)^4}{(0.18)^4 \times 5.6 \times 10^{11}} = 5.32 \times 10^{-13} \text{ mol/L}$$

39. $\alpha_1 = 0.005 = \sqrt{K_a} \qquad (\because C_1 = 1 \text{ mol L}^{-1})$

Molarity of the diluted solution,

$$C_2 = \frac{2}{32} = \frac{1}{16} \text{mol L}^{-1}$$

$$\alpha_2 = \sqrt{\frac{K_a}{C_2}} = 0.005\sqrt{16} = 0.02$$

$$[H_3O^+] = C_2\alpha_2 = \frac{1 \times 0.02}{16} = 1.25 \times 10^{-3} \text{M}$$

40.

	Na_2CO_3	+ HCl $\longrightarrow$	NaCl	+ $NaHCO_3$
Meq before reaction	$\frac{30}{106} \times 1000 = 283$	$150 \times 1 = 150$		
Meq after reaction	133	0	150	150

The solution contains Na_2CO_3 and HCO_3^- and thus, acts as (a) buffer.

$$\therefore \quad pH = -\log K_a + \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$pH = -\log K_a + \log(133/150)$$

$$pH = -\log 5.63 \times 10^{-11} + \log(133/150) = 10.249 - 0.052$$

$$pH = 10.197$$

41. If no precipitate is to occur

Here, $[Ag^+][Cl^-] \le K_{sp}$

$$[Cl^-] = 0.01\ M$$

$$[Ag^+](0.01) \le 1.8 \times 10^{-10}$$

$$[Ag^+] \le 1.8 \times 10^{-8}\ M$$

The maximum concentration of free, uncomplexed Ag^+ permitted in solution is 1.8×10^{-8} M. This means that almost all the Ag^+ (0.10 M) must be complexed.

$$\therefore Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2^+]$$

$$\therefore \quad [NH_3] = ?$$

$$[Ag^+] = 1.8 \times 10^{-8} M$$

$$[Ag(NH_3)_2^+] = 0.10\ M$$

$$\therefore \quad K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.6 \times 10^7$$

$$\frac{0.10}{1.8 \times 10^{-8}[NH_3]^2} = 1.6 \times 10^7$$

$$[NH_3]^2 = 0.347$$

$$[NH_3] = 0.589\ M$$

The concentration calculated above is that of free, uncomplexed NH_3.

$[NH_3]$ required by 0.1 M Ag^+ in the formation of $[Ag(NH_3)_2^+]$ = 0.2 M

Hence, total $[NH_3] = 0.589 + 0.2\ M = 0.789\ M$

42.

$$\underset{(Base)}{N_1V_1} = \underset{(Acid)}{N_2V_2}$$

$$2.5 \times \frac{2}{5} = \frac{2}{15} \times V_2 \text{ or } V_2 = \frac{15}{2} = 7.5\ mL$$

$$BOH + HCl \longrightarrow BCl + H_2O$$

2.5 mL of $\frac{2}{5}$ M base contains, base $= 2.5 \times \frac{2}{5} = 1$ mmol

$\therefore$ Salt BCl formed = 1mmol

Volume of solution = 2.5 mL + 7.5 mL = 10 mL

$\therefore$ Concentration of salt [BCl] in the solution

$$= \frac{1}{10}\ M = 0.1\ M$$

For salt of weak base and strong acid

$$[H^+] = \sqrt{\frac{K_wC}{K_b}} = \sqrt{\frac{10^{-14} \times 0.1}{10^{-12}}} = 3.2 \times 10^{-2}\ M$$

43.

Salt	Solubility product	Solubility
MX	$S_1^2 = 4.0 \times 10^{-8}$	$S_1 = 2 \times 10^{-4}$
MX_2	$4S_2^3 = 3.2 \times 10^{-14}$	$S_2 = 2 \times 10^{-5}$
M_3X	$27S_3^4 = 2.7 \times 10^{-15}$	$S_3 = 1 \times 10^{-4}$

Thus, order of solubilities = $MX > M_3X > MX_2$

44. (i) $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+; K_1 = 3.5 \times 10^{-3}$

(ii) $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+; K_2 = 1.7 \times 10^{-3}$

On the basis of above reactions,

$$K_1 = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]} \quad \ldots(i)$$

$$K_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+[NH_3]} \quad \ldots(ii)$$

For the formation of $[Ag(NH_3)_2]^+$

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$\text{Formation constant, } K = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \quad \ldots(iii)$$

From Eqs. (i) and (ii)

$$K = K_1 \times K_2 = 3.5 \times 10^{-3} \times 1.7 \times 10^{-3}$$

$$= 5.95 \times 10^{-6} \approx 6.08 \times 10^{-6}$$

45. CH_3NH_2 (base) on reaction with HCl (acid) give a salt of weak base and strong acid as $CH_3NH_3^+Cl^-$.

	CH_3NH_2	+ $HCl \longrightarrow$	$CH_3NH_3^+Cl^-$
At $t = 0$	0.1 mol	0.08 mol	0
After reaction	(0.1 − 0.08) = 0.02 mol	0	0.08 mol

So, it acts as basic buffer solution due to presence of weak base and its salt in solution of one litre.

$$pOH = -\log K_b \times \log \frac{[salt]}{[base]}$$

$$pOH = -\log K_b \times \log \frac{[CH_3NH_3^+Cl^-]}{[CH_3NH_2]}$$

$$= -\log(5 \times 10^{-4}) + \log \frac{[0.08]}{[0.02]}$$

$$= -\log 5 + 4 \log 10 + \log 4$$

$$= -0.699 + 4 + 0.602 = 3.903$$

$$pH = 14 - pOH = 14 - 3.903$$

$$= 10.097 = -\log[H^+]$$

$$[H^+] = 8.0 \times 10^{-11}$$

46. $NaX + H_2O \rightleftharpoons NaOH + HX$

HX is a weak acid, so NaX is a salt of weak acid and strong base.

Hydrolysis constant of NaX,

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}} = 1 \times 10^{-9}$$

Again, $K_h = \frac{h^2}{V} = Ch^2$

(where, h = degree of hydrolysis)

$$1 \times 10^{-9} = 0.1 \times h^2$$

$$h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8} \Rightarrow h = 1 \times 10^{-4}$$

% of degree of hydrolysis of NaX salt

$$= 1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01\%$$

47. In the required equation NH_3 is on LHS, so invert the equation (i)

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g); K_5 = \frac{1}{K_1} \quad \ldots(iv)$$

Moreover, there are three moles of H_2O, so multiply Eq. (iii) by 3

$$3H_2(g) + \frac{3}{2}O_2(g) \rightleftharpoons 3H_2O(g); K_6 = K_3^3 \quad \ldots(v)$$

(because when a reaction is multiplied by n, K becomes K^n).

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2$$

On adding Eqs. (iv), (ii) and (v) we get

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

$$K_4 = K_2 \times K_5 \times K_6$$

[because equilibrium constants are multiplied, when two or more reactions are added.]

On putting the values of K_5 and K_6, we get

$$K_4 = K_2 \cdot \frac{1}{K_1} \cdot K_3^3 = \frac{K_2K_3^3}{K_1}$$

48. At 330 K,

$$[H^+][OH^-] = K_w = 1 \times 10^{-13.6}$$

$$[H^+](10^{-4}\ M) = 1 \times 10^{-13.6}$$

$$[H^+] = \frac{1 \times 10^{-13.6}}{10^{-4}} = 10^{-9.6}$$

$$pH = -\log[H^+] = -\log(10^{-9.6}) = 9.6$$

49. % ionic character $= \frac{\mu_{observed}}{\mu_{calculated}} \times 100$

$$\mu_{observed} = 6.104 \times 10^{-30}\ Cm$$

$$\mu_{calculated} = e \times d$$

$$= 1.6 \times 10^{-19} C \times 9.17 \times 10^{-11} m$$

$$= 1.467 \times 10^{-29}\ Cm$$

$$\therefore \% \text{ ionic character} = \frac{6.104 \times 10^{-30}}{1.467 \times 10^{-29}} \times 100 = 41.6\%$$

50. pH = 1 $\therefore [H^+] = 10^{-1} = 0.1M$

pH = 2 $\therefore [H^+] = 10^{-2} = 0.01M$

For dilution of HCl, $M_1V_1 = M_2V_2$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10\ L$$

Volume of water to be added = 10 − 1 = 9 L

51. Concentration $= \frac{\text{mass}}{\text{molar mass} \times V\ (\text{mL})}$

$$\therefore [CH_3COOH] = \frac{5 \times 1000}{60 \times 500}$$

[Molar mass of CH_3COOH = 60 g mol^{-1}]

$$= 0.166\ M$$

Similarly, $[CH_3COONa] = \frac{7.5 \times 1000}{82 \times 500} = 0.183\ M$

For the buffer of CH_3COOH—CH_3COONa,

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= 4.76 + \log\left[\frac{0.183}{0.166}\right]$$

$$= 4.76 + \log(1.10)$$

$$= 4.76 + 0.042 = 4.80$$

$$\therefore 4.76 < pH < 5.0$$

52. (i) $\underset{s_1\ mol\ L^{-1}}{Hg_2Cl_2} \rightleftharpoons \underset{s_1}{Hg_2^{2+}} + \underset{2s_1}{2Cl^-}$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$= (s_1)(2s_1)^2 = s_1 \cdot 4s_1^2 = 4s_1^3$$

$$\therefore \text{Solubility, } s_1 = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

(ii) $\underset{s_2\ mol\ L^{-1}}{Cr_2(SO_4)_3} \rightleftharpoons \underset{2s_2}{2Cr^{3+}} + \underset{3s_2}{3SO_4^{2-}}$

$$K_{sp} = [Cr^{3+}]^2[SO_4^{2-}]^3 = (2s_2)^2(3s_2)^3$$

$$= 4s_2^2 \times 27s_2^3 = 108s_2^5$$

$$\therefore \text{Solubility, } s_2 = \left(\frac{K_{sp}}{108}\right)^{1/5}$$

(iii) $\underset{s_3\ mol\ L^{-1}}{BaSO_4} \rightleftharpoons \underset{s_3}{Ba^{2+}} + \underset{s_3}{SO_4^{2-}}$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (s_3)^2$$

$$\therefore \text{Solubility, } s_3 = (K_{sp})^{1/2}$$

(iv) $\underset{s_4\ mol\ L^{-1}}{CrCl_3} \rightleftharpoons \underset{s_4}{Cr^{3+}} + \underset{3s_4}{3Cl^-}$

$$K_{sp} = [Cr^{3+}][Cl^-]^3 = (s_4)(3s_4)^3 = 27s_4^4$$

$$\therefore \text{Solubility, } s_4 = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

53. 5.0×10^{-2} M NaOH $\equiv [OH^-] = 5 \times 10^{-2}$ M

$$[H^+][OH^-] = 1 \times 10^{-14}$$

$$[H^+] \cdot 5 \times 10^{-2} = 1 \times 10^{-14}$$

$$[H^+] = \frac{1 \times 10^{-14}}{5 \times 10^{-2}} = 2 \times 10^{-13}$$

$$pH = -\log[H^+] = -\log(2 \times 10^{-13})$$

$$= 12.69 \approx 12.70$$

54. We know that acidic strength $\propto K_a$ value.

Thus, on the basis of K_a value, order of acidic strength is

$HCN < HNO_2 < HF$

Conjugate base of a strong acid is weak.

Therefore, the order of base strength of conjugate base is

$F^- < NO_2^- < CN^-$

55. Let the degree of dissociation $= x$

	A	+	$2B$	$\rightleftharpoons$	$2C$	+	D
Initial concentration	1		1.5		0		0
At equilibrium	$(1-x)$		$(1.5-2x)$		$2x$		x

Given, $(1-x) = (1.5-2x)$

$$1 = 1.5 - 2x + x$$

$$1 = 1.5 - x$$

$$x = 1.5 - 1 = 0.5$$

Equilibrium constant for the reaction

$$K_C = \frac{[C]^2[D]}{[A][B]^2} = \frac{(2x)^2(x)}{(1-x)(1.5-2x)^2}$$

$\because$ $x = 0.5$

$$K_C = \frac{(2 \times 0.5)^2 (0.5)}{(1-0.5)(1.5-2\times 0.5)^2}$$

$$= \frac{(1) \times (0.5)}{(0.5)(0.5)^2} = \frac{0.5}{0.5 \times 0.25} = \frac{0.5}{0.125} = 4$$

56. Concentration of CO_3^{2-} ions $= 1.0 \times 10^{-4}$ M

For precipitation $K_{sp} \le [Ba^{2+}][CO_3^{2-}]$

Given, $K_{sp} = 5.1 \times 10^{-9}$

Hence, minimum concentration of Ba^{2+} ions should be

$$= \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}} = 5.1 \times 10^{-5} \text{ M}$$

57. $HQ = H^+ + Q^-$

$[H^+] = \sqrt{K_a C}$ by Ostwald's dilution law

$$[H^+] = 10^{-pH} = 10^{-3} \text{ M}$$

$$C = 0.1 \text{ M}$$

Thus, $10^{-3} = \sqrt{K_a \times 0.1}$ or $10^{-6} = K_a \times 0.1$

$\therefore$ $K_a = 1 \times 10^{-5}$

58. $Ca(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3OH^-(aq)$

$$\begin{array}{ccc} s & s & 3s \end{array}$$

$$K_{sp} = [Cr^{3+}][OH^-]^3$$

$$1.6 \times 10^{-30} = (s)(3s)^3$$

$$1.6 \times 410^{-30} = 27(s)^4$$

$$s^4 = \frac{\frac{1.6 \times 10^{-30}}{27}}{\sqrt[4]{\frac{1.6 \times 10^{-30}}{27}}}$$

59.

$$\begin{array}{lccccc} & HA & \rightleftharpoons & H^+ & + & A^- \\ \text{At } t=0 & 1 & & 0 & & 0 \\ \text{At } t=t & (1-10^{-5}) & & (10^{-5}) & & (10^{-5}) \end{array}$$

$$[A^+] = [H^+]$$

$$\Rightarrow \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[10^{-5}][10^{-5}]}{[1-10^{-5}]}$$

Since, $1 >>> 10^{-5}$, therefore, $(1-10^{-5}) \approx 1$

$\therefore$ $K_a = 1 \times 10^{-10}$

60. Only in reaction (ii) $H_2PO_4^-$, gives H^+ to H_2O, thus behaves as an acid.

61. $K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13}$

$$[Ag^+] = 0.05 \text{ M}$$

Moles of KBr $= 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$

Weight of KBr $= 1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

62. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = 10^{-4}$$

pOH = 4 and pH = 10

63. $K_{sp(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$

$$[Ba^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}}$$

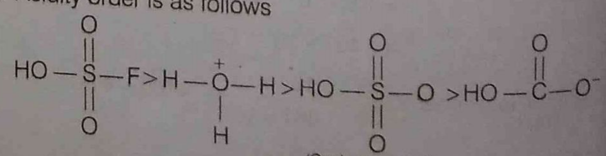
$$[Ba^{2+}] = 5.1 \times 10^{-5} \text{ M}$$

64. For salt of a weak acid and weak base,

$$pH = 7 + \frac{1}{2}[pK_a - pK_b] = 7 + \frac{1}{2}[4.80 - 4.78]$$

$$= 7 + \frac{1}{2}(0.02) = 7.01$$

65. Acidity order is as follows



(Conjugate anion) decreases acidity

66. From the aqueous buffered solution of HA, 50% HA is ionised.

$$[HA]=[A^-]$$

Buffer solution of weak acid

$$HA \longrightarrow \text{acidic buffer}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$= pK_a + \log 1$$

$$pH = pK_a = 4.5$$

$$pOH = pK_w - pH$$

$$pOH = 14 - 4.5 = 9.5$$

67. $AgIO_{3(s)} \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$

$$K_{sp} = [Ag^+][IO_3^-]$$

$$1.0\times10^{-8} = (s)(s)$$

$$1.0\times10^{-8} = s^2$$

$$s = \sqrt{1.0\times10^{-8}}$$

$$s = 1.0\times10^{-4}\ \text{mol/L}$$

In 1000 mL, moles of $AgIO_3$ dissolved $= 1\times10^{-4}$ moles

In 100 mL, moles of $AgIO_3$ dissolved $= 1\times10^{-5}$ moles

Mass of $AgIO_3$ in 100 mL $= 1\times10^{-5}\times283 = 2.83\times10^{-3}$ g

68.

$$MX_2 = \underset{S}{M^{2+}} + \underset{2S}{2X^-}$$

$$K_{sp} = [M^{2+}][X^-]^2$$

$$K_{sp} = (S)(2S)^2 = 4S^3$$

$$4S^3 = 4\times10^{-12}$$

$$S = 1\times10^{-4}\ M$$

$$M^{2+} = S = 1\times10^{-4}\ M$$

69. Loss of H^+ from an acid results in the formation of conjugate base.

$$OH^- \longrightarrow \underset{\text{conjugate base}}{O^{2-}} + H^+$$

70.

$$pH = -\log[H^+]$$

$$[H^+] = \text{antilog}[-pH] = \text{antilog}[5.4]$$

$$= \text{antilog}\,[1\times10^{-5.4}]$$

$$= 3.98\times10^{-6}\ M$$

71. HPO_4^{2-} is the conjugate base of $H_2PO_4^-$.

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

72. For the solute, $A_xB_y \rightleftharpoons xA + yB$

$$K_{sp} = x^x y^y (s)^{x+y}$$

Thus, $\quad M\times4 \rightleftharpoons M^{4+} + 4x^-$

$$x = 1,\ y = 4$$

$$K_{sp} = (1)^1\,(4)^4\,(s)^{(1+4)} = 256\,s^5$$

$$s = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

73. In 1×10^{-8} M HCl solution, H_2O is also present and undergoes self ionisation.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$[H^+] = 10^{-7}\ \text{M at } 25^\circ C$$

H^+ from HCl decreases self ionisation which decreases $[H^+]$ concentration, hence net concentration must be smaller than 10^{-7} M.

74. Basicity of a substance refers to their proton affinity.

The N-atom of NH_3 being smaller in size and more electron negative than P and S it can easily donates their electrons to the proton. Whereas O-atom of H_2O cannot donate their electrons easily, therefore, NH_3 possesses highest proton affinity.

75. $AB_2 \rightleftharpoons A^{2+} + 2B^-$

$$K_{sp} = [A^{2+}][B^-]^2$$

$$= (s)\,(2s)^2 = 4s^3$$

$$= 4(1\times10^{-5})^3$$

$$= 4\times10^{-15}$$

76. 0.005 M $(CH_3COO)_2Ca$

$$\underset{(0.005\ M)}{(CH_3COO)_2Ca} \longrightarrow Ca^{2+} + \underset{(2\times0.005\,=\,0.01)}{2CH_3COO^-}$$

$$[CH_3COO^-] = 0.01\ M$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \underset{\text{alkaline}}{OH^-}$$

$$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

$$= 7 + 2.37 + \frac{\log 0.01}{2}$$

$$= 7 + 2.37 - 1 = 8.37$$

77.

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^{2-} + OH^-$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$$

$\Rightarrow H_2PO_2^-$ is a conjugate base of H_3PO_3 which does not give, H^+. is a conjugate base of $H_2PO_3^-$ and does not undergo further ionization.

78. (a) $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = (s)\,(2s)^2 = 4s^3$$

79. NaCl is the salt of strong acid and strong base. It is not a buffer as aqueous solution of NaCl is itself an exact neutral solution.

Unit Test 2

(Physical Chemistry-I)

DAY 11

1. The free energy for the following reactions are as follows

$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l), \Delta G° = -1234\,kJ$

$C(s) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \Delta G° = -394\,kJ$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \Delta G° = -237kJ$

The standard free energy change for the following reaction is **[NCERT Exemplar]**

$H_2(g) + 2C(s) \rightarrow C_2H_2(g)$

(a) −209 kJ (b) −2259 kJ
(c) +209 kJ (d) +2259 kJ

2. In a closed insulated container, a liquid is stirred with a paddle to increase the temperature. Which of the following is true?

(a) $\Delta E + W \neq 0, q = 0$ (b) $\Delta E = 0,\ W = q \neq 0$
(c) $\Delta E = W = q \neq 0$ (d) $W = 0, \Delta E = q \neq 0$

3. The internal energy change when a system goes from state A to B is 40 kJ mol^{-1}. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy ?

(a) 40 kJ (b) > 40 kJ
(c) < 40 kJ (d) Zero

4. Which species possesses negative value of specific heat?

(a) Ice (b) Water
(c) Vapours (d) Saturated vapours

5. An ideal gas heat engine operates in Carnot cycle between 227°C and 127°C. It absorbs 6×10^4 cal of heat at high temperature. Amount of heat converted to work is

(a) 1.2×10^4cal (b) 4.8×10^4cal
(c) 6×10^4cal (d) 2.4×10^4cal

6. In evaporation of water, ΔH and ΔS are :

(a) +, + (b) +, −
(c) −, + (d) −, −

7. $A \longrightarrow B$, $\Delta H = +$ ve. Graph between $\log_{10} p$ and $\frac{1}{T}$ is a straight line of slope $\frac{1}{4.606}$. Hence, ΔH is

(a) 1 (b) 2
(c) 4 (d) −1

8. The heat of atomisation of $PH_3(g)$ is 228 kcal mol^{-1} and that of $P_2H_4(g)$ is 355 kcal mol^{-1}. The energy of the P—P bonds (in kcal) is

(a) 102 (b) 51
(c) 26 (d) 204

9. The difference between heats of reaction at constant pressure and constant volume for the reaction,

$$2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$$

at 25°C, in kJ, is

(a) −7.43 (b) +3.72
(c) −3.72 (d) +7.43

10. 1 mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95K) $\longrightarrow$ (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta E = 30.0$ L atm. The change in enthalpy (ΔH) of the process in L atm is

(a) 40.0 (b) 42.3
(c) 44.0
(d) not defined because pressure is not constant

11. $\Delta H_{vap} = 30$ kJ mol^{-1} and $\Delta S_{vap} = 75$ J mol^{-1} K^{-1}. Find temperature of vapours, at one atmosphere.

(a) 400 K (b) 350 K
(c) 298 K (d) 250 K

12. The polymerisation of ethene to linear polythene is represented by the reaction.

$$n(CH_2{=}CH_2) \longrightarrow -\!\!(CH_2{-}CH_2)\!\!-_n$$

Given that the average enthalpies of bond dissociation for C=C and C—C at 298 K are +590 and +331 kJ mol^{-1} respectively. The enthalpy of polymerisation per mole of ethene at 298 K, is

(a) 72 kJ (b) 27 kJ
(c) 1144 kJ (d) 172 kJ

13. When 1 mole of an ideal gas is compressed to half its initial volume and simultaneously heated to twice its initial temperature, the change in entropy (ΔS) is
(a) $C_V \ln 2$
(b) $C_p \ln 2$
(c) $R \ln 2$
(d) $(C_V - R)\ln 2$

14. The enthalpy changes of formation of the gaseous oxides of nitrogen (N_2O and NO) are positive because of
(a) the high bond energy of the nitrogen molecule
(b) the high electron affinity of oxygen atoms
(c) the high electron affinity of nitrogen atoms
(d) the tendency of oxygen to form O^{2-} ion

15. 1.0 g of pure calcium carbonate was found to require 50 mL of dilute HCl for complete reaction. The strength of the HCl solution is given by
(a) 0.2 N (b) 0.4 N
(c) 2.0 N (d) 4.0 N

16. What is the molarity of H_2SO_4 solution that has a density 1.84 g/cc at 35°C and contains solute 98% by weight?
(a) 4.18 M
(b) 1.84 M
(c) 8.41 M
(d) 18.4 M

17. The lowering in vapour pressure caused by the addition of 100 g of sucrose (molecular mass = 342) to 1000 g of lowering in water, if the vapour pressure of pure water at 25°C is 23.8 mm Hg, is
(a) 0.012 mm Hg (b) 0.125 mm Hg
(c) 1.15 mm Hg (d) 1.25 mm Hg

18. Two solutions of KNO_3 and CH_3COOH are prepared separately. Molarity of both is 0.1 M and their osmotic pressures are p_1 and p_2 respectively. The correct relationship between the osmotic pressures is
(a) $p_1 = p_2$ (b) $p_1 > p_2$
(c) $p_2 > p_1$ (d) $\frac{p_1}{p_1 + p_2} + \frac{p_2}{p_1 + p_2}$

19. The osmotic pressure of a 5% (w/V) solution of cane sugar at 150°C is
(a) 3.078 atm (b) 4.078 atm
(c) 5.078 atm (d) 2.45 atm

20. Which will show maximum depression in freezing point when concentration is 0.1 M?
(a) Urea (b) $BaCl_2$
(c) $Al_2(SO_4)_3$ (d) KBr

21. A 5% solution of sugar cane (mol wt. = 342) is isotonic with 1% solution of x. The mol. wt. of x is
(a) 34.2 (b) 68.4
(c) 136.2 (d) 171.2

22. In a saturated solution of the sparingly soluble strong electrolyte, $AgIO_3$ (molecular mass = 283) the equilibrium which sets in, is

$$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

If the solubility product constant, K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of the $AgIO_3$ contained in 100 mL of its saturated solution?
(a) 28.3×10^{-2} g (b) 2.83×10^{-3} g
(c) 1.0×10^{-7} g (d) 1.0×10^{-4} g

23. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.5 atm pressure. Ammonium hydrogen sulphate decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches at equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for the decomposition of NH_4HS at this temperature, is
(a) 0.11 (b) 0.17
(c) 0.18 (d) 0.30

24. For the reaction,
$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$; $K_c = 1.8 \times 10^{-6}$ at 184°C
($R = 0.00831$ kJ mol^{-1} K^{-1})

When K_p and K_c are compared at 184°C, it is found that
(a) whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure.
(b) $K_p = K_c$
(c) K_p is less than K_c
(d) K_p is greater than K_c

25. The pK_a for acid A is greater than pK_a for acid B. The strong acid is
(a) acid B (b) acid A
(c) Both A and B (d) Neither A nor B

26. Given pH of a solution A is 3 and it is mixed with another solution having pH 2. If both are mixed, resultant pH of the solution will be
(a) 3.2 (b) 1.9 (c) 3.4 (d) 3.5

27. For the reaction,
$CuSO_4 \cdot 5\,H_2O(s) \rightleftharpoons CuSO_4 \cdot 3\,H_2O(s) + 2\,H_2O\,(g)$
K_p at 298 K is 1.086×10^{-4} atm^2 and vapour pressure of water is 23.8 torr. The salt $CuSO_4 \cdot 5H_2O$ will be efforescent when the relative humidity is
(a) 80% (b) 60%
(c) 50% (d) less than 33.3%

28. The species, which acts as a Lewis acid but not a Bronsted acid is
(a) NH_2^- (b) O^{2-}
(c) BF_3 (d) OH^-

29. 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 the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost decrease in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

30. 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

(a) 0.0001% (b) 0.01%
(c) 0.1% (d) 0.15%

31. A sample of $Na_2CO_3 \cdot H_2O$ weighing 0.62 g is added to 100 mL of 0.1 N $(NH_4)_2SO_4$ solution. What will be the resulting solution?

(a) Acidic (b) Neutral
(c) Basic (d) None of these

32. At infinite dilution, the percentage ionisation for both strong and weak electrolyte is

(a) 1% (b) 20%
(c) 50% (d) 100%

33. A litre of solution is saturated with AgCl. To this solution if 1.0×10^{-4} moles of solid NaCl are added, what will be the $[Ag^+]$ assuming no volume change?

(a) More (b) Less
(c) Equal (d) Zero

34. Which hydroxide will have lowest value of solubility product at normal temperature (25°C)?

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

35. When solid potassium cyanide is added in water, the

(a) pH will increase
(b) pH will decrease
(c) pH will remain same
(d) electrical conductivity will not change

36. Heat obtained due to expansion of 1 mole of H_2 gas at 1000 K from 10 L to 100 L under isothermal reversible condition is absorbed by an engine having a sink at 300 K. Useful work obtained is

(a) – 1382 cal (b) – 3224 cal
(c) 1382 cal (d) 3224 cal

37. The enthalpy of hydrogenation of 1-pentene is + 126 kJ mol^{-1}. The enthalpy of hydrogenation of 1,3-pentadiene is + 230 kJ mol^{-1}. Hence, resonance (delocalisation) energy of 1,3-pentadiene is

(a) 22 kJ (b) 104 kJ
(c) 252 kJ (d) 11 kJ

38. An aqueous solution of liquid 'X' [mol. weight 56] 28% by weight has a vapour pressure 150 mm. Find the vapour pressure of 'X' if vapour pressure of water is 155 mm of Hg.

(a) 110 mm (b) 150 mm (c) 220 mm (d) 125 mm

39. A monoprotonic weak acid [HA] is ionised 5% in 0.1 M aqueous solution. What is equilibrium constant for its ionisation?

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

(a) 9.5×10^{-2} (b) 2.63×10^{-4}
(c) 2.303×10^{-3} (d) 5×10^{-3}

40. A buffer solution with pH 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 0.1 M NH_4OH. $[K_b = 1.8 \times 10^{-5}]$

(a) 3.4 (b) 2.6 (c) 1.5 (d) 1.9

Directions (Q. Nos. 41 to 43) *Aqueous calcium chloride solution is mixed with sodium oxalate and precipitate of calcium oxalate formed is filtered and dried. Its saturated solution was prepared and 250 mL of this solution was titrated with 0.001 M $KMnO_4$ solution, when 6.0 mL of this was required.*

41. Which is the indicator in the above titration?

(a) Methyl orange (b) Phenolphthalein
(c) Sulphuric acid (d) $KMnO_4$ itself

42. Number of moles of $KMnO_4$ required in this titration is

(a) 6.0×10^{-3} (b) 6×10^{-6}
(c) 250 (d) 2.5×10^{-1}

43. Number of moles of oxalate present in given saturated solution of calcium oxalate is

(a) 6×10^{-6} (b) 3×10^{-6} (c) 1.5×10^{-6} (d) 1.5×10^{-5}

Directions (Q. Nos. 44 and 45) *Iron metal is produced commercially by reducing iron (III) oxide in iron ore with carbon monoxide as follows*

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3\ CO_2(g)$$

	$Fe_2O_3(s)$	$CO(g)$	$Fe(s)$	$CO_2(g)$
ΔH_f (kJ/mol)	– 824.2	– 110.5	0	– 393.5
$\Delta S°$ (J/Kmol)	87.4	197.6	27.3	213.6

44. The standard free energy change for the reaction at 25°C, is

(a) + 15.0 kJ (b) – 29.3 kJ
(c) – 15.0 kJ (d) – 24.8 kJ

45. Mark out the correct statement(s).

(a) The reverse reaction becomes spontaneous at a lower temperature
(b) The reverse reaction becomes spontaneous at a higher temperature
(c) The reverse reaction is not spontaneous at any temperature
(d) None of the above

Directions (Q. Nos. 46 to 50) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation of Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

46. Statement I On mixing equal volumes of 1 M HCl and 2 M CH_3COONa, an acidic buffer solution is formed.

Statement II Resultant mixture contains CH_3COOH and CH_3COONa which are parts of acidic buffer.

47. Statement I The pH of a basic buffer mixture is given as

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{salt}]}$$

Statement II The pH of an acidic buffer mixture is given by

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

48. Statement I The pK_a of a weak acid becomes equal to pH of the solution at the mid point of its titration.

Statement II The molar concentrations of proton acceptor and proton donor become equal at the mid point of titration of a weak acid.

49. Statement I Heat of neutralisation is always less than zero.

Statement II Neutralisation involves reaction between an acid and a base.

50. Statement I The molality of the solution does not change with change in temperature.

Statement II The molality is expressed in units of moles per 1000 g of solvent.

Answer

1. (c)	**2.** (a)	**3.** (d)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (b)
11. (a)	**12.** (a)	**13.** (d)	**14.** (a)	**15.** (b)	**16.** (d)	**17.** (b)	**18.** (b)	**19.** (c)	**20.** (c)
21. (b)	**22.** (b)	**23.** (a)	**24.** (d)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (c)	**29.** (d)	**30.** (b)
31. (a)	**32.** (d)	**33.** (b)	**34.** (d)	**35.** (a)	**36.** (d)	**37.** (a)	**38.** (a)	**39.** (b)	**40.** (d)
41. (d)	**42.** (b)	**43.** (d)	**44.** (b)	**45.** (c)	**46.** (a)	**47.** (d)	**48.** (a)	**49.** (b)	**50.** (a)

Hints & Solutions

1. (a) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l), \quad \Delta G° = -123\,\text{kJ}$

(b) $C(s) + O_2(g) \longrightarrow CO_2(g), \quad \Delta G° = -394\,\text{kJ}$

(c) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \quad \Delta G° = -237\,\text{kJ}$

Add Eq. (b) + (c) and then subtract from (a), to get,

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g), \quad \Delta G° = -209\,\text{kJ}$$

2. For insulated container, $q = 0$.

3. In case of cyclic process, $\Delta E = 0$.

4. Specific heat of a substance reflects its ability to absorb heat energy. A negative value of specific heat shows that there is no absorption of heat. Therefore, specific heat of saturated vapours is negative.

5. $\eta = \frac{T_2 - T_1}{T_2} = \frac{500-400}{500} = \frac{1}{5}$

$$W = \eta \times Q = \frac{1}{5} \times 6 \times 10^4$$
$$= 1.2 \times 10^4$$

6. For evaporation of water energy is supplied to the system. Thus, it is an endothermic reaction. Hence, ΔH will be positive. But when water changes to vapour, its randomness increases. Thus, ΔS will be positive.

7. By Clapeyron – Clausius equation

$$\log p = -\frac{\Delta H}{2.303\,RT} + \text{constant}$$

$$\frac{\Delta H}{2.303\,R} = \frac{1}{4.606}$$

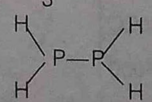
$$\Delta H = \frac{2.303 \times 2}{4.606} = 1\ \text{cal}$$

8. Bond dissociation energy of

$$PH_3(g) = 228\ \text{kcal mol}^{-1}$$

$$\text{P–H bond energy} = \frac{228}{3} = 76\,\text{kcal mol}^{-1}$$

P_2H_4



Bond energy of

$$4\,(P—H) + (P—P) = 355 \text{ kcal mol}^{-1}$$

$$4 \times 76 + (P—P) = 355 \text{ kcal mol}^{-1}$$

$$\therefore \quad P—P \text{ bond energy} = 51 \text{ kcal mol}^{-1}$$

9. $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta n_g = 12 - 15 = -3$$

$$\Delta H - \Delta E = -3 \times 8.314 \times 298 = -7.43 \text{ kJ}$$

10. $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta n_g = 1 \text{ mol},$$

$$\Delta T = 245 - 95 = 150 \text{ K}$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$\Delta E = 30.0 \text{ L atm}$$

$$\Delta H = 30 + 1 \times 0.0821 \times 150 = 42.3 \text{ L atm}$$

11. $\Delta H_{vap} = 30 \text{ kJ/mol} = 30 \times 10^3 \text{ J mol}^{-1}$

$$\Delta S_{vap} = 75 \text{ J mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 0,$$

$$\therefore \quad \Delta H = T\Delta S$$

$$30 \times 10^3 = T \times 75$$

$$T = \frac{30 \times 10^3}{75} = 400 \text{ K}$$

12. In this polymerisation reaction, every molecule of ethene involves breaking of one C ═ C (double bond) and formation of two C—C single bonds.

The amount of energy required to break one mole of $>C{=}C<$ (double bond) into C— C (single bond) = 590 kJ.

The energy released in the formation of two moles of C—C single bond = $2 \times 331 = 662$ kJ

Net energy released per mole of ethene = $662 - 590 = 72$ kJ

Enthalpy of polymerisation per mole of ethene at 298 K,

$$\Delta H = 72 \text{ kJ mol}^{-1}$$

13. When there is simultaneously change in temperature and volume (or pressure)

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

$$= C_V \ln\left(\frac{2}{1}\right) + R\ln\frac{1}{2}$$

$$= C_V \ln 2 - R\ln 2 = (C_V - R)\ln 2$$

14. The enthalpy changes of formation of the gaseous oxides of nitrogen are positive due to high bond energy of the nitrogen molecule.

15. Meq. of HCl = M eq. of $CaCO_3$

$$N \times 50 = \frac{1}{50} \times 1000$$

$$N = \frac{1 \times 1000}{50 \times 50} = 0.4\text{N}$$

16. (*d*) 98% H_2SO_4 means 98 g H_2SO_4 in 100 g solution.

$$\text{Volume of solution} = \frac{100}{1.84} \text{ cc} = 54.3 \text{ cc}$$

$$\text{Molarity} = \frac{1}{54.3} \times 1000 = 18.4 \text{ M}$$

17. Molecular mass of sucrose = 342

$$\text{Moles of sucrose} = \frac{100}{342} = 0.292 \text{ mol}$$

$$\text{Moles of water } (N) = \frac{1000}{18} = 55.5 \text{ mol}$$

Vapour pressure of pure water $p° = 23.8$ mm Hg

$$\frac{\Delta p}{p°} = \frac{n}{n+N}$$

$$\frac{\Delta p}{23.8} = \frac{0.292}{0.292 + 55.5}$$

$$\Delta p = \frac{23.8 \times 0.292}{55.792} = 0.125 \text{ mm Hg}$$

18. KNO_3 dissociates completely while CH_3COOH dissociates to a smaller extent, hence $p_1 > p_2$.

19. $C = \frac{5 \times 1000}{342 \times 100} = \frac{50}{342} \text{mol L}^{-1}$

$$\pi = \frac{50}{342} \times 0.082 \times 423 = 5.07 \text{ atm}$$

20. $KBr = K^+ + Br^- = 2$ ions

$$BaCl_2 = Ba^{2+} + 2\,Cl^- = 3 \text{ ions}$$

$$Al_2(SO_4)_3 = 2Al^{3+} + 3SO_4^{2-} = 5 \text{ ions}$$

Urea is not ionise.

Hence, $Al_2(SO_4)_3$ shows maximum depression in freezing point.

21. For isotonic solutions,

$$\frac{w_1}{m_1} = \frac{w_2}{m_2}$$

$$\frac{5}{342} = \frac{1}{m_2}$$

$$m_2 = 68.4$$

22. $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$

Let solubility of $AgIO_3$ be S.

$$K_{sp} = [Ag^+]\,[IO_3^-]$$

$$\Rightarrow \quad 1.0 \times 10^{-8} = S^2 \text{ or } S = 1 \times 10^{-4} \text{ mol L}^{-1}$$

In 1000 mL, moles of $AgIO_3$ dissolved = 1×10^{-4} mol.

In 100 mL, moles of $AgIO_3$ dissolved = 1×10^{-5} mol

Mass of $AgIO_3$ in 100 mL,

$$= 1 \times 10^{-5} \times 283 = 2.83 \times 10^{-3}$$

23. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

	$NH_4HS(s)$	$NH_3(g)$	$H_2S(g)$
Initially	1	0.5	0
At equilibrium		$(0.5 + x)$	x

Total pressure at equilibrium

$$= p_{NH_3} + p_{H_2S} = 0.5 + x + x = 0.84$$
$$x = 0.17 \text{ atm}$$
$$p_{NH_3} = 0.50 + 0.17 = 0.67 \text{ atm}$$
$$p_{H_2S} = 0.17 \text{ atm}$$
$$K_p = p_{NH_3} \cdot p_{H_2S}$$
$$= 0.67 \times 0.17 = 0.114 \text{ atm}$$

24. $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$$K_c = 1.8 \times 10^{-6} \text{ at } 184°C \ (= 457 \text{ K})$$
$$R = 0.00831 \text{ kJ mol}^{-1} \text{ K}^{-1}$$
$$K_p = K_c (RT)^{\Delta n_g}$$

where, Δn_g = gaseous products − gaseous reactants

$$= 3 - 2 = 1$$
$$K_p = 1.8 \times 10^{-6} \times 0.00831 \times 457 = 6.836 \times 10^{-6}$$

Thus, $K_p > K_c$

25. B is strong because those acids which have lower pK_a value, are strong.

26. pH of the solution $A = 3$

$$[H^+]_A = 10^{-3} \text{ M}$$

pH of the solution $B = 2$

$$[H^+]_B = 10^{-2} \text{ M}$$
$$[H^+] = 10^{-3} + 10^{-2} = 11 \times 10^{-3}$$
$$\text{pH} = -\log (11 \times 10^{-3})$$
$$= 3 - \log 11 = 3 - 1.04 = 1.9$$

27. An efflorescent salt is one that loses water to the atmosphere. This will occur if in the equilibrium water vapour pressure, with the salt is greater than the water vapour pressure in the atmosphere. For the given hydrated salt, equilibrium is

$$CuSO_4 \cdot 5H_2O\,(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O\,(g)$$
$$K_p = p^2_{H_2O} = 1.086 \times 10^{-4} \text{ atm}^2$$
$$\therefore \quad p_{H_2O} = 1.042 \times 10^{-2} \text{ atm} = 7.92 \text{ torr}$$

Since, p_{H_2O} is less than the vapour pressure of water in air at the same temperature, $CuSO_4 \cdot 5\,H_2O$ will not always effloresce. It will effloresce only on a dry day, when the partial pressure of moisture in the air is less than 7.92 torr.

Relative humidity $= \dfrac{7.92}{23.8} = 0.333 = 33.3\%$

Thus, this salt will effloresce when the relative humidity is less than 33.3%.

28. BF_3 acts as Lewis acid but not as a Bronsted acid.

29. Aspirin is a weak acid. Due to common ion effect, it is unionised in acid medium but completely ionised in alkaline medium.

30. $X^- + H_2O \rightleftharpoons HX + OH^-$

$$K_h = \frac{10^{-14}}{10^{-5}}$$

So, $$x = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$$
$$= 100 \times 10^{-4} = 10^{-2} = 0.01$$

So, degree of hydrolysis = 0.01%.

31. Gram equivalent of $(NH_4)_2SO_4 = \dfrac{100}{1000} \times \dfrac{1}{10} \times 66 = 0.66$

Gram equivalent of $Na_2CO_3 \cdot H_2O = \dfrac{0.62}{62} = 0.01$

Left $(NH_4)_2SO_4 = 0.66 - 0.01 = 0.65$

Since, $(NH_4)_2SO_4$ is a salt of strong acid and weak base therefore solution will be acidic in nature.

32. According to Ostwald's dilution law,

degree of ionisation $\propto$ dilution

$\therefore$ at infinite dilution, strong and weak both electrolytes will be 100% ionised.

33.
$$\begin{array}{lccc} & AgCl \longrightarrow & Ag^+ & + \ Cl^- \\ & & x & x \\ \text{after adding NaCl} & & x & x + 1 \times 10^{-4} \end{array}$$

$[Ag^+]$ decreases due to common ion effect.

34. $Be(OH)_2$ has lowest solubility and hence, lowest solubility product.

35. $KCN + H_2O \rightleftharpoons KOH + HCN$;

KOH is a strong base and HCN is a weak acid, due to which solution will be basic in nature. Therefore, pH of the solution will increase.

36. $-W = q = 2.303\ nRT \log \dfrac{V_2}{V_1}$

$$= 2.303 \times 1 \times 2 \times 1000 \log \frac{100}{10} = 4606 \text{ cal}$$
$$\eta = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2} \quad \text{or} \quad 1 - \frac{T_1}{T_2} = 1 - \frac{q_1}{q_2}$$
$$\text{or} \quad \frac{T_1}{T_2} = \frac{q_1}{q_2} \quad \text{or} \quad \frac{300}{1000} = \frac{q_1}{4606}$$
$$q_1 = 1381.8 = 1382 \text{ cal}$$
$$W = q_2 - q_1 = 4606 - 1382 = 3224 \text{ cal}$$

37. $CH_2{=}CHCH_2CH_2CH_3 + H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3$;

$$\Delta H = 126 \text{ kJ mol}^{-1}$$

$CH_2{=}CHCH{=}CHCH_3 + 2H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3$;

$$\Delta H = 230 \text{ kJ mol}^{-1}$$

Theoretical value of hydrogenation of two [C=C] bonds = 252 kJ mol^{-1}

Thus, resonance energy = 252 − 230 = 22 kJ

38. According to Raoult's law for liquid mixtures,

$$p_t = p°_A + p°_B$$
$$\therefore \quad p_t = p°_A \times \left[\frac{\dfrac{w_A}{M_A}}{\dfrac{w_A}{M_A} + \dfrac{w_B}{M_B}}\right] + p°_B \times \left[\frac{\dfrac{w_B}{M_B}}{\dfrac{w_A}{M_A} + \dfrac{w_B}{M_B}}\right]$$

Given that, $w_A = 28\,g$, $w_{H_2O} = 72\,g$ $p_A^\circ = ?$

$p_{H_2O} = 155$, $M_A = 56\,g$, $M_{H_2O} = 18\,g$

and $p_s = 150$ mm

$$\therefore \quad 150 = p_A^\circ \times \left[\frac{\frac{28}{56}}{\frac{28}{56}+\frac{72}{18}}\right] + 155 \times \left[\frac{\frac{72}{18}}{\frac{28}{56}+\frac{72}{18}}\right]$$

$$150 = p_A^\circ \times \frac{1}{2} \times \frac{2}{9} + 155 \times 4 \times \frac{2}{9}$$

$$\therefore \quad p_A^\circ = 110 \text{ mm}$$

39. $H_2O(l)$ is taken as pure liquid, hence is not included in equilibrium.

	$HA(aq) + H_2O(l)$	$\rightleftharpoons H_3O^+(aq)$	$+ A^-(aq)$
Initial	0.1 M	0	0
Equilibrium	$-\frac{0.1\times5}{100}$	$+\frac{0.1\times5}{100}$	$+\frac{0.1\times5}{100}$
Conc.	0.095 M	0.005 M	0.005 M

$$K_c = \frac{[H_3O^+][A^-]}{[HA]} = \frac{0.005 \times 0.005}{0.095} = 2.63 \times 10^{-4}$$

40. $pOH = -\log K_b + \log\left[\frac{\text{salt}}{\text{acid}}\right]$

$$pOH = -\log[1.8\times10^{-5}] + \log\left[\frac{\text{salt}}{1.0}\right]$$

$$5 = 4.7 + \log\left[\frac{\text{salt}}{1.0}\right]$$

$$\therefore \quad \log\left[\frac{\text{salt}}{1.0}\right] = 5 - 4.7 = 0.3$$

$$\left[\frac{\text{salt}}{1.0}\right] = \text{antilog } 0.3$$

$$[\text{salt}] = 1.9$$

41. MnO_4^- (after complete oxidation of $C_2O_4^{2-}$) imparts its own colour.

42. Millimoles of $KMnO_4 = MV = 0.001 \times 6 \times 10^{-3} = 6 \times 10^{-6}$

43. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

Moles of $C_2O_4^{2-} \equiv \frac{5}{2}$ moles of MnO_4^-

$$= 6 \times 10^{-6} \times \frac{5}{2} = 1.5 \times 10^{-5}$$

44. $\Delta H^\circ = [2\Delta H^\circ_{f(Fe)} + 3\Delta H^\circ_{f(CO_2)}] - [\Delta H^\circ_{f(Fe_2O_3)} + 3\Delta H^\circ_{f(CO)}]$

$$= [2(0) + 3(-393.5)] - [1\times(-824.2) + 3(-110.5)]$$

$$= -24.8 \text{ kJ}$$

and $\Delta S^\circ = [2S^\circ_{(Fe)} + 3S^\circ_{(CO_2)}] - [S^\circ_{(Fe_2O_3)} + 5S^\circ_{(CO)}]$

$$= [(2\times27.3) + (3\times213.6)] - [(1\times87.4) + (3\times197.6)]$$

$$= +15.0 \text{ J/K} = 15 \times 10^{-3} \text{ kJ/K}$$

$$\therefore \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -24.8 - 298 \times 15 \times 10^{-3} = -29.3 \text{ kJ}$$

45. On reversing the reaction, ΔH° becomes positive and ΔS° becomes negative. Therefore, ΔG° becomes positive. Hence, the reaction is not spontaneous at any temperature.

46. Statement II is the correct explanation of statement I.

47. For basic buffer, $pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$

and for acidic buffer, $pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

48. Statement II is the correct explanation of statement I.

49. Heat of neutralisation refers to the amount of heat liberated in the combination of H^+ and OH^- ions in the solution to form one mole of water.

50. Statement II is the correct explanation of statement I.

Day 12

Oxidation and Reduction

Concepts of Oxidation *and* Reduction

Loss of electron by an atom is called oxidation or de-electronation while gain of electron by an atom is called reduction or electronation.

Oxidants or Oxidising Agents are the substances which

(i) oxidise other,
(ii) get reduced,
(iii) gain electrons (*i.e.*, their oxidation number decreases during a reaction)

Reductants or Reducing Agents are the substances which

(i) reduce others,
(ii) get oxidised,
(iii) loss electrons (*i.e.*, their oxidation number increases during a reaction)

Some Important Oxidants

1. Molecules of most electronegative elements such as O_2, O_3, halogens.
2. Oxides of metals and non-metals such as MgO, CaO, CrO_3, H_2O, CO_2 etc.

3. The compounds having either of an element in their highest oxidation state such as $K_2Cr_2O_7$, $KMnO_4$, $HClO_4$, H_2SO_4, HNO_3, $FeCl_3$, $HgCl_2$, $KClO_3$ etc.

Permanganate ion acts as strong oxidising agent and in acidic medium it always produces 5 electrons per formula unit irrespective of the reducing agent.

Some Important Reductants

1. All metals such as Na, Al, Zn etc., and some non-metals, *e.g.*, C, S, P, H_2 etc.
2. Metallic hydrides such as NaH, LiH, KH, CaH_2 and halogen acids such as HCl, HBr, HI.
3. The compounds having either of an element in their lowest oxidation state such as $H_2C_2O_4$, $FeSO_4$, Hg_2Cl_2, Cu_2O, $SnCl_2$ etc.

Equivalent weights of Oxidizing Agent (*OA*) or Reducing Agent (RA)

$$= \frac{\text{Molar mass of OA / RA agent}}{\text{Number of electrons lost or gained per formula unit of RA / OA}}$$

H_2O_2 is both oxidising and reducing agent but its equivalent weight as either oxidising or reducing agents are the same, i.e., 17.

Oxidation Number

The real or imaginary charge, which an atom appears to have in its combined state is called oxidation number of that atom.

- *Valency of an element is always a whole number. It can neither be zero nor fractional. While oxidation number may be positive or negative. It can be zero or fractional.*
- *Fractional oxidation state is only the average oxidation state of an element when two or more of its atoms are present in different oxidation states in a given compound.*

Rules for Assigning Oxidation Number

The oxidation number of an element or atom can be calculated with the help of following rules

(i) The oxidation number of an element in its elementary state is zero.

(ii) Oxidation number of an ion is equal to the electrical charge present on it.

(iii) Oxidation number of a compound is zero.

(iv) Oxidation number of fluorine is always −1 in all of its compounds.

(v) The oxidation number of alkali metals is always +1 and those of alkaline earth metals is +2.

(vi) Oxidation number of hydrogen is +1 except in ionic hydrides, where it is −1.

(vii) Two oxidation numbers of N are −3 and +3, when it is bonded with less electronegative and more electronegative atoms respectively.

(viii) Oxidation number of oxygen is −2 except in $OF_2(+2)$, $O_2F_2(+1)$, peroxides (−1) and superoxides (−1/2).

(ix) The oxidation number of halogens is always −1 in metal halides.

(x) In interhalogen compounds, the more electronegative of the two halogens gets the oxidation number of −1.

Oxidation number of metals in amalgams and carbonyls for e.g., $[Fe(CO)_5]$ is zero.

Redox Reactions

The reaction, which involves oxidation and reduction as its two half reactions is called **redox reaction.** *A redox change occurs simultaneously.*

Types of Redox Reactions

These are of three types as follows

1. **Intermolecular Redox Reactions**

Which involve the reaction between two substances, one of them is oxidant and other is reductant, e.g.,

$$\underset{\text{reductant}}{10FeSO_4} + \underset{\text{oxidant}}{2KMnO_4} + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

These are further divided into two types

(i) **Combination reactions** in which two atoms or molecules (in their zero oxidation state) combine together and one gets oxidised while the other gets reduced.

$$\underset{\text{reductant}}{\overset{0}{C}} + \underset{\text{oxidant}}{\overset{0}{O_2}} \longrightarrow \overset{+4\ -2}{CO_2}$$

(ii) **Displacement reactions** in which an atom or ion in a compound is replaced by an atom or ion. These are further of two types

Metal displacement reactions in which metal is displaced.

$$\underset{\text{oxidant}}{CuSO_4} + \underset{\text{reductant}}{Zn} \longrightarrow Cu + ZnSO_4$$

Non-metal displacement reactions in which non-metal is displaced.

$$\underset{\text{reductant}}{2Na} + \underset{\text{oxidant}}{2H_2O} \longrightarrow 2NaOH + H_2$$

2. **Intramolecular Redox Reactions**

Which involve oxidation of one element of a compound as well as reduction of other element of the same compound. Decomposition reactions are also intramolecular redox reactions, but to be a redox reaction, it is essential that one of the products of decomposition must be in the elemental state. *e.g.*,

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

3. **Autoredox** or **Disproportionation Reactions**

Which involves oxidation and reduction of the same element, *e.g.*, $Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^{-1} + H_2O$

Balancing of Redox Reactions

Redox reactions can be balanced through

1. ion electron method
2. oxidation number method.

1. Ion Electron Method

The method involves the following steps

- Write redox reaction in ionic form.
- Split redox reaction into oxidation half and reduction half reactions.
- Balance atoms of each half-reactions by using simple multiples.
- For balancing H and O, add H^+ ion and H_2O to the appropriate sides, similarly add OH^- and H_2O to the appropriate sides.
- Balance the charge on both the sides and multiply one or both half-reactions by suitable number to equalise number of electrons in both equations.
- Add the two balance half-reactions and cancel common terms.

2. Oxidation Number Method

The method involves the following steps

- Assign oxidation number to the atoms in the equation and write separate equations for atoms undergoing oxidation and reduction.
- Find the change in oxidation number in each equation and make the change equal in both the equations by multiplying with suitable integers.
- After adding both the equations complete the balancing (by balancing H and O).

Redox Titrations

The redox titrations is a type of titration based on a redox reaction between the analyte and titrant. Redox titration may involve the use of a redox indicator and/or a potentiometer.

Types of Redox Titrations

The different types of redox titrations are given below

1. **Potassium Permanganate Titrations**

In which reducing agents like $FeSO_4$, Mohr's salt $[(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O]$, H_2O_2, As_2O_3, oxalic acid $(COOH)_2$ etc, are directly titrated against $KMnO_4$ in acidic medium. *e.g.*,

$$\underset{\text{ferrous ion}}{5Fe^{2+}} + \underset{\text{permanganate ion}}{MnO_4^-} + 8H^+ \longrightarrow \underset{\text{ferric ion}}{5Fe^{3+}} + Mn^{2+} + 4H_2O$$

In these titrations, $KMnO_4$ is self-indicator.

2. **Potassium Dichromate Titrations**

In which, the same reducing agents listed above are directly titrated against $K_2Cr_2O_7$ in acidic medium, *e.g.*,

$$\underset{\text{ferrous ion}}{6Fe^{2+}} + \underset{\text{dichromate ion}}{Cr_2O_7^{2-}} + 14H^+ \longrightarrow 2Cr^{3+} + \underset{\text{ferric ion}}{6Fe^{3+}} + 7H_2O$$

In this case, diphenylamine is the indicator.

3. **Ceric Sulphate Titrations**

In which, the reducing agents are directly titrated against $Ce(SO_4)_2$, *e.g.*,

$$\underset{\text{ferrous ion}}{Fe^{2+}} + \underset{\text{ceric ion}}{Ce^{4+}} \longrightarrow \underset{\text{ferric ion}}{Fe^{3+}} + \underset{\text{cerous ion}}{Ce^{3+}}$$

The indicators used are diphenyl amine or diphenylbenzidine.

4. **Sodium Thiosulphate Titrations**

In which sodium thiosulphate is a reducing agent and titrated against iodine. *These are of two types*

(i) **Iodimetric Titrations** which involves direct use of iodine as the oxidising agent, using starch as an indicator, *e.g.*,

$$I_2 + \underset{\text{thiosulphate ions}}{2S_2O_3^{2-}} \longrightarrow 2I^- + \underset{\text{tetrathionate ions}}{S_4O_6^{2-}}$$

(ii) **Iodometric Titrations** in which oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$ etc are treated with KI. In this reaction, I_2 is liberated quickly, which is titrated against sodium thiosulphate solution using starch as an indicator, *e.g.*,

$$\underset{\text{permanganate ion}}{2MnO_4^-} + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + \underset{\text{iodine}}{5I_2} + 8H_2O$$

- *The equivalence point (end point) refers the condition where equivalents of one species react with same number of equivalents of other species.*
- *If oxidation of KI with H_2O_2 (in acidic medium) is carried out in presence of limited amount of $Na_2S_2O_3$, the produced I_2 gives blue colour with starch like an alarm. The reaction is known as clock reaction.*

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

These reactions are used to study the rates of redox reactions.

Practice Zone

DAY 12

1. The oxidation numbers of phosphorus in $Ba(H_2PO_2)_2$ and xenon in Na_4XeO_6 are respectively

(a) +3 and +4
(b) +2 and +6
(c) +1 and +8
(d) −1 and −6

2. In which of the following pairs, there is greatest difference in the oxidation number of the underlined elements?

(a) $\underline{N}O_2$ and $\underline{N}_2O_4$
(b) $\underline{P}_2O_5$ and $\underline{P}_4O_{10}$
(c) $\underline{N}_2O$ and $\underline{N}O$
(d) $\underline{S}O_2$ and $\underline{S}O_3$

3. Nitric oxide acts as a reducing agent in the reaction

(a) $4NH_3 + 5O_2 \longrightarrow 2NO + 6H_2O$
(b) $2NO + 3I_2 + 4H_2O \longrightarrow 2NO_3^- + 6I^- + 8H^+$
(c) $2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$
(d) $2NO + H_2S \longrightarrow N_2O + S + H_2O$

4. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is not correct in this respect? **[NCERT Exemplar]**

(a) The oxidation number of hydrogen is always +1.
(b) The algebraic sum of all the oxidation numbers in a compound is zero.
(c) An element in the free or the uncombined state bears oxidation number zero.
(d) In all its compounds, the oxidation number of fluorine is −1.

5. Which of the following is not a reducing agent?

(a) SO_2
(b) H_2O_2
(c) CO_2
(d) NO_2

6. Amongst the following, identify the species with an atom in +6 oxidation state.

(a) MnO_4^-
(b) $Cr(CN)_6^{3-}$
(c) NiF_6^{2-}
(d) CrO_2Cl_2

7. In standardisation of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is

(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as molecular weight

8. The oxidation number of sulphur in S_8, S_2F_2 and H_2S respectively are

(a) 0, +1 and −2
(b) +2, +1 and −2
(c) 0, + 1 and + 2
(d) −2, + 1 and − 2

9. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

10. $C_2H_6(g) + nO_2 \longrightarrow CO_2(g) + H_2O(l)$

In this equation, ratio of the coefficients of CO_2 and H_2O is

(a) 1 : 1
(b) 2 : 3
(c) 3 : 2
(d) 1 : 3

11. Which of the following is a redox reaction?

(a) Formation of glucose from CO_2 and water
(b) Reaction of potassium cyanide with silver cyanide
(c) Hydration of rubidium
(d) Reaction of barium chloride with sulphuric acid

12. In which of the following, the oxidation number of oxygen has been arranged in increasing order?

(a) $BaO_2 < KO_2 < O_3 < OF_2$
(b) $OF_2 < KO_2 < BaO_2 < O_3$
(c) $BaO_2 < O_3 < OF_2 < KO_2$
(d) $KO_2 < OF_2 < O_3 < BaO_2$

13. In the reaction,

$$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

(a) bromine is oxidised and the carbonate radical is reduced
(b) bromine is reduced and the carbonate radical is oxidised
(c) bromine is neither reduced nor oxidised
(d) bromine is both reduced and oxidised

14. In a reaction, 4 mole of electrons are transferred to 1 mole of HNO_3. The possible product obtained due to reduction is

(a) 0.5 mole of N_2 (b) 0.5 mole of N_2O
(c) 1 mole of NO_2 (d) 1 mole of NH_3

15. The oxidation numbers of phosphorus varies from

(a) −1 to +1 (b) −3 to +3
(c) −3 to +5 (d) −5 to +1

16. Reaction, $2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$,

is used for commercial preparation of bromine from its salts. Suppose we have 50 mL of a 0.06 M solution of NaBr. What volume of a 0.05 M solution of Cl_2 is needed to react completely with the Br^- ?

(a) 50 mL (b) 1200 mL
(c) 30 mL (d) 60 mL

17. The equivalent weight of $Na_2S_2O_3$ in the reaction,

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

is

(a) M (b) $M/8$
(c) $M/0.5$ (d) $M/2$

18. What will be the value of the equivalent weight of $KBrO_3$ in the following equation

$$2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O$$

(a) $M/4$ (b) $M/6$
(c) $M/10$ (d) $M/5$

19. The compound that can work both as an oxidising as well as reducing agent is

(a) $KMnO_4$ (b) H_2O_2
(c) $Fe_2(SO_4)_3$ (d) $K_2Cr_2O_7$

20. In which of the following reactions, hydrogen is acting as an oxidising agent ?

(a) With iodine to give hydrogen iodide
(b) With lithium to give lithium hydride
(c) With nitrogen to give ammonia
(d) With sulphur to give hydrogen sulphide

21. In which of the following compounds, an element exhibits two different oxidation states? **[NCERT Exemplar]**

(a) NH_2OH (b) NH_4NO_3
(c) N_2H_4 (d) N_3H

22. When SO_2 is passed through an acidified solution of potassium dichromate, the oxidation state of S changes from

(a) +4 to 0 (b) +4 to +2
(c) +4 to +6 (d) +6 to +4

23. In which of the compounds does manganese exhibit highest oxidation number?

(a) MnO_2 (b) Mn_3O_4
(c) K_2MnO_4 (d) $MnSO_4$

24. When the following half-reaction is balanced

$$CN^- \longrightarrow CNO^-$$

Which of the following statements is true regarding the balance half-reaction?

(a) carbon is losing two electrons per atom
(b) oxidation number of carbon increases from +1 to +3
(c) oxidation number of nitrogen remains constant
(d) statements (a) and (c) both are true

25. The equivalent weights of $KMnO_4$ in an acidic, a neutral and an alkaline medium are respectively (Molecular wt. of $KMnO_4 = 158$)

(a) 31.60, 79, 158 (b) 31.60, 52.67, 79
(c) 31.60, 52.67, 158 (d) 52.67, 158, 31.60

26. A particular acid rain water has SO_3^{2-}. If a 25 mL sample of this water requires 34.08 mL of 0.01964 M $KMnO_4$ for this titration, what is the molarity of SO_3^{2-} in acid rain?

(a) 0.0669 (b) 0.0267
(c) 0.1339 (d) 0.669

27. Cericammonium sulphate and potassium permanganate are used as oxidising agents in acidic medium for oxidation of ferrous ammonium sulphate to ferric sulphate. The ratio of number of moles of orceric ammonium sulphate required per mole of ferrous ammonium sulphate to the number of potassium permaganate required per mole of ferrous ammonium sulphate, is

(a) 5.0 (b) 0.2
(c) 0.6 (d) 2.0

Directions (Q. Nos. 28 to 30) *Oxidation involves loss of electrons while reduction involves gain of electrons. In a redox reaction reductant is oxidised to lose electrons. These electrons are taken up by an oxidant to get itself reduced. Oxidation-reduction occur simultaneously. The redox reactions are of three types.*
These are intermolecular, intramolecular and disproportionation reactions. In a conjugate pair of redox, the one having higher oxidation number acts as oxidant and other is its conjugate reductant.

28. The reaction,

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

is an example of reaction of

(a) disproportionation (b) intermolecular redox
(c) intramolecular redox (d) None of these

29. Two moles of N_2H_4 loses twenty moles of electrons to form 2 moles of a new compound X. If all the nitrogens are present in new compound and there is no change in oxidation number of hydrogen, the oxidation state of nitrogen in X will be

(a) −7 (b) −3
(c) +3 (d) +7

30. The oxidation number of four sulphur atoms in tetrathionate ion are
(a) 2.5, 2.5, 2.5, 2.5 (b) 5, 0, 0, 5
(c) 3, 2, 2, 3 (d) 4, 1, 1, 4

Directions *(Q. Nos. 31 and 32) $KMnO_4$ and $K_2Cr_2O_7$ are widely used as volumetric reagents for analytical estimation of iron, hydrogen peroxide, iodide, ozone, sulphite, nitrite etc. Reaction is carried out in acidic medium.*

31. Equivalents of MnO_4^- and $Cr_2O_7^{2-}$ per mol of the ion in acidic medium are in the ratio of
(a) 1 : 1 (b) 1 : 5 (c) 6 : 1 (d) 5 : 6

32. 5.5 g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ required 5.4 mL of 0.1 N $KMnO_4$ solution for complete oxidation. The mole of hydrated ferric sulphate present in the mixture is
(a) 9.5×10^{-3} mol (b) 9.7×10^{-2} mol
(c) 0.53×10^{-3} mol (d) 19×10^{-3} mol

Directions *(Q. Nos. 33 to 36) Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. Statement I Oxidation number of chromium in CrO_5 is + 6.
Statement II Oxidation number of each oxygen atom is –1.5.

34. Statement I 1 mole of FeC_2O_4 is oxidised by 0.6 mole of MnO_4^- in acidic medium.
Statement II MnO_4^- oxidises both Fe^{2+} as well as $C_2O_4^{2-}$.

35. Statement I Bleaching action of SO_2 is temporary. whereas bleaching action of Cl_2 is permanent.
Statement II Bleaching by SO_2 and Cl_2 is due to oxidation.

36. Statement I Conversion of black lead painting is made to white by the action of H_2O_2.
Statement II Sulphur is oxidised to SO_4^{2-}.

37. Six moles of Cl_2 undergo a loss and gain of 10 moles of electrons to form two oxidation states of Cl in an autoredox change. What are the two oxidation states of Cl in this change?
(a) +5, – 1 (b) +7, – 1
(c) +3, 0 (d) +3, – 1

38. 0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30 cm^3 of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. What is the percentage of MnO_2 in the sample ? (At. wt. of Mn = 55)
(a) 38.3% (b) 52.2%
(c) 13.05% (d) 26.1 %

39. It requires 40 mL of 0.5 M Ce^{4+} to titrate 10 mL of 1 M Sn^{2+} to Sn^{4+}. What is the oxidation state of cerium in the reduced product ?
(a) +4 (b) +3 (c) +2 (d) +1

40. A 1.1 g sample of copper ore is dissolved and the $Cu^{2+}(aq)$ is treated with excess KI. The liberated I_2 requires 12.12 mL of 0.1 M $Na_2S_2O_3$ solution for titration. What is percentage of copper, by mass in the ore?
(a) 5% (b) 10%
(c) 7% (d) 8%

41. 0.56 g of lime stone was treated with oxalic acid to give CaC_2O_4. The precipitate decolourised 45 mL of 0.2 N $KMnO_4$ in acid medium. Calculate % of CaO in lime-stone.
(a) 57% (b) 45%
(c) 80% (d) 90%

42. Which order of compounds is according to the decreasing order of the oxidation state of nitrogen?
(a) HNO_3, NO, NH_4Cl, N_2 (b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2 (d) NO, HNO_3, NH_4Cl, N_2

43. 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
(a) 1 (b) 3
(c) 5 (d) 7

44. The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is
(a) 4 (b) 5
(c) 6 (d) 7

45. Consider the titration of potassium dichromate solution with acidified Mohr's salt solution using dimethylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is
(a) 3 (b) 4
(c) 5 (d) 6

46. Oxidation states of the metal in the minerals haematite and magnetite, respectively are
(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

AIEEE & JEE Main *Archive*

47. Which one of the following cannot function as an oxidising agent? **[JEE Main Online 2013]**

(a) I^- (b) S(s)
(c) $NO_3^-(aq)$ (d) $Cr_2O_7^{2-}$

48. Given, $x\,Na_2HAsO_3 + y\,NaBrO_3 + z\,HCl \longrightarrow$

$$NaBr + H_3AsO_4 + NaCl$$

The value of x, y and z in the above redox reaction are respectively. **[JEE Main Online 2013]**

(a) 2, 1, 2 (b) 2, 1, 3
(c) 3, 1, 6 (d) 3, 1, 4

49. Oxidation state of sulphur in anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ increases in the order **[JEE Main Online 2013]**

(a) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$ (b) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$
(c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$ (d) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

50. Consider the following reaction:

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O.$$

The values of x, y and z in the reaction are respectively. **[IIT JEE Main 2013]**

(a) 2, 5 and 8 (b) 2, 5 and 16
(c) 5, 2 and 8 (d) 5, 2 and 16

51. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl **[AIEEE 2008]**

(a) oxidises oxalic acid to carbon dioxide and water
(b) gets oxidised by oxalic acid to chlorine
(c) furnishes H^+ ions in addition to those from oxalic acid
(d) reduces permanganate to Mn^{2+}

52. What products are expected from the disproportionation reaction of hypochlorous acid? **[AIEEE 2006]**

(a) $HClO_3$ and Cl_2O
(b) $HClO_2$ and $HClO_4$
(c) HCl and Cl_2O
(d) HCl and $HClO_3$

53. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is **[AIEEE 2005]**

(a) +3 (b) +2
(c) +6 (d) +4

54. Among the properties (*A*) reducing, (*B*) oxidising and (*C*) complexing, the set of properties shown by CN^- ion towards metal species is **[AIEEE 2004]**

(a) *A*, *B*
(b) *B*, *C*
(c) *C*, *A*
(d) *A*, *B*, *C*

55. Several blocks of magnesium are fixed to the bottom of a ship to **[AIEEE 2003]**

(a) keep away the sharks
(b) make the ship lighter
(c) prevent action of water and salt
(d) prevent puncturing by under sea rocks

56. Oxidation number of Cl in $CaOCl_2$ (bleaching powder) is **[AIEEE 2002]**

(a) zero, since it contains Cl_2
(b) −1, since it contains Cl^-
(c) +1, since it contains ClO^-
(d) +1 and −1, since it contains ClO^- and Cl^-

57. MnO_4^- is a good oxidising agent in different medium changing to

$$MnO_4^- \longrightarrow Mn^{2+} \longrightarrow MnO_4^{2-} \longrightarrow MnO_2 \longrightarrow Mn_2O_3$$

Changes in oxidation number respectively, are **[AIEEE 2002]**

(a) 1, 3, 4, 5
(b) 5, 4, 3, 2
(c) 5, 1, 3, 4
(d) 2, 6, 4, 3

58. Which of the following is a redox reaction? **[AIEEE 2002]**

(a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$
(b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
(c) $Ca(OH)_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$
(d) $2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$

Answers

1. (c)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (d)	**7.** (b)	**8.** (a)	**9.** (a)	**10.** (b)
11. (a)	**12.** (a)	**13.** (d)	**14.** (b)	**15.** (c)	**16.** (c)	**17.** (a)	**18.** (d)	**19.** (b)	**20.** (b)
21. (b)	**22.** (c)	**23.** (c)	**24.** (d)	**25.** (c)	**26.** (a)	**27.** (a)	**28.** (b)	**29.** (c)	**30.** (b)
31. (d)	**32.** (a)	**33.** (c)	**34.** (a)	**35.** (c)	**36.** (a)	**37.** (a)	**38.** (d)	**39.** (b)	**40.** (c)
41. (b)	**42.** (b)	**43.** (c)	**44.** (b)	**45.** (d)	**46.** (d)	**47.** (a)	**48.** (c)	**49.** (c)	**50.** (b)
51. (d)	**52.** (d)	**53.** (a)	**54.** (c)	**55.** (c)	**56.** (d)	**57.** (c)	**58.** (d)		

Hints & Solutions

1. $\overset{+2}{Ba}(\overset{+1}{H_2}\overset{x}{P}\overset{-2}{O_2})_2$

$\therefore \quad 2 + 2[2 \times (+1) + x + 2 \times (-2)] = 0$

or $\quad 2 + 4 + 2x - 8 = 0$ or $x = +1$

and $\quad \overset{+1}{Na_4}\overset{x}{Xe}\overset{-2}{O_6}$

$\therefore \quad 4 \times 1 + x + 6 \times (-2) = 0$ or $x = +8$

2. (a) $\overset{+4}{N}O_2$ and $\overset{+4}{N_2}O_4$; Difference = 0

(b) $\overset{+5}{P_2}O_5$ and $\overset{+5}{P_4}O_{10}$; Difference = 0

(c) $\overset{+1}{N_2}O$ and $\overset{+2}{N}O$; Difference = +2 − 1 = +1

(d) $\overset{+4}{S}O_2$ and $\overset{+6}{S}O_3$; Difference = +6 − 4 = +2

3. $2\overset{+2}{N}O + 3I_2 + 4H_2O \longrightarrow 2\overset{+5}{N}O_3^- + 6I^- + 8H^+$

Hence, NO acts as a reducing agent and reduces I_2 to I^- since the oxidation number of nitrogen changes from +2 in NO to +5 in NO_3^-.

4. Oxidation number of hydrogen is +1 except in ionic hydrides, where it is −1.

5. In CO_2, the oxidation number of C, *i.e.*, +4 is already the maximum and it cannot increase its oxidation number further hence, does not act as a reducing agent.

6. Oxidation number of Cr in CrO_2Cl_2 is

$x + 2 \times (-2) + 2 \times (-1) = 0$ or $x - 4 - 2 = 0$ or $x = +6$

7. $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

It is a six electron change

$\therefore$ Eq. wt. of $K_2Cr_2O_7 = \frac{1}{6}$ (molecular weight)

8. $\overset{0}{S_8}, \overset{+1}{S_2}\overset{-1}{F_2}, \overset{+1}{H_2}\overset{-2}{S}$

Here, oxidation number of S in S_8, S_2F_2 and H_2S respectively are 0, +1, −2.

9.
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

Thus, the coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ in the above balanced equation respectively are 2, 5, 16.

10. The balanced equation is

$$2C_2H_6 + 5O_2 \longrightarrow 4CO_2 + 6H_2O$$

Ratio of the coefficient of CO_2 and H_2O is 4 : 6 and 2 : 3.

11. Oxidation

$$6\overset{+4}{C}O_2 + 6H_2\overset{-2}{O} \xrightarrow{\text{Sunlight}} \overset{0}{C_6}H_{12}O_6 + 6\overset{0}{O_2}$$

Reduction

Since, oxidation and reduction both occurs simultaneously in the above equation, so it is a redox reaction.

12. $Ba\overset{-1}{O_2} < K\overset{-0.5}{O_2} < \overset{0}{O_3} < \overset{+2}{O}F_2$

13. $3\overset{0}{Br_2} + 6CO_3^{2-} + 3H_2O \longrightarrow 5\overset{-1}{Br^-} + \overset{+5}{Br}O_3^- + 6HCO_3^-$

Br_2 is reduced to Br^- (oxidation number decreases from zero to −1) and Br_2 is oxidised to BrO_3^- (oxidation number increases from zero to +5).

14. Reduction half - reaction $H\overset{+5}{N}O_3 + 4e^- \longrightarrow \frac{1}{2}\overset{+1}{N_2}O$

15. Highest negative oxidation state for p-block elements = number of electrons in valence shell −8 and highest positive oxidation state for p-block elements = group number −10

$= 5 - 8$ to $15 - 10 = -3$ to $+5$

16. $2Br^- \longrightarrow Br_2 + 2e^-$ (Valence factor for $Br^- = -1$)

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ (Valence factor for $Cl_2 = 2$)

Meq. of Cl_2 = Meq. of Br^-

$0.05 \times 2 \times V = 50 \times 0.06 \times 1$

$\therefore \quad V = 30$ mL

17. $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

$$E_{Na_2S_2O_3} = \frac{2M}{2} = M$$

18. $2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O$

$$E_{KBrO_3} = \frac{\text{mol. wt.}}{\text{no. of electrons gained}} = \frac{2BrO_3^-}{10}$$

$$= \frac{BrO_3^-}{5} = \frac{KBrO_3}{5} = \frac{M}{5}$$

19. The oxidation number of O in H_2O_2 is −1. It can either increases to zero in O_2 or decreases to −2 in H_2O. Therefore, H_2O_2 can act both as an oxidising as well as a reducing agent.

20. $2Li^0 + \overset{0}{H_2} \longrightarrow 2\overset{+1}{Li}\overset{-1}{H}$

21. NH_4NO_3 is an ionic compound exist in the form of NH_4^+ ; NO_3^-

In NH_4^+ ; $x + 4 = +1$ or $x = -3$

In NO_3^- ; $x - 6 = -1$ or $x = +5$

22. $K_2Cr_2O_7 + 4H_2SO_4 + 3\overset{+4}{S}O_2 \longrightarrow$

$K_2SO_4 + Cr_2(SO_4)_3 + 3\overset{+6}{S}O_3 + 4H_2O$

Oxidation number of S changes from +4 in SO_2 to +6 in SO_3.

23. Highest oxidation number of Mn in K_2MnO_4 is $2 + x - 8 = 0$ or $x = +6$, while in all other compounds oxidation number of Mn is lower than 6.

24. In the given redox reaction, $C^- \equiv N \longrightarrow O^- — C \equiv N$

Oxidation number of nitrogen is remaining unchanged at − 3. Oxidation number of carbon is increasing from + 2 to + 4. Hence, (a) and (c) are the only correct response. Therefore option (d) is correct.

25. $\overset{+7}{KMnO_4} \xrightarrow[\text{medium}]{\text{Acidic}} Mn^{2+}; E = \frac{M}{5} = \frac{158}{5} = 31.60$

$\overset{+7}{KMnO_4} \xrightarrow[\text{medium}]{\text{Neutral}} \overset{+4}{MnO_2}; E = \frac{M}{3} = \frac{158}{3} = 52.67$

$\overset{+7}{KMnO_4} \xrightarrow[\text{medium}]{\text{slightly Alkaline}} \overset{+6}{MnO_4^{2-}}; E = M = 158$

26. $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$

Meq. of SO_3^{2-} = Meq. of $KMnO_4$

$$N \times 25 = 34.08 \times 0.01964 \times 5$$

$$N_{SO_3^{2-}} = 0.1339$$

$$M_{SO_3^{2-}} = \frac{0.1339}{2} = 0.0669 \quad [\because S^{4+} \longrightarrow S^{6+} + 2e^-]$$

27. $Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$

$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \longrightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$

$$\therefore \frac{\text{Moles of cericammonium sulphate}}{\text{Moles of potassium permanganate}} = \frac{1}{1/5} = 5.0$$

28. The reaction is an example of intermolecular redox reactions.

$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow$
$2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$

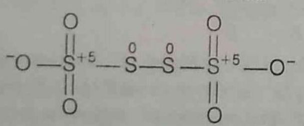
$2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e^-$

$Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$

29. $\because \; 2N_2H_4 \longrightarrow 2X + 20\,e^-$

$\therefore \; N_2H_4 \longrightarrow X + 10e^-$

As two atoms of nitrogen lose ten electrons *i.e.*, 5 electrons each. Hence, oxidation state = − 2 + 5 = + 3

30. 

[Structure of tetrathionate ion]

31. $\underset{+7}{MnO_4^-} \longrightarrow \underset{+2}{Mn^{2+}}$ O.N. change 5

$\underset{+12}{Cr_2O_7^{2-}} \longrightarrow \underset{+6}{2Cr^{3+}}$ 6

1 mole of $MnO_4^- \equiv 5$ equivalents of MnO_4^-

1 mole of $Cr_2O_7^{2-} \equiv 6$ equivalents of $Cr_2O_7^{2-}$

32. Redox reactions : $\overset{7+}{Mn} + 5e^- \longrightarrow \overset{2+}{Mn}$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

It must be known that only $FeSO_4 \cdot 7H_2O$ will react with $KMnO_4$ to bring in redox change.

$\because$ Meq. of $FeSO_4.7H_2O$ = Meq. of $KMnO_4$

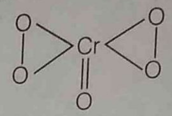
or $\frac{w}{E} \times 1000 = 5.4 \times 0.1$ or $\frac{w}{278} \times 1000 = 0.54$

or $w = 0.150$ g

$\therefore$ Weight of $Fe_2(SO_4)_3 \cdot 9H_2O = (5.5 - 0.150)$ g = 5.350 g

and mole of $Fe_2(SO_4)_3 \cdot 9H_2O = \frac{5.350}{562} = 9.5 \times 10^{-3}$ mol

33. In CrO_5, four oxygen atoms are in −1 oxidation state.



$$x + 1(-2) + 4(-1) = 0$$

$$x = +6$$

34. Statement II is the correct reason of statement I.

35. $Cl_2 + H_2O \longrightarrow 2HCl + O$

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

36. $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

37. Oxidation $\dot{Cl_2} \longrightarrow 2\overset{5+}{Cl} + 10e^-$

Reduction $5\dot{Cl_2} + 10e^- \longrightarrow 10\,Cl^-$

Total redox reaction $6\,Cl_2 \longrightarrow 2\overset{5+}{Cl} + 10\,Cl^-$

38. $MnO_2 \xrightarrow{HCl} Cl_2 \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} NaI + Na_2S_4O_6$

The reactions suggest

Meq. of MnO_2 = Meq. of Cl_2 formed
= Meq. of I_2 liberated
= Meq. of $Na_2S_2O_3$ used

$$\frac{\omega_{MnO_2}}{M/2} \times 1000 = 0.1 \times 1 \times 30$$

[$\because$ Valency factor for $Na_2S_2O_3 = 1$]

or $w_{MnO_2} = \frac{0.1 \times 1 \times 30 \times M}{2 \times 100} = \frac{0.1 \times 1 \times 30 \times 87}{2000}$

or $w_{MnO_2} = 0.1305$

$\therefore$ Percentage of $MnO_2 = \frac{0.1305}{0.5} \times 100 = 26.1\%$

39. $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

$ne^- + Ce^{4+} \longrightarrow Ce^{(4-n)+}$

$\because$ Meq. of Ce^{4+} = Meq. of Sn^{2+}

or $40 \times 0.5 \times n = 1 \times 2 \times 10$

$\therefore$ $n = 1$

Hence, $Ce^{4+} + e^- \longrightarrow Ce^{3+}$

40. $Cu^{2+} + e^- \longrightarrow Cu^+$

$2I^- \longrightarrow I_2 + 2e^-$

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

Meq. of Cu^{2+} = Meq. of liberated I_2
= Meq. of used $Na_2S_2O_3$

$$\frac{w_{Cu^{2+}}}{M/1} \times 1000 = 12.12 \times 0.1 \times 1$$

$$w_{Cu^{2+}} = \frac{12.12 \times 0.1 \times 63.6}{1000}$$

$$w_{Cu^{2+}} = w_{Cu} = 0.077 \text{ g}$$

$$\% \text{ of Cu} = \frac{0.077}{1.1} \times 100 = 7\%$$

41. $CaCO_3 \xrightarrow{\text{Oxalic acid}} CaC_2O_4 \xrightarrow{KMnO_4}$ decolourises

Redox changes :

For CaC_2O_4 $\quad \overset{3+}{C_2} \longrightarrow 2C^{4+} + 2e^-$

For $KMnO_4$ $\quad 5e^- + \overset{7+}{Mn} \longrightarrow Mn^{2+}$

$\because$ Meq. of $CaCO_3$ = Meq. CaC_2O_4 = Meq. of $KMnO_4$ and Meq. of $CaCO_3$ = Meq. of CaO (since CaO is present in $CaCO_3$)

$\therefore$ Meq. of CaO = Meq. of $KMnO_4$

$$\frac{w}{56/2} \times 1000 = 45 \times 0.2$$

$$w_{CaO} = 0.252 \text{ g}$$

% of CaO in lime stone $= \frac{0.252}{0.56} \times 100 = 45\%$

42. Let oxidation number of N be x

In HNO_3 — $+1 + x + 3(-2) = 0$ or $x = +5$

In NO — $x - 2 = 0$ or $x = +2$

In N_2 — $x = 0$

In NH_4Cl — $x + y - 1 = 0$ or $x = -3$

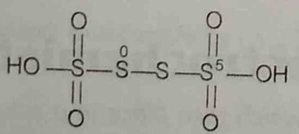
Thus the order of oxidation states of nitrogen is

$$HNO_3 > NO > N_2 > NH_4Cl$$

43. Br_2 is disproportionated in basic medium as

$$3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$

44. $Na_2S_4O_6$ is a salt of $H_2S_4O_6$ which has the following structure.



The difference in oxidation number of two types of sulphur = 5

45. Haematite is Fe_2O_3, in which oxidation number of ion is (III). Magnetite is Fe_3O_4 which is infact a mixed oxide ($FeO \cdot Fe_2O_3$), hence, iron is present in both (II) and (III) oxidation state.

46. $2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$.

47. In I^-, iodine is present in its lowest possible oxidation state. Further reduction in oxidation state is not possible. That's why its further reduction is not possible. Hence, it cannot function as oxidising agent.

48. $3Na_2HAsO_3 + NaBrO_3 + 6HCl \rightarrow NaBr + 3H_3AsO_4 + 6NaCl$

49. Let the oxidation state of S be x.

SO_3^{2-} $\quad x + (-2) \times 3 = -2$

$x - 6 = -2$

$\therefore$ $x = +4$

$S_2O_4^{2-}$ $\quad 2 \times x + (-2)4 = -2$

$2x - 8 = -2$

$2x = 6$ or $x = +3$

$S_2O_6^{2-}$ $\quad 2x + (-2)6 = -2$

$2x = 10 \Rightarrow x = +5$

$\therefore$ The increasing order of oxidation states is

$$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$$

50. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10\,CO_2 + 8H_2O$

$x = 2, y = 5, z = 16$

51. Mohr's salt [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) is a reducing agent involving $1e^-$ change while $K_2Cr_2O_7$ is an oxidising agent involving $6e^-$ change, *i.e.*,

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Thus, 1 mole of $Cr_2O_7^{2-}$ ion will oxidise 6 moles of Mohr's salt.

52. $3HOCl \longrightarrow 2HCl + HClO_3$

53. $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

$Cr_2O_7^{2-}$ is reduced to Cr^{3+}

Thus, final state of Cr is +3.

54. CN^- is a better complexing agent (*C*) as well as a reducing agent (*A*)

Thus, properties (*A*) and (*C*) are shown.

Property (*C*) : $Ni^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-}$

Property (*A*) :

$$\overset{II}{Cu}Cl_2 + 5KCN \longrightarrow K_3[\overset{I}{Cu}(CN)_4] + \frac{1}{2}(CN)_2 + 2KCl$$

(CN reduces Cu^{2+} to Cu^+)

55. To prevent action of water and salt, a number of blocks of magnesium are fixed to the bottom of a ship.

56. $CaOCl_2$ is written basically as Ca(OCl)Cl

$OCl^- \longrightarrow$ Cl has +1 oxidation state

$Cl^- \longrightarrow$ Cl has −1 oxidation state

57. $\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$ change in oxidation number 5

$\longrightarrow MnO_4^{2-}$ change in oxidation number 1

$\longrightarrow \overset{+4}{Mn}O_2$ change in oxidation number 3

$\longrightarrow \overset{+3}{Mn_2}O_3$ change in oxidation number 4

58. (a) $\overset{+1}{Na}\overset{-1}{Cl} + \overset{+1}{K}\overset{-1}{NO_3} \longrightarrow \overset{+1}{Na}\overset{-1}{NO_3} + \overset{+1}{K}\overset{-1}{Cl}$

change in oxidation number.

(b) $\overset{+2}{Ca}\overset{-2}{C_2O_4} + 2\overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Ca}\overset{-1}{Cl_2} + \overset{+1}{H_2}\overset{-2}{C_2O_4}$

(c) $\overset{+2}{Ca}\overset{-1}{(OH)_2} + 2\overset{-3}{N}\overset{+1}{H_4}\overset{-1}{Cl} \longrightarrow \overset{+2}{Ca}\overset{-1}{Cl_2} + 2\overset{-3}{N}\overset{+1}{H_3} + 2\overset{+1}{H_2}\overset{-2}{O}$

in all these cases during reaction, there is no change in oxidation state of ion or molecule or constituent atom, these are simply ionic reactions.

(d) $2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$

$Ag^+ \longrightarrow$ Ag gain of e^-, reduction

$Zn \longrightarrow Zn^{2+}$ loss of e^-, oxidation.

Day 13

Electrochemistry

Day 13

Outlines ...

- Concepts of Electrochemistry
- Conductors
- Electrolysis
- Kohlrausch's Law
- Electrochemical Cell
- EMF of Cell
- Nernst Equation
- Batteries
- Fuel Cells

Concept of Electrochemistry

The study of the chemical reactions which take place in a solution at the interface of an electron conductor and an ionic conductor is considered under the branch of chemistry namely as electrochemistry.

Conductors

The substance which can conduct electricity are called **conductors**. On the basis of species that conduct electricity (current), conductors are of two types *viz*, metallic conductors and electrolytic conductors.

(i) **Metallic or electronic conductors** can conduct current by transfer of free electrons.

(ii) **Electrolytic conductors** can conduct current by the mobility of ions. This process is known as **electrolytic conduction**.

Conductance in Electrolytic Solutions

The power of an electrolyte to conduct electric current is called conductance or conductivity. Just like metallic conductors, electrolytic solutions also obey Ohm's law.

1. **Conductance** (C)

Reciprocal of resistance is called **conductance**, *C*.

$C = \frac{1}{\text{Resistance}} = \frac{1}{R}$. Its unit is mho ($\Omega^{-1}$) or Siemens (S).

2. **Conductivity** or **Specific Conductance** (κ)

The resistance of any conductor varies directly as its length (l) and inversely as its cross sectional area (a) *i.e.*, $R \propto \frac{l}{a}$ or $R = \rho \frac{l}{a}$

where, ρ is called the resistivity or specific resistance.

If $l = 1$ cm and $a = 1\,\text{cm}^2$ then $R = \rho$

$\therefore \quad \kappa = \frac{1}{\rho_1} = \frac{l}{a} \times \text{conductance } (C)$

where, $\frac{l}{a}$ = cell constant, it is determined with the help of conductivity bridge, where a standard solution of KCl is used.

The unit of specific conductance (κ) is $\text{ohm}^{-1}\,\text{cm}^{-1}$ or S cm^{-1}.

3. **Molar Conductivity** (Λ_m)

It is the conducting power of all the ions produced by one gram mole of an electrolyte in a given solution.

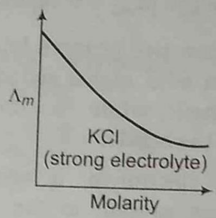
Thus, $\Lambda_m = \frac{\kappa \times 1000}{\text{molarity}}$

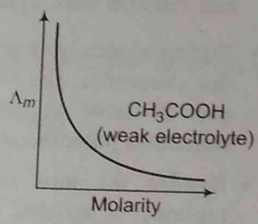
Theunits for molar conductivity

$= \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ or $\text{S cm}^2\ \text{mol}^{-1}$

Variation of Molar and Equivalent Conductivities with Concentration

In case of strong electrolytes, electrolytes, like KCl, have high value of conductance even at low concentration and there is no rapid increase in their equivalent or molar conductance on dilution.





In case of weak electrolytes, electrolytes, like acetic acid, have a low value of conductance at high concentration and there is a rapid increase in the value of equivalent conductance (molar conductance) with dilution.

Limiting Molar Conductivity or Infinite Conductivity (Λ_m° or Λ_m^∞)

It is the molar conductivity of electrolyte when concentration of electrolyte approaches zero (*i.e.*, at infinite dilution).

4. **Equivalent Conductivity** (Λ_{eq})

It is the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

Thus, $\Lambda_{eq} = \frac{\kappa \times 1000}{\text{normality}}$. The units for equivalent conductivity $= \text{ohm}^{-1}\,\text{cm}^2\,(\text{g eq})^{-1}$ or $\text{S cm}^2\,(\text{g eq})^{-1}$

5. **Effect of Dilution on Conductivity**

Equivalent as well as molar conductivity $\propto$ dilution and Specific conductivity $\propto \frac{1}{\text{dilution}}$

Electrolysis

Electrolysis is a process in which electric energy is used to bring some chemical changes. It is carried out in an ***electrolytic cell*** *which involves conversion of electric energy to chemical energy.*

Electrolytic cell

⊕ Anode	⊖ Cathode
• Oxidation	• Reduction
• More E°_{oxi}, gets oxidised easily	• More E°_{red}, gets reduced easily

where, E°_{oxi} = standard oxidation potential *i.e.*, at standard conditions (1 atm, 298 K and 1M) tendency to lose electrons.

E°_{red} = standard reduction potential *i.e.*, at standard conditions (1 atm, 25°C and 1M) tendency to gain electrons.

- Decreasing order of oxidation potential;

  $I^- > Br^- > Cl^- > OH^- > F^- > NO_2^- > NO_3^- > SO_3^{2-} > SO_4^{2-}$

- Increasing order of reduction potential;

  All metal, more reactive than hydrogen [E°_{red} = less than zero] < Hydrogen [E°_{red} = zero] < metals less reactive than hydrogen [E°_{red} = + ve] like Cu, Ag etc.

- During electrolysis when two or more ions complete at the electrodes, the ion with higher reduction potential gets liberated at cathode while the one with lower reduction potential at the anode.

- Besides the ions of electrolyte, if some other ions (cations or anions) are present in the solution, then which of the two or more ions gets discharged at each electrode depends upon their relative discharge potential. Usually ions with lower discharge potential are discharged in preference to those which have high discharge potential.

- *For aqueous solution of salt:*

  (i) If metal is less reactive (like Ag, Cu) than hydrogen, metal will be deposited at cathode.

  (ii) If metal is more reactive than hydrogen, H_2 gas will be liberated at cathode.

In aqueous solution containing any of the cation $Li^+, Na^+, Ba^{2+}, Ca^{2+}$, Mg^2 or Al^{3+}, it is water which is reduced at cathode and not the metal cations. In aqueous solution of the SO_4^{2-} and NO_3^-, anions are not oxidised, it is water which is oxidised.

Faraday's Laws of Electrolysis

The quantitative relationships based on the electrochemical researches published by Faraday. These two laws given by the Faraday are given below.

First Law

Deposited mass of the substance is directly proportional to passed charge in a voltameter.

$$w \propto Q$$
$$w = ZQ$$
$$w = Zit$$

where, w = mass,

Q = charge (in coulomb)

i = current (in amperes)

t = time (in second)

Z = electrochemical equivalent.

$$= \frac{\text{equivalent wt.}}{96500\text{ C}} \qquad \left[\text{Equivalent wt.} = \frac{\text{atomic wt.}}{\text{valency}}\right]$$

1 Faraday = charge of one mole of electrons

$$1F = 6.022 \times 10^{23} \times 1.6 \times 10^{-19}$$
$$= 96500 \text{ C (approx.)}$$

No. of gram equivalents = No. of Faradays of electricity,

i.e., 1 g eq of any substance = 1F of electricity

Other forms of Faraday first law expression are

$$w = ZQ = \frac{E}{F} \times Q$$
$$= \frac{Q}{F} \times \frac{M}{Z}$$
$$= \frac{it}{F} \times \frac{M}{Z}$$

One Faraday or 96500 C or 1 mole of e^- cause the reduction of 1 mole of monovalent cation or 1/2 mole of divalent cation or 1/3 mole of trivalent cation.

Second Law

The number of equivalents of any substance produced by a given quantity of electricity during electrolysis are same.

$$\frac{w_A}{w_B} = \frac{E_A}{E_B}$$

where, w_A = deposited mass of substance A,

E_A = equivalent wt. of A

w_B = deposited mass of substance B,

E_B = equivalent wt. of B

Kohlrausch's Law

It states that molar conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions i.e., anions and cations.

e.g.,

$$\Lambda^\circ_m CH_3COOH = \lambda^\circ_m CH_3COO^- + \lambda^\circ_m H^+$$

$$\Lambda^\circ_m Al_2(SO_4)_3 = 2 \times \lambda^\circ_m Al^{3+} + 3 \times \lambda^\circ_m SO_4^{2-}$$

Applications of Kohlrausch's Law

(i) For the determination of equivalent/molar conductivity at infinite dilution.

(ii) For the determination of degree of dissociation.

Degree of dissociation (α)

$$= \frac{\text{molar conductance at a given concentration}}{\text{molar conductance at infinite dilution}}$$

$$= \frac{\Lambda^c_m}{\Lambda^\infty_m}$$

(iii) For the calculation of dissociation constant of a weak electrolyte.

$$K_a = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$$

[$\because$ For weak electrolyte, $\alpha <<< 1$]

Here, K_a = equilibrium dissociation constant

C = molar concentration of weak electrolyte

(iv) For the determination of solubility of sparingly soluble salt.

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda^\circ_m}$$

- *Transport number is the fraction of current carried by an ion. It decreases with increase in concentration.*
- *Transport number of cation*

$$(n_c) = \frac{\text{current carried by cation}}{\text{total current}} = \frac{u_c}{u_c + u_a}$$

- *Transport number of anion* $(n_a) = \dfrac{u_a}{u_c + u_a}$

Absolute ionic mobilities is defined as the speed of ions in cm per second at infinite dilution under a potential gradient of 1 V/cm. Its units are cm s^{-1} N cm^{-1}.

Electrochemical Cell

An electrochemical cell or simple a cell a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge.

Electrochemical cells are of the following two types

1. Electrolytic Cells

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

$$H_2SO_4\,(l) \xrightarrow[\text{(acidified/dil)}]{H^+} H_2O(g) + O_2(g) + \text{dil } H_2SO_4$$

2. Galvanic or Voltaic Cells

It is a device in which a redox reaction used to convert chemical energy into electrical energy.

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

The two types are therefore the reverse of each other.

Electrode and Half-Cell

When used in electrochemical studies, a strip of metal, M used is called **electrode**. The metal strip is immersed in a solution containing the metal ion M^{n+}. The combination of the metal electrode and solution is called a **half-cell**.

Three kinds of interactions are possible between metal atom on the electrode and metal ion in solution.

(i) A metal ion M^{n+} may collide with the electrode and undergo no change.

(ii) A metal ion M^{n+} may collide with the electrode, gain n electrons and be converted to a metal atom M. The ion is reduced. $M^{n+}(aq) + ne^- \longrightarrow M(s)$

(iii) A metal atom M on the electrode may lose n electrons and enter the solution as ion M^{n+}. The metal atom is oxidised.

$$M\,(s) \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} M^{n+}\,(aq) + ne^-$$

	Electrolytic cell		Voltaic or Galvanic cell	
	Anode	Cathode	Anode	Cathode
Sign	+	−	−	+
Electron flow	out	in	out	in
Half-reaction	oxidation	reduction	oxidation	reduction

Salt-bridge

It is a U-shaped tube contains a gel permeated with a solution of an inert electrolyte such as Na_2SO_4. The ions of the inert electrolyte do not react with the other ions in the solutions and they are not oxidised or reduced at the electrodes. The salt-bridge is necessary to complete the electrical circuit and to maintain electrical neutrality in both compartments (by flow of ions).

Representation of a Cell

- The anode is written on the left hand side and cathode on the right hand side.
- A vertical line (|) or semicolon (;) indicates a contact between two phases.
- The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution.
- The cathode of the cell is represented by writing the cation of the electrolyte first and then metal.
- The salt bridge which seperates the two half-cells is indicated by two parallel vertical lines.
- Sometimes molar concentration or signs are also indicated on the electrodes.

Consider the Daniell cell with following cell reaction :

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

In writing a cell diagram, following points are considered. We divide the cell into two half-cells

	The anode	The cathode
Reaction	Oxidation takes place $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$	Reduction takes place $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
Terminal	Negative	Positive
Side	LHS	RHS
Diagram	$Zn(s) Zn^{2+}(aq)$	$Cu^{2+}(aq) / Cu(s)$

Complete cell diagram may be represent as follows

Anode half-cell Salt bridge Cathode half-cell

$$Zn(s) \,|\, Zn^{2+}(aq) \,||\, Cu^{2+}(aq) \,|\, Cu(s)$$

Electrons flow this way

Phase boundary Phase boundary

If oxidised or reduced part is a gas, use Pt electrode saturated with that gas

e.g., (anode)

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$$

$$Pt(H_2)\,|\,H^+(aq)$$

(cathode)

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

$$H^+(aq)\,|\,Pt(H_2)$$

- If oxidised and reduced parts are in ionic state, use Pt electrode.

e.g.,

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

$$Pt\,|\,Fe^{2+}(aq), Fe^{3+}(aq)$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

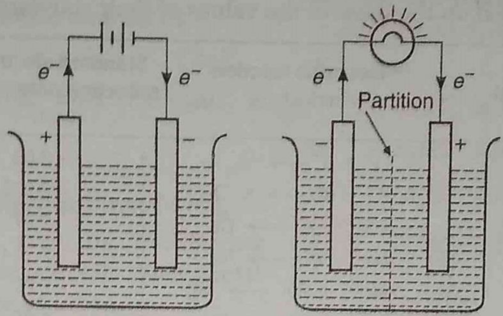
$$MnO_4(aq)\,Mn^{2+}(aq)\,|\,Pt$$

Difference between Electrolytic and Electrochemical Cells

The main points of difference between these two cells are

1. The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done is called electrolytic cell while **galvanic** or **voltaic** cell is a device in which **redox** reaction is used to convert chemical energy to electrical energy.
2. In 'electrolytic cell', anode is positive electrode, while cathode is negative electrode. On the other hand, in 'galvanic cell' anode is negative electrode and cathode is positive electrode.
   In both the cells anode is always the site of oxidation and cathode is of reduction.
3. In electrolytic cell, ions are discharged at both the electrodes, while in galvanic cell ions are discharged only at cathode.

4. In electrolytic cell, both the electrodes are fitted in same compartment, while in galvanic cell both the electrodes are fitted in different compartments.



(a) Electrolytic cell (emf is applied to cell)

(b) Voltaic or galvanic cell (emf is generated by cell)

5. Besides salt bridge in both the cells, both the electrodes are connected externally with the help of a wire connected through a voltmeter. Flow of current and electrons occur through this wire.

EMF of Cell

In electrochemical cell, the electrodes in different half-cells have different reduction potential. As a result of this, different flow of electrons is seen from the electrode with higher tendency to lose electrons to other electrode. This difference in electrode potential of electrodes is called electromotive force or cell potential of a cell. This is the driving force for all cell reactions.

Standard Electrode Potential and emf

If we connect two different electrodes, electrons will flow from the electrode of higher negative electric charge density to the electrode with a lower negative electric charge density. A property closely related to the density of negative electric charge is called the electrode potential. Potential difference between the metal and the metal ion in which electrode is dipped, is called electrode potential denoted as E.

In the standard state, when pressure is 1 atm, (latest IUPAC correction use 1 bar) and concentration is 1 M, electrode potential is called standard electrode potential denoted as E°. Temperature is generally taken as 298K (*i.e.*, 25°C)

According to international convention, standard reduction potentials are now called standard electrode potentials. If the standard electrode potential of a half-cell is 0.34 V, it means it is the standard reduction potential $E^\circ_{M^{n+}/M}$, of the half-cell M^{n+}/M with half-cell reaction $M^{n+} + ne^- \longrightarrow M$

- If $E^\circ_{ox} = xV$, then $E^\circ_{red} = -xV$

  $E^\circ_{Cu^{2+}/Cu} = 0.34$ V, then $E^\circ_{Cu^{2+}/Cu} = -0.34$ V
- E°_{cell} or E_{cell} is the potential difference between the two half-cells. Since the potential difference is the driving force for electrons, it is also called the electromotive force (emf) of the cell or the cell potential or the cell voltage.
- This driving force pushes the negatively charged electrons away from the anode (–ve electrode) and pulls them towards the cathode (+ ve electrode). The SI unit of cell potential is the volt (V) and the potential of a galvanic cell is defined as the positive quantity.

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$
$$E_{cell} = E_{ox} + E_{red}$$

For such cases take values according to the reaction. Electrons should be equal in both half-cell reactions.

» Standard Hydrogen Electrode, SHE used as a reference electrode. Its reduction potential is taken as zero. It is represented as Pt, H_2(1 atm) | H^+(1 M) or H^+ (1M)|H_2 (1 atm), Pt depending upon whether it acts as anode or cathode respectively.

» The difference between the potential required for the evolution of gas and the standard electrode potential of that gas is called over voltage/over potential.

Electrochemical Series

The arrangement of metals in decreasing order of tendency to lose electrons (e^-) is called **electrochemical series** or it is the series in which the elements are arranged on the basis of the values of their standard reduction potential at 25°C.

Element	Electrode reaction (reduction)	Standard electrode reduction potential E° (volt)
Li	$Li^+ + e^- \longrightarrow Li$	– 3.05
K	$K^+ + e^- \longrightarrow K$	– 2.925
Ca	$Ca^{2+} + e^- \longrightarrow Ca$	– 2.87
Na	$Na^+ + e^- \longrightarrow Na$	– 2.714
Mg	$Mg^{2+} + 2e^- \longrightarrow Mg$	– 2.37
Al	$Al^{3+} + 3e^- \longrightarrow Al$	– 1.66
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	– 0.7628
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	– 0.74
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	– 0.44
Cd	$Cd^+ + 2e^- \longrightarrow Cd$	– 0.403
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	– 0.25
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	– 0.14
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.00
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	+ 0.337
I_2	$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.535
Ag	$Ag^+ + e^- \longrightarrow Ag$	+ 0.799
Hg	$Hg^{2+} + 2e^- \longrightarrow Hg$	+ 0.885
Br_2	$Br_2 + e^- \longrightarrow 2Br^-$	+ 1.08
Cr_2	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
Au	$Au^{3+} + 3e^- \longrightarrow Au$	+ 1.50
F_2	$F_2 + 2e^- \longrightarrow 2F^-$	+ 2.87
Li	$Li^+ + e^- \longrightarrow Li$	– 3.05

Increasing tendency for reduction
Increasing tendency to accept electrons (e^-)
Increasing strength as oxidising agent

Increasing strength as oxidising agent
Increasing tendency to lose electrons (e^-)
Increasing tendency for oxidation

Nernst Equation

The relationship between electrode potential and concentration of solution is called nernst equation.

$$E_{cell} \text{ or } EMF = E^\circ_{cell} - \frac{2.303RT}{nF} \log Q$$

where, n = total number of electrons lost or gained

$1F = 96500C$, $T = 298$ K

$R = 8.314$ J/K

Q = reaction coefficient of overall reaction $= \frac{[O.S.]}{[R.S.]}$

where, [O.S.] = concentration of oxidised state

[R.S.] = concentration of reduced state

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

- *The emf of a standard cell does not change with temperature. Weston cell is a common example of standard cell.*
- *The standard electrode potential of a half-cell has a fixed value. It does not change, if the half-reaction is multiplied with an integer.*

Applications of Nernst Equation

There are two important applications of Nernst equation are given below.

(i) To find equilibrium constant

At equilibrium, E_{cell} = zero

$$\therefore \quad E^\circ_{cell} = \frac{0.0591}{n} \log K$$

where, K = equilibrium constant.

(ii) To find Gibb's free energy change

$$\Delta G^\circ = -n E^\circ_{cell} F$$

ΔG° = standard Gibbs free energy change

Some Important Relationship in Electrochemistry

1. **Relationship between Cell Potential and Gibbs Energy Change (ΔG)**

In an electrochemical cell, maximum work done (ΔG) is given by $\Delta G = nF \times E_{cell}$

where, F = Faraday's constant

n = number of moles of electrons transferred.

A galvanic cell does electrical work by transferring electrical charge through an external circuit. When small amount of current is drawn from the cell then

$$-\Delta G = W_{elec.}$$

(i) If ΔG of the system is positive then the process would be possible only if the surrounding do electrical work on the system (as in electrolysis).

(ii) If ΔG of the system is negative then the system does electric work on the surroundings (as in galvanic cells). For a voltaic cell, the work is done on the surroundings, thus given a negative sign. Hence,

$$\Delta G = W_{max} = -nFE_{cell}$$

and the standard free energy ($\Delta G°$) is given by,

$$\Delta G° = -nFE°_{cell}$$

2. **Relation Between Cell Potential ($E°_{cell}$), Free Energy ($\Delta G°$) and K**

The relation between cell potential ($E°_{cell}$), free energy ($\Delta G°$) and equilibrium constant (K_c) is given by,

$$\Delta G° = -2.303RT \log K_c$$

as $\quad \Delta G° = nFE°_{cell}$ and $E°_{cell} = \dfrac{2.303\ RT}{nF} \log K_c$

where, n is the number of moles of electrons transferred in the balanced equation for the process to which you apply the Nernst equation.

3. **Relation Between Standard Potentials of Half-cells Containing a Metal in different Oxidation State**

If two half-reactions having potentials $E_1°$ and $E_2°$ are combined to give a third half-reaction having a potential $E_3°$, then

$$\Delta G_3° = \Delta G_1° + \Delta G_2°$$

or $\quad -n_3FE_3° = -n_1FE_1° - n_2FE_2°$

or $\quad n_3E_3° = n_1E_1° + n_2E_2°$

or $\quad E_3° = \dfrac{n_1E_1° + n_2E_2°}{n_3}$

Lead Accumulator

In lead accumulator the electrodes are made of lead and the electrolyte consists of dilute sulphuric acid. The electrodes are usually cast from a lead alloy containing 7–12% of antimony (to give increased hardness and corrosion resistance) and a small amount of tin (for better casting properties).

The electrodes are coated with a paste of lead (II) oxide (PbO) and finely divided lead; after insertion into the electrolyte a 'forming' current is passed through the cell to convert the PbO on the negative plate into a sponge of finely divided lead. On the positive plate the PbO is converted to lead (IV) oxide (PbO_2). The equation for the overall reaction during discharge is

$$PbO_2 + 2H_2SO_4 + Pb \longrightarrow 2PbSO_4 + 2H_2O$$

The reaction is reversed during charging. Each cell gives an emf of about 2 V and in motor vehicles a 12-V battery of six cells is usually used. The lead-acid battery produces 80–120 kJ per kilogram.

Batteries

*A cell or a **battery** (arrangement of 1 or more cells connected in series) is basically a galvanic cell and used where the chemical energy of redox reaction is converted into electrical energy. There are two types of batteries*

1. Primary Batteries

The primary batteries are those in which the cell reaction occurs only once and the battery becomes dead after use over a period of time and cannot be reused again, *e.g.*, dry cells like Leclanche cell, mercury cell etc. Hence, primary batteries are not rechargeable. *e.g.*, dry cell, mercury cell.

(i) **Dry cell or Leclanche cell** is also called primary voltaic cell.

In it the electrode reactions are

At anode $\quad Zn\,(s) \longrightarrow Zn^{2+} + 2e^-$

At cathode

$M_nO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

The cell potential is 1.6 V.

(ii) Another type of dry cell is **mercury cell.**

The electrode reactions for the cell are

At anode $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

At cathode $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall cell reaction is

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

2. Secondary Batteries

These are also called **reversible galvanic** or **voltaic cell**. Secondary batteries are rechargeable because on charging reaction becomes reverse *e.g.*, lead storage battery, nickel cadmium cell etc.

In lead storage battery, a solution of sulphuric acid surrounds the plates and acts as electrolyte. The battery consist of 6 cells, each contains lead anode and lead oxide cathode. The cell potential is 12 V. The half-cell reactions, when the battery is being used up are **At anode** $Pb(s) + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e^-$

At cathode $PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$

Overall reaction

$Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4(s) + 2H_2O$

During charging follows following reactions

At anode

$PbSO_4(s) + 2H_2O \longrightarrow PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^-$

At cathode $PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}$

Overall reaction

$2PbSO_4(s) + 2H_2O \longrightarrow Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-}$

Fuel Cells

Fuel cells are another means by which chemical energy may be converted into electrical energy. Energy can be obtained indefinitely from a fuel cell as long as outside supply of fuel is maintained. e.g., $H_2 - O_2$ *fuel cell.*

This cell was used as a primary source of electrical energy on the moon flights. The overall cell reaction produces water, which was used for drinking by the astronauts.

The half-reactions are

At anode

$$2H_2(g) + 4OH^-(aq) \longrightarrow H_2O(l) + 4e^-$$

At cathode

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

Overall cell reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Efficiency of the Fuel Cell

The efficiency of the fuel cell is the ratio of change in Gibbs energy ΔG to the heat of combustion ΔH and mathematically can be given as,

$$\eta = \frac{\Delta G}{\Delta H} \times 100$$

where,

η = thermodynamic efficiency of a fuel cell

ΔH = heat of combustion

ΔG = work done

$= -nFE^\circ_{cell}$.

Corrosion and its Prevention

Corrosion is basically an electrochemical phenomenon. A metal is oxidised by loss of electrons to oxygen and form metal oxide. *e.g.*, conversion of iron to rust $[Fe_2O_3 \cdot xH_2O]$, the tarnishing of silver (due to formation of Ag_2S), development of a green coating on copper and bronze.

Corrosion of iron, known as **rusting**, occurs in the presence of water and oxygen.

At anode $2Fe\ (s) \rightarrow 2Fe^{2+}(aq) + 4e^-$

At cathode $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O\ (l)$

The overall reaction,

$2Fe\ (s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O\ (l)$

Fe^{2+} ions further oxidised by atmospheric oxygen to Fe^{3+} ions and form hydrated ferric oxide $[Fe_2O_3 \cdot xH_2O]$.

$$4\,Fe^{2+} + O_2 + 4\,H_2O \longrightarrow 2Fe_2O_3(s) + 8H^+(aq)$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{hydrated ferric oxide (rust)}}{Fe_2O_3 \cdot xH_2O}$$

Rusting of iron can be prevented by the following methods

- Barrier protection through coating of paints or electroplating.
- Galvanisation or coating of surface with tin metal.
- By the use of antirust solutions.

Practice Zone

DAY 13

1. A current of 2 A is passed for 5 h through a molten tin salt to deposit 22.2 g tin. What is the oxidation state of tin in salt ? [At. wt. of Sn = 118.69 g]
(a) +2 (b) +5
(c) +3 (d) +4

2. The reaction,
$$\frac{1}{2}H_2(g) + AgCl(s) \rightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$
occurs in the galvanic cell
(a) $Ag|AgCl(s)|KCl(aq)||AgNO_3(aq)|Ag(s)$
(b) $Pt|H_2(g)|HCl\ (aq)||AgNO_3(aq)|Ag(s)$
(c) $Pt|H_2(g)|HCl(aq)||AgCl(s)|Ag(s)$
(d) $Pt|H_2(g)|KCl(aq)||AgCl(s)|Ag(s)$

3. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively
(a) H_2, O_2 (b) O_2, H_2
(c) O_2, Na (d) O_2, SO_2

4. When a lead storage battery is discharged,
(a) SO_2 is evolved
(b) lead sulphate is consumed
(c) lead is formed
(d) sulphuric acid is consumed

5. Of the following metals that cannot be obtained by electrolysis of the aqueous solution of their salts are
(a) Ag and Mg (b) Ag and Al
(c) Mg and Al (d) Cu and Cr

6. The standard reduction potential values of the three metallic cations X, Y and Z are 0.52, −3.03 and −1.18V respectively. The order of reducing power of the corresponding metals is
(a) $Y > Z > X$ (b) $X > Y > Z$
(c) $Z > Y > X$ (d) $Z > X > Y$

7. A gas X at 1atm is bubbled through a solution containing a mixture of 1MY^- and 1MZ^- at 25°C. If the order of reduction potentials is $Z > Y > X$, then
(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Y
(d) Y will reduce both X and Y

8. For the electrochemical cell, $M|M^+||X^-|X$,
$$E^\circ(M^+/M) = 0.44\ V \text{ and } E^\circ(X/X^-) = 0.33\ V$$
From this data, one can deduce that
(a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction.
(b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77$ V
(d) $E_{cell} = -0.77$ V

9. $\Lambda^0_{m\,(NH_4OH)}$ is equal to .... **[NCERT Exemplar]**
(a) $\Lambda^0_{m\,(NH_4OH)} + \Lambda^0_{m\,(NH_4Cl)} - \Lambda^0_{(HCl)}$
(b) $\Lambda^0_{m\,(NH_4Cl)} + \Lambda^0_{m\,(NaOH)} - \Lambda^0_{(NaCl)}$
(c) $\Lambda^0_{m\,(NH_4Cl)} + \Lambda^0_{m\,(NaCl)} - \Lambda^0_{(NaOH)}$
(d) $\Lambda^0_{m\,(NaOH)} + \Lambda^0_{m\,(NaCl)} - \Lambda^0_{(NH_4Cl)}$

10. When the sample of copper with the zinc impurity is to be purified by electrolysis, the appropriate electrodes are

	Cathode	Anode
(a)	pure zinc	pure copper
(b)	impure zinc	pure copper
(c)	impure zinc	impure sample
(d)	pure copper	impure sample

11. For the reactions,
$$C + O_2 \longrightarrow CO_2,\qquad \Delta H = -393\ kJ$$
$$2\,Zn + O_2 \longrightarrow 2\,ZnO,\qquad \Delta H = -412\ kJ$$
(a) carbon can oxidise zinc
(b) oxidation of carbon is not possible
(c) oxidation of zinc is not feasible
(d) zinc can oxidise carbon

12. The standard reduction potential for Fe^{2+}/Fe and Sn^{2+}/Sn electrodes are −0.44 and −0.14 V respectively. For the cell reaction; $Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$, the standard emf is
(a) +0.30 V (b) − 0.58 V (c) +0.58 V (d) − 0.30 V

13. For the reaction,
$$Zn(s) + Cu^{2+}(0.1M) \longrightarrow Zn^{2+}(1M) + Cu(s)$$
taking place in a cell, E°_{cell} is 1.10 V. E_{cell} for the cell will be $\left(2.303\frac{RT}{F} = 0.0591\right)$
(a) 1.80 V (b) 1.07 V (c) 0.82 V (d) 2.14 V

14. The Edison storage cell is represented as

$$Fe(s)|FeO(s)|KOH(aq)|Ni_2O_3(s)|NiO(s)|Ni(s)$$

the half-cell reactions are :

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-; \quad E^\circ = +0.40V$$

$$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-; E^\circ = -0.87V$$

What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?

(a) 127 kJ
(b) 245.11 kJ
(c) 90.71 kJ
(d) 122.55 kJ

15. The standard reduction potentials at 298 K for the following half reactions are given against each

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s); \quad -0.762 \text{ V}$$
$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s); \quad -0.740 \text{ V}$$
$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g); \quad 0.00 \text{ V}$$
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq); \quad 0.770 \text{ V}$$

Which is the strongest reducing agent?

(a) Zn (s) (b) Cs (s)
(c) H_2 (g) (d) $Fe^{3+}(aq)$

16. The electric charge for electrode deposition of one gram equivalent for substance is

(a) one ampere for one second
(b) 96500 C per second
(c) charge on one mole of electrons
(d) one ampere for an hour

17. Conductivity (unit siemen's) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is

(a) $S\ m\ mol^{-1}$ (b) Sm^2mol^{-1}
(c) $S^{-2}m^2mol$ (d) $S^2m^2mol^{-2}$

18. What will be the emf for the given cell?

$$Pt|H_2(p_1)|H^+(aq)|H_2(p_2)|Pt$$

(a) $\frac{RT}{F}\ln\frac{p_1}{p_2}$ (b) $\frac{RT}{2F}\ln\frac{p_1}{p_2}$
(c) $\frac{RT}{F}\ln\frac{p_2}{p_1}$ (d) None of these

19. In the cell reaction;

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s), \ E^\circ_{cell} = 0.46V$$

By doubling the concentration of Cu^{2+}, E_{cell} is

(a) doubled
(b) halved
(c) increases but less than double
(d) decreases by a small fraction

20. In the electrolytic cell, flow of electrons is from

(a) cathode to anode in solution
(b) cathode to anode through external supply
(c) cathode to anode through internal supply
(d) anode to cathode through internal supply

21. Which of the following statement is correct? **[NCERT Exemplar]**

(a) E_{Cell} and $\Delta_r G$ of cell reaction both are extensive properties
(b) E_{Cell} and $\Delta_r G$ of cell reaction both are intensive properties
(c) E_{Cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property
(d) E_{Cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property

22. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l); \quad E^\circ = 1.51 \text{ V}$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad E^\circ = 1.38 \text{ V}$$

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq); \ E^\circ = 0.77 \text{ V}$$

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq) \quad E^\circ = 1.40 \text{ V}$$

Identify the incorrect statement regarding the quantitative estimation of gaseous $Fe(NO_3)_2$.

(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

23. Electrolysis of molten NaCl leads to the formation of

(a) sodium and hydrogen
(b) sodium and oxygen
(c) hydrogen and oxygen
(d) sodium and chlorine

24. NaCl is manufactured by the electrolysis of brine solution. The products of the reaction are

(a) Cl_2 and H_2 (b) Cl_2 and Na – Hg
(c) Cl_2 and Na (d) Cl_2 and O_2

25. How many Faradays are required to reduce 1mol of BrO_3^- to Br^-?

(a) 3 (b) 5
(c) 6 (d) 4

26. The unit of ionic mobility is

(a) $m^{-2}V^{-1}s^{-1}$ (b) $m^2V^{-1}s^{-1}$
(c) $m^{-2}Vs^{-1}$ (d) $m^2V^{-2}s^{-1}$

27. The value of the reaction quotient, Q for the cell

$$Zn(s)|Zn^{2+}(0.01M)||Ag^+(1.25\ M)|Ag(s) \text{ is}$$

(a) 156 (b) 125
(c) 1.25×10^{-2} (d) 6.4×10^{-3}

Directions *(Q. Nos. 28 to 30) Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry.*

The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes.

(Atomic mass : Na =23, Hg=200;1F=96500C).

28. The total number of moles of chlorine gas evolved is

(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0

29. If the cathode is a Hg electrode, the maximum weight (in gram) of amalgam formed from this solution is

(a) 200 (b) 225 (c) 400 (d) 446

30. The total charge (in coulomb) required for complete electrolysis is

(a) 24125 (b) 48250 (c) 96500 (d) 193000

Directions *(Q. Nos. 31 and 32) The electrochemical cell shown below is a concentration cell.*

$\frac{M}{M^{2+}}$ *(saturated solution of a sparingly soluble salt, MX_2) $||\, M^{2+}$ ($0.00001\ mol\ dm^{-3} M$).*

The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298 K, is 0.059 V.

31. The solubility product (K_{sp} ; $mol^3\ dm^{-9}$) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.059$ V)

(a) 1×10^{-15} (b) 4×10^{-15}

(c) 1×10^{-12} (d) 4×10^{-12}

32. The value of ΔG (kJ mol^{-1}) for the given cell is (Take $1F = 96500\ C\ mol^{-1}$)

(a) – 5.7 (b) 5.7 (c) 11.4 (d) – 11.4

Directions *(Q. Nos. 33 to 38) Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

33. Statement I The standard reduction potential of M^{n+}/M electrode increases with increase in activity of M^{n+} ion.

Statement II The standard reduction potential is given by

$$E_{red} = E^{\circ}_{red} + \frac{0.059}{n} \log [M^{n+}]$$

34. Statement I Galvanised iron does not rust.

Statement II Zinc has more negative electrode potential than iron.

35. Statement I For the Daniell cell $Zn|Zn^{2+}||Cu^{2+}|Cu$ with $E_{cell} = 1.1V$, the application of opposite potential greater than 1.1V results into flow of electron from cathode to anode.

Statement II Zinc is deposited at anode and Cu is deposited at cathode.

36. Statement I Anode is the electrode at which oxidation occurs and cathode is the electrode at which reduction occurs.

Statement II Anode and cathode in electrochemical cells and electrolytic cells have opposite polarity.

37. An inaccurate ammeter and silver coulometer is connected in series in an electric circuit through which a constant direct current flows. If ammeter reads 0.6 ampere throughout one hour, the silver deposited on coulometer was found to be 2.16 g. What % error is in the reading of ammeter ? [Assume 100% current efficiency].

(a) 1% (b) 0.54%

(c) 0.06 % (d) 10%

38. Same quantity of charge is being used to liberate iodine (at anode) and a metal M (at cathode). The mass of metal M liberated is 0.617 g and the liberated iodine is completely reduced by 46.3 mL of 0.124 M sodium thiosulphate. What is the total time to bring this change if 10 A current is passed through solution of metal iodide?

(a) 55.4 s (b) 25.2 s

(c) 5.54 s (d) 16.8 s

39. What is the current efficiency of an electrodeposition of Cu metal from $CuSO_4$ solution in which 9.80 g copper is deposited by the passage of 5 A current for 2 h ?

(a) 50% (b) 82.8%

(c) 41.4 % (d) 100%

40. X g of silver is plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 h at a current of 8.46 A. What is the area of the tray if the thickness of silver plating is 0.00254 cm?

[Given, density of silver = 10.5 g cm^{-3}]

(a) $10.7 \times 10^4\ cm^2$

(b) $1.02 \times 10^4\ cm^2$

(c) $4.1 \times 10^3\ cm^2$

(d) $10.2 \times 10^4\ cm^2$

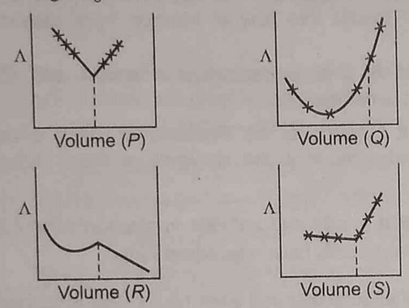
41. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to reaction,

$$2Cl^-(aq) + 2H_2O \longrightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

A direct current of 25 A with a current efficiency of 62% is passed through 20 L of NaCl solution (20% by weight). How long it take to produce 1 kg of Cl_2 ?

(a) 30.20 h (b) 12.17 h (c) 48.71 h (d) 14.61 h

42. $AgNO_3$ (*aq*) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) *versus* the volume of $AgNO_3$ is



(a) *P* (b) *Q* (c) *R* (d) *S*

43. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H_2 gas at the cathode is ($1F = 96500$ C mol^{-1})

(a) 9.65×10^4 s (b) 19.3×10^4 s
(c) 28.95×10^4 s (d) 38.6×10^4 s

44. The rusting of iron takes place as follows

$$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l); \quad E^\circ = +1.23 \text{ V}$$
$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \quad E^\circ = -0.44 \text{ V}$$

Calculate ΔG° for the net process.

(a) -322 kJ mol^{-1}
(b) -161 kJ mol^{-1}
(c) -152 kJ mol^{-1}
(d) -76 kJ mol^{-1}

45. $Zn \mid Zn^{2+}(a = 0.1M) \| Fe^{2+}(a = 0.01M) \mid Fe$.

The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(a) $10^{0.32/0.0591}$ (b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.295}$

AIEEE & JEE Main *Archive*

46. Electrode potentials (E°) are given below

$$Cu^+/Cu = +0.52 \text{ V}$$
$$Fe^{3+}/Fe^{2+} = +0.77 \text{ V}$$
$$\frac{1}{2}I_2(s)/I^- = +0.54 \text{ V}$$
$$Ag^+/Ag = +0.88 \text{ V}$$

Based on the above potentials strongest oxidizing agent will be **[JEE Main Online 2013]**

(a) Cu (b) Fe^{3+} (c) Ag^+ (d) I_2

47. A solution of copper sulphate ($CuSO_4$) is electrolysed for 10 min with a current of 1.5 A. The mass of copper deposited at the cathode (atomic mass of Cu = 63u) is **[JEE Main Online 2013]**

(a) 0.3892 g (b) 0.2938 g
(c) 0.2398 g (d) 0.3928 g

48. Given, $E^0_{\frac{1}{2}Cl_2/Cl} = 1.36$ V, $E^0_{Cr^{3+}/Cr} = -0.74$ V,

$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V, $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V

The correct order of reducing power of the species (Cr, Cr^{3+}, Mn^{2+} and Cl^-) will be **[JEE Main Online 2013]**

(a) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$ (b) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$
(c) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$ (d) $Cr^{3+} < Cl^- < Cr < Mn^{2+}$

49. Given, $E^0_{Cr^{3+}/Cr} = -0.74$ V; $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E^0_{Cl/Cl^-} = 1.36$ V

Based on the data given above, strongest oxidising agent will be **[IIT JEE Main 2013]**

(a) Cr^{3+} (b) Mn^{2+} (c) MnO_4^- (d) Cl^-

50. Four successive members of the first row transition elements are listed below with atomic numbers.

Which one of them is expected to have the highest $E^0_{M^{3+}/M^{2+}}$ value? **[IIT JEE Main 2013]**

(a) Mn ($Z = 25$) (b) Fe ($Z = 26$) (c) Co ($Z = 27$) (d) Cr ($Z = 24$)

51. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are -0.76, -0.23 and -0.44 V respectively. The reaction $X + Y^2 \longrightarrow X^2 + Y$ will be spontaneous when **[AIEEE 2012]**

(a) X = Ni, Y = Fe (b) X = Ni, Y = Zn
(c) X = Fe, Y = Zn (d) X = Zn, Y = Ni

52. The reduction potential of hydrogen half-cell will be negative if **[AIEEE 2011]**

(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M
(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M
(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M
(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

53. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 Sm^{-1}. If resistance of the 0.4 M solution of the same electrolyte is 260 Ω, its molar conductivity is [AIEEE 2011]

(a) 6250 $Sm^2\ mol^{-1}$
(b) $6.25 \times 10^{-4}\ Sm^2\ mol^{-1}$
(c) $625 \times 10^{-4}\ Sm^2\ mol^{-1}$
(d) 62.5 $Scm^2\ mol^{-1}$

54. Consider the following cell reaction,

$$2\,Fe(s) + O_2(g) + 4\,H^+\,(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l);$$
$$E^\circ = 1.67\ V$$

At $[Fe^{2+}] = 10^{-3}$ M, $P_{(O_2)} = 0.1$ atm and pH = 3, the cell potential at 25°C is

(a) 1.47 V (b) 1.77 V
(c) 1.87 V (d) 1.57 V

55. The correct order of $E^\circ_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is [AIEEE 2010]

(a) Mn > Cr > Fe > Co (b) Cr > Fe > Mn > Co
(c) Fe > Mn > Cr > Co (d) Cr > Mn > Fe > Co

56. Given, $E^\circ_{Fe^{3+}/Fe} = -0.036$ V, $E^\circ_{Fe^{2+}/Fe} = -0.439$ V

The value of standard electrode potential for the charge, $Fe^{3+}\,(aq) + e^- \longrightarrow Fe^{2+}\,(aq)$ will be [AIEEE 2009]

(a) – 0.072 V (b) 0.385 V
(c) 0.770 V (d) – 0.270 V

57. Given, $E^0_{Cr^{3+}/Cr} = -0.72$ V; $E^\circ_{Fe^{2+}/Fe} = -0.42$ V

The potential for the cell

$Cr \mid Cr^{3+}(0.1M) \mid\mid Fe^{2+}(0.01M) \mid Fe$ is [AIEEE 2009]

(a) – 0.339 V (b) – 0.26 V (c) 0.26 V (d) 0.339 V

58. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.2 M solution of the electrolyte will be [AIEEE 2006]

(a) 124×10^{-4} S m^2 mol^{-1} (b) 1240×10^{-4} S m^2 mol^{-1}
(c) 1.24×10^{-4} S m^2 mol^{-1} (d) 12.4×10^{-4} S m^2 mol^{-1}

59. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (atomic mass = 27u; 1 F = 96500 C). The cathode reaction is

$$Al^{3+} + 3e^- \rightarrow Al$$

To prepare 5.12 kg of aluminium metal by this method required electricity will be [AIEEE 2005]

(a) 5.49×10^1C (b) 5.49×10^4C
(c) 1.83×10^7C (d) 5.49×10^7C

60. The standard emf of a cell, involving one electron change is found to be 0.591V at 25°C. The equilibrium constant of the reaction is (1F = 96500 C mol^{-1}) [AIEEE 2004]

(a) 1.0×10^1 (b) 1.0×10^5
(c) 1.0×10^{10} (d) 1.0×10^{30}

Answers

1. (a)	**2.** (c)	**3.** (a)	**4.** (d)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (b)	**9.** (b)	**10.** (d)
11. (a)	**12.** (d)	**13.** (b)	**14.** (b)	**15.** (a)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (d)	**20.** (d)
21. (c)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (c)	**26.** (b)	**27.** (d)	**28.** (b)	**29.** (d)	**30.** (d)
31. (b)	**32.** (d)	**33.** (a)	**34.** (a)	**35.** (a)	**36.** (b)	**37.** (d)	**38.** (a)	**39.** (b)	**40.** (b)
41. (c)	**42.** (d)	**43.** (b)	**44.** (a)	**45.** (b)	**46.** (c)	**47.** (b)	**48.** (a)	**49.** (c)	**50.** (c)
51. (d)	**52.** (c)	**53.** (b)	**54.** (d)	**55.** (a)	**56.** (c)	**57.** (a)	**58.** (d)	**59.** (d)	**60.** (c)

Hints & Solutions

1. Equivalents of tin $= \dfrac{i \cdot t}{96500}$

or $\dfrac{22.2}{\text{Eq. wt.}} = \dfrac{2 \times 5 \times 60 \times 60}{96500}$

Eq. wt. = 59.5

$\therefore$ Valency of tin $= \dfrac{\text{At. wt.}}{\text{Eq. wt.}} = \dfrac{118.69}{59.5} \approx 2$ (an integer)

Thus, $Sn^{2+} + 2e^- \longrightarrow Sn$

2. H_2 undergoes oxidation and $AgCl(Ag^+)$ undergoes reduction. Therefore, cell may be represent, as

$$Pt \mid H_2(g) \mid HCl(aq) \mid\mid AgCl(s) \mid Ag(s).$$

3. At cathode, H^+ is more easily reduced than Na^+ to give H_2 and at anode, OH^- oxidised to give O_2.

4. When a lead storage battery is discharged, H_2SO_4 is consumed.

5. Mg and Al have lower reduction potentials than H_2O. Hence, H_2O is reduced more easily to give H_2 gas at the cathode.

6. Greater the reduction potential, less is the reducing power.

7. Greater the reduction potential, stronger is the oxidising agent. Hence, *Y* is stronger oxidising agent than *X* but weaker than *Z*.

8. EMF for (b) is +ve $= E^0_{red}(M) + E^0_{oxi}(X)$

$= 0.44 + (-0.33) = 0.11$V

9. According to Kohlrausch's law

$\Lambda^{o}_{m(NH_4Cl)} + \Lambda^{o}_{m(NaOH)} = \Lambda^{o}_{m(NH_4OH)} + \Lambda^{o}_{m(NaCl)}$

or, $\Lambda^{o}_{m(NH_4OH)} = \Lambda^{o}_{m(NH_4Cl)} + \Lambda^{o}_{m(NaOH)} - \Lambda^{o}_{m(NaCl)}$

10. Impure sample is made the anode and pure copper acts as the cathode.

11. Zinc can lose electrons to form Zn^{2+} and carbon can gain electrons to form carbide ion (C^{4-}).

Thus, zinc is oxidised by carbon.

12. $E^{\circ}_{cell} = E^{\circ}_{oxi}(Sn) + E^{\circ}_{red}(Fe) = +0.14 + (-0.44) = -0.30$ V

13. $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\left(\frac{Zn^{2+}}{Cu^{2+}}\right)$

$= 1.10 - \frac{0.0591}{2}\log\frac{1}{0.1} = 1.07$ V

14. Given, $E^{\circ}_{FeO/Fe} = -0.87V$; and $E^{\circ}_{Ni_2O_3/NiO} = 0.40V$

$\therefore$ $E^{\circ}_{Fe/FeO} = +0.87$ V

and $E^{\circ}_{NiO/Ni_2O_3} = -0.40$ V

Since E°_{oxi} for Fe / FeO > E°_{oxi} for NiO / Ni_2O_3

$\therefore$ Redox changes

At anode $Fe + 2OH^- \longrightarrow FeO(s) + H_2O(l) + 2e^-$

At cathode $Ni_2O_3(s) + H_2O(l) + 2e^- \longrightarrow 2NiO(s) + 2OH^-$

Overall reaction

$Fe(s) + Ni_2O_3(s) \longrightarrow FeO(s) + 2NiO(s)$

Hence, $E^{\circ}_{cell} = E^{\circ}_{anode} - E^{\circ}_{cathode}$

$= 0.87 - (-0.40)$

or $E^{\circ}_{cell} = 1.27$ V

and $\Delta G^{\circ} = nFE^{\circ}_{cell}$

$= 2 \times 1.27 \times 96500$

$= 245110$ J $= 245.11$ kJ

15. Less the reduction potential, weaker is the oxidising agent or stronger is the reducing agent.

16. One gram equivalent is deposited by 1F *i.e.*, charge on 1 mole electrons.

17. $\text{Conductivity} = \kappa \times \frac{\text{area} \times \text{conc.}}{\text{length}}$

or $\kappa = \frac{\text{conductivity} \times \text{length}}{\text{area} \times \text{conc.}} = \frac{S \times m}{m^2 \times mol\ m^{-3}}$

$= Sm^2mol^{-1}$

18. RHS, $2H^+ + 2e^- \rightleftharpoons H_2(p_2)$

LHS, $H_2(p_1) \rightleftharpoons 2H^+ + 2e^-$

Overall reaction $H_2(p_1) \rightleftharpoons H_2(p_2)$

$E = E^{\circ} - \frac{RT}{nF}\ln\frac{p_2}{p_1}$

$= 0 - \frac{RT}{2F}\ln\frac{p_2}{p_1} = \frac{RT}{2F}\ln\frac{p_1}{p_2}$

19. $E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln\frac{[Cu^{2+}]}{[Ag^+]^2}$

Doubling (Cu^{2+}) decreases the emf by a small fraction.

20. In electrolytic cell, flow of electron is possible from anode to cathode through internal supply.

21. E_{Cell} is an intensive property because it does not depend on the system size or the amount of material in the system while $\Delta_r G$ of a cell reaction is an extensive property because it depends on the amount of material in the system.

22. The reaction between MnO_4^- and HCl may be represented as follows:

$2MnO_4^-(aq) + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$

Thus, on the basis of this reaction following electrochemical cell will be represented

Pt $Cl_2(g)$ (1 atm) | Cl^- (aq) || $MnO_4^-(aq)$ | $Mn^{2+}(aq)$

Since, $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

From given data, $E^{\circ}_{cell} = 1.51 - 1.40 = 0.11$ V

E^- cell is positive, hence ΔG° is negative. Thus, above cell reaction is feasible but MnO_4^- ion can oxidise, Fe^{2+} to Fe^{3+} and Cl^- to Cl_2 in aqueous medium also. Therefore, for quantitative estimation of aqueous $Fe(NO_3)_2$ it is not a suitable reagent.

23. Electrolysis of molten NaCl gives Na and Cl_2.

24. Electrolysis of brine solution (saturated NaCl solution) gives Cl_2 and H_2.

25. $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$

$\therefore$ Number of Faraday required = 6

26. Ionic velocity is in ms^{-1} and electric field strength is in Vm^{-1}, so ionic mobility is $(ms^{-1})/Vm^{-1}$ or $m^2V^{-1}s^{-1}$.

27. The cell reaction is

$Zn(s) \longrightarrow Zn^{2+}(0.01M) + 2e^-$

$[Ag^+(1.25M) + e^- \longrightarrow Ag(s)] \times 2$

$Zn(s) + 2Ag^+(1.25)M \longrightarrow Zn^{2+}(0.01M) + 2Ag(s)$

$Q = \frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{0.01}{(1.25)^2} = 6.4 \times 10^{-3}$

28. 4.0 M NaCl, 500 mL (0.5L)

Moles of NaCl $= 4 \times 0.5 = 2$

2 mol NaCl $\equiv$ 2 mol Cl^-

$\underset{2\ mol}{2Cl^-} \longrightarrow \underset{1\ mol}{Cl_2}$

29. $\underset{2\ mol}{Na + Hg} \longrightarrow \underset{2\ mol}{Na-Hg}$

2 moles of amalgam $= 23 \times 2 + 2 \times 200 = 446$ g

30. $2Cl^- \longrightarrow Cl_2 + 2e^-$

Total charge $= 2 \times 96500C = 193000C$

31. The solubility equilibrium for MX_2 is

$$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2X^-(aq)$$

Solubility product, $K_{sp} = [M^{2+}][X^-]^2$

$$= 10^{-5} \times (2 \times 10^{-5})^2$$
$$= 4 \times 10^{-15}$$

($\because$ In saturated solution of MX_2, $[X^-] = 2[M^{2+}]$)

32. $\Delta G = -nFE = \dfrac{-2 \times 0.059 \times 96500}{1000}$ kJ $= -11.4$ kJ mol^{-1}

33. Both the statements are true and statement II is the correct explanation of statement I.

34. Galvanised iron *i.e.*, iron coated with zinc does not rust easily as zinc has more negative electrode potential (– 0.76 V) than iron.

35. In a Daniell cell, $Zn|Zn^{2+}||Cu^{2+}|Cu$

$$E_{cell} = 1.1V$$

The reaction of oxidation half-cell is

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The reaction of reduction half-cell is

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

So, $\quad Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

because Zn is oxidised, it is deposited at anode and Cu is reduced, so it is deposited at cathode. If the opposite potential is greater than 1.1 V, then the electrons flow from cathode to anode. So, both the statements are true and correct explanation.

36. Statement II is not the correct explanation of statement I, but both are facts.

37. $$\frac{\text{wt.}}{\text{Eq. wt.}} = \frac{i \cdot t}{96500}$$

or $$\frac{2.16}{108} = \frac{i \times 60 \times 60}{96500}$$

or $$i = 0.54\text{ A}$$

Error in reading of ammeter $= 0.60 - 0.54 = 0.06$ A

$\therefore$ $$\%\text{ error} = \frac{0.06}{0.60} \times 100 = 10\%$$

38. Eq. of metal = Eq. of iodine = Eq. of hypo $= \dfrac{it}{96500}$

$\therefore$ $$\frac{0.617}{\text{Eq. wt.}} = \frac{46.3}{1000} \times 0.124 \times 1$$

$[\because 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$ and Eq. wt. $= \dfrac{\text{Mol. wt.}}{2}$ h

$\therefore$ Eq. wt. $= 107.47]$

Hence, $$\frac{0.617}{107.47} = \frac{10 \times t}{96500}$$
$$t = 55.4\text{ s}$$

39. $$\frac{\text{wt.}}{\text{Eq. wt.}} = \frac{it}{96500}$$

or $$\frac{9.8}{63.5/2} = \frac{i \times 2 \times 60 \times 60}{96500}$$

$\therefore$ $$i = 4.14\text{ A}$$

$\therefore$ Current efficiency $= \dfrac{\text{theoretical value of } i}{\text{practical value of } i} \times 100$

$$= \frac{4.14}{5} \times 100 = 82.8\%$$

40. $$\frac{w_{Ag}}{\text{Eq. wt.}_{Ag}} = \frac{it}{96500}$$

or $$w_{Ag} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500}$$

or $$w_{Ag} = 272.18\text{ g.}$$

Volume of Ag $= \dfrac{272.18}{10.5} = 25.92$ cm^3

$\therefore$ Surface area $= \dfrac{25.92}{0.00254} = 1.02 \times 10^4$ cm^2

41. The redox changes are

At anode $\quad 2Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode $\quad 2e^- + 2H_2O \longrightarrow 2OH^- + H_2$

Now $$\frac{w}{\text{Eq. wt.}} = \frac{it}{96500}$$

Given, $\quad w_{Cl_2} = 10^3$ g, Eq. wt.$_{Cl_2} = 35.5$ and

$$i = \frac{25 \times 62}{100} = 15.5\text{ A}$$

Hence, $$t = \frac{10^3 \times 96500}{35.5 \times 15.5}$$
$$= 175374.83\text{ s}$$
$$= 48.71\text{ h}$$

42. As $AgNO_3$ is added to solution, KCl will be displaced according to following reaction.

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

For every mole of KCl displaced from solution, one mole of KNO_3 comes in solution resulting in almost constant conductivity. As the end point is reached, added $AgNO_3$ remain in solution increasing ionic concentration, hence conductivity increases. Hence, option (d) is correct.

43. $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

For 0.01 mol H_2, 0.02 mole of electrons are consumed.

Charge required $= 0.02 \times 96500$ C $= i \times t$

Time required $= \dfrac{0.02 \times 96500}{10 \times 10^{-3}}$

$$= 19.3 \times 10^4\text{ s}$$

44. Reactions,

(i) $Fe(s) \rightarrow Fe^{2+} + 2e^-, E^\circ = +0.44V$

and $\quad \Delta G_1^\circ = -nE^\circ F = -2 \times 0.44 \times F$

(ii) $2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O(l), E^\circ = +1.23V$

and $\quad \Delta G_2^\circ = -2 \times (+1.23) \times F$

Net reaction

$$Fe(s) + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O\,(l)$$

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$
$$= -2\times(+0.44) + (-2\times 1.23)$$
$$= -0.88 - 2.46$$
$$= -3.34\,F = -3.34\times 96500\,J$$
$$= -322.31\,kJ$$
$$\approx -322\,kJ$$

45. For cell $Zn\,|\,Zn^{2+}(a = 0.1M)\,||\,Fe^{2+}(a = 0.01M)\,|\,Fe$

The half cell reactions are

(i) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

(ii) $Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$

$$Zn(s) + Fe^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Fe(s)$$

On applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log_{10}\frac{[Zn^{2+}]}{[Fe^{2+}]}$$

$$0.2905 = E^\circ_{cell} - \frac{0.0591}{2}\log_{10}\frac{0.1}{0.01}$$

$$0.2905 = E^\circ_{cell} - 0.0295\times\log_{10}10$$

$$0.2905 = E^\circ_{cell} - 0.0295\times 1$$

$$\therefore \quad E^\circ_{cell} = 0.2905 + 0.0295 = 0.32V$$

At equilibrium, ($E_{cell} = 0$)

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log_{10}K_c$$

$$\therefore \quad 0 = E^\circ_{cell} - \frac{0.0591}{n}\log_{10}K_c$$

$$\text{or} \quad E^\circ_{cell} = \frac{0.0591}{2}\log_{10}K_c$$

$$0.32 = \frac{0.0591}{2}\log_{10}K_c \quad \text{or } K_c = 10^{0.32/0.0295}$$

46. More positive value of electrode potential represents that Ag^+ is the strongest oxidizing agent.

47. From Faraday's first law,

Mass of Cu deposited,

$$w = Zit = \frac{E}{96500}\cdot i\cdot t$$
$$= \frac{63}{2\times 96500}\times 1.5\,A\times 10\times 60\,s$$
$$= 0.2938g$$

48. More the negative value of reduction potential, higher the reducing power. Thus, the correct order of reducing tendency is

$$\underset{(1.51\,V)}{Mn^{2+}} < \underset{(1.36\,V)}{Cl^-} < \underset{(1.33\,V)}{Cr^{3+}} < \underset{(-0.74\,V)}{Cr}$$

49. As per data mentioned MnO_4^- is strongest oxidising agent as it has maximum SRP value.

50. $E^0_{Mn^{+3}/Mn^{+2}} = 1.57\,V$, $E^\circ_{Fe^{+3}/Fe^{+2}} = 0.77\,V$

$E^0_{Co^{+3}/Co^{+2}} = 1.97\,V$; $E^\circ_{Cr^{+3}/Cr^{+2}} = -0.41$

51. A cell reaction is spontaneous if $\Delta G^\circ < 0$

Since, $\Delta G^\circ = -nFE^\circ_{cell}$

Thus, $E^\circ_{cell} > 0$

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

red

$$X + Y^{2+} \longrightarrow X^{2+} + Y$$

ox

(a) If $X = Ni$, $Y = Fe$

$$Ni + Fe^{2+} \longrightarrow Ni^{2+} + Fe$$
$$E^\circ_{Ni/Ni^{2+}} = +\,0.23\,V$$
$$E^\circ_{Fe^{2+}/Fe} = -\,0.44\,V$$

Thus, $$E^\circ_{cell} = E^\circ_{Ni/Ni^{2+}} + E^\circ_{Fe^{2+}/Fe}$$
$$= -\,0.21\,V$$
$$E^\circ_{cell} < 0$$

(b) If $X = Ni$, $Y = Zn$

$$Ni + Zn^{2+} \longrightarrow Ni^{2+} + Zn$$
$$E^\circ_{Ni/Ni^{2+}} = 0.23\,V$$
$$E^\circ_{Zn^{2+}/Zn} = -\,0.76\,V$$
$$\therefore \quad E^\circ_{cell} = -\,0.53\,V$$
$$E^\circ_{cell} < 0$$

(c) $X = Fe$, $Y = Zn$

$$Fe + Zn^{2+} \longrightarrow Fe^{2+} + Zn$$
$$E^\circ_{cell} = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Zn^{2+}/Zn}$$
$$= 0.44 - 0.76 = -\,0.32\,V$$
$$E^\circ_{cell} < 0$$

(d) $X = Zn$, $Y = Ni$

$$Zn + Ni^{2+} \longrightarrow Zn^{2+} + Ni$$
$$E^\circ_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{Ni^{2+}/Ni}$$
$$= 0.76 - 0.23 = 0.53\,V$$
$$E^\circ_{cell} > 0 \text{ (spontaneous)}$$

52. Reduction hydrogen half-cell is

$$H^+(xM)\,|\,Pt(H_2)$$

Half-cell reaction is

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

Reaction quotient $= Q = p_{H_2}/[H^+]^2, n = 2$

$$E_{red} = E^{\circ}_{red} - \frac{0.0591}{n} \log Q$$

$$= 0 - \frac{0.0591}{2} \log Q$$

	p_{H_2}	$[H^+]$	$Q = \frac{p_{H_2}}{[H^+]^2}$	E_{red}
(a)	1 atm	2.0 M	0.25	+ve
(b)	1 atm	1.0 M	1.0	0
(c)	2 atm	1.0 M	2.0	–ve
(d)	2 atm	2.0 M	0.50	+ve

53. Specific conductance = conductance × cell constant

$$1.3 = \frac{1}{50} \times \text{cell constant}$$

$\therefore$ Cell constant $= 1.3 \times 50\ m^{-1} = 65\ m^{-1} = \left(\frac{65}{100}\right) cm^{-1}$

$$\text{Molar conductivity} = \frac{1000 \times \text{conductance} \times \text{cell constant}}{\text{molarity}}$$

$$= \frac{1000}{0.4} \times \frac{1}{260} \times \frac{65}{100}$$

$$= 6.25\ \text{Scm}^2\ \text{mol}^{-1}$$

$$= 6.25 \times 10^{-4}\ \text{Sm}^2\ \text{mol}^{-1}$$

54. The half reactions are,

$$[Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-] \times 2$$

$$O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O$$

$$2Fe(s) + O_2(g) + 4H^+ \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$E = E^{\circ} - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4\ (0.1)} = 1.57\ V$$

55. Usually across the first transition series, the negative values for standard electrode potential decrease except for Mn due to stable d^5-configuration.

So, correct order of E° is Mn > Cr > Fe > Co

56. Given, $Fe^{3+} + 3e^- \longrightarrow Fe;\ E^{\circ}_1 = -0.036\ V$ ...(i)

$Fe^{2+} + 2e^- \longrightarrow Fe;\ E^{\circ}_2 = -0.439\ V$ ...(ii)

We need to calculate

$Fe^{3+} + e^- \longrightarrow Fe^{2+};\ E^{\circ}_3 = ?$ ...(iii)

We can obtain then (iii) be subtracting (ii) from (i) but we can not obtain E°_3 that way because electrode potential is intensive property. That's when we determine E°_3 calculating

$$\Delta G_3 = \Delta G_1 - \Delta G_2$$

(ΔG is an extensive property)

$$\Delta G_3 = 3 \times 0.036 - 2 \times 0.439$$

$$nFE^{\circ}_3 = (0.108 - 0.878)\,F$$

$$-1 \times F \times E^{\circ}_3 = -0.770$$

$$E^{\circ}_3 = 0.770\ F$$

57. $E^{\circ}_{cell} = -0.42 - (-0.72) = 0.30\ V$

The cell reaction is

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe,\ n = 6$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6} \times 4 = 0.30 - 0.04 = 0.26\ V$$

58. Where, $R = 100\ \Omega$

$$\kappa = \frac{1}{R}\left(\frac{l}{a}\right)$$

$\frac{l}{a}$ (cell constant) $= 1.29 \times 100\ m^{-1} = 129\ m^{-1}$

$R = 520\ \Omega;\ C = 0.2\ M$

μ (molar conductivity) = ?

$\mu = \kappa \times V$

Hence, $\mu = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6} m^3$

$= 12.4 \times 10^{-4}\ \text{Sm}^2\ \text{mol}^{-1}$

59. $Al^{3+} + 3e^- \rightarrow Al$

$w = ZQ$

where, w = amount of metal

$= 5.12\text{kg} = 5.12 \times 10^3 g$

Z = electrochemical equivalent

$$= \frac{\text{equivalent weight}}{96500}$$

$$= \frac{\text{atomic mass}}{\text{number of electrons} \times 96500}$$

$$= \frac{27}{3 \times 96500}$$

$$5.12 \times 10^3 = \frac{27}{3 \times 96500} \times Q$$

$$Q = \frac{5.12 \times 10^3 \times 3 \times 96500}{27} C = 5.49 \times 10^7 C$$

60. Relation between K_{eq} and E°_{cell} is

$$E^{\circ}_{cell} = \frac{2.303RT}{nF} \log K_{eq}$$

$$E^{\circ}_{cell} = \frac{0.0591}{n} \log K_{eq} \text{ (at 298K)}$$

$$0.591 = \frac{0.0591}{1} \log K_{eq}$$

$\therefore$ $\log K_{eq} = 10$

$\therefore$ $K_{eq} = 1 \times 10^{10}$

Day 14

Chemical Kinetics

Day 14
Outlines ...

Concept of Chemical Kinetics

Chemical kinetics is the branch of chemistry which addresses the rate of chemical reaction. It include the investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition rates.

Rate of a Reaction

The rate or speed or velocity of a reaction is the rate of change of concentration of reactants or products in unit time. When a reaction occurs, the concentration of reactants starts decreasing while the concentration of products starts increasing.

$$A \rightarrow B$$

Rate of reaction can be defined in two ways

(i) **Average rate of reaction,**

$$r_{av} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

The units of rate of a reaction are mol L^{-1} s^{-1} or mol L^{-1} min^{-1}.

(ii) **Instantaneous rate of reaction** (r_{inst}) can be calculated from r_{av} in the limit $\Delta t \to 0$ and is represented as

$$r_{inst} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

In general for a reaction, $aA + bB \longrightarrow cC + dD$

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Factors Affecting the Rate of Reaction

The rate of chemical reactions depends upon a number of factors such as

(i) Concentration
(ii) Nature of reactants
(iii) Temperature
(iv) Presence of catalyst
(v) Exposure to radiations

Rate Constant and Rate Law

According to law of mass action, The rate of a chemical reaction is directly proportional to the product of effective concentrations of reacting species, each raised to a suitable power may or may not be equal to the respective stoichiometric coefficients. For a general reaction, $aA + bB \longrightarrow$ Products; Rate $= k[A]^a[B]^b$

where, k is **rate constant** or **velocity constant** or **specific reaction rate.**

The above expression is called **rate law** as it describes the functional dependence of the reaction rate upon concentration of various reactants. Rate law cannot be deduced from balanced equation. It is obtained experimentally.

Unit of k in terms of concentration, Rate $= k[A]^x$

where, x = order of reaction $\frac{\text{mol}}{\text{L} \cdot \text{time}} = k\left[\frac{\text{mol}}{\text{L}}\right]^x$

$\therefore$ Unit of $k = (\text{mol})^{1-x} \cdot \text{L}^{x-1}\text{s}^{-1}$

Order of Reaction

The sum of the coefficients (or powers) of the reacting species that are involved in the rate law expression for the reaction represents the order of the reaction.

For the reaction, $aA + bB \longrightarrow cC + dD$

According to law of mass action, $\frac{dx}{dt} = k[A]^a[B]^b$

According to rate law (rate equation), $\frac{dx}{dt} = k[A]^\alpha[B]^\beta$

Overall order of reaction $= \alpha + \beta$

The order of reaction can only be determined by experiments.

Zero Order Reaction

Reactions in which the concentration of reactants do not change with time and the concentration rates remain constant throughout are said to be zero order reactions.

$$k = -\frac{[C_t] - [C_0]}{t}$$

where, C_0 = initial concentration of the reactant

C_t = concentration of the reactant at any time t

$$t_{1/2} = \frac{C_0}{2k}$$

where, k = rate constant, $t_{1/2}$ = half-life period

For a zero order reaction, half-life period is directly proportional to the initial concentration of reactant and units of rate constant and rate of reaction are same, i.e., mol $\text{L}^{-1}\,\text{s}^{-1}$.

First Order Reaction

The **first order reaction** is defined as "The reaction in which the reaction rate is determined by the change of one concentration term of the reactant only", *e.g.*, In the reaction

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)}$$

where, t = time, a = initial concentration

k = rate constant,

$(a–x)$ = concentration of a after time 't'

$$t_{1/2} = \frac{0.693}{k}, \quad t_{1/2} = \text{half-life period}$$

For any reaction, half life period $t_{1/2} \propto \frac{1}{a^{n-1}}$

where, a = initial concentration, n = order of reaction

Rate equation for first order gas phase reactions

$$k = \frac{2.303}{t}\log\frac{p_0}{p_0 - p_t}$$

where, p_0 = initial pressure
p_t = pressure after time t

In a sequence of reactions $A \xrightarrow{k_A} B \xrightarrow{k_B} C$ [B] is maximum when,

$$t = \frac{2.303}{(k_A - k_B)}\log_{10}\left(\frac{k_A}{k_B}\right)$$

Second Order Reaction

The reaction is said to be of **second order** if its reaction rate is determined by the variation of two concentration terms of reactants. It can be represented as

$$k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$, when both the reactants are same.

Transformation of O_3 into O_2 is an example of negative order reaction order w.r.t. O_2 is −1.

Third Order Reactions

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

$$-\frac{\Delta R}{\Delta t} \text{ or } \frac{\Delta P}{\Delta t} = k[A]^3 \quad \text{(For } 3P \rightarrow \text{product)}$$

or $$-\frac{\Delta R}{\Delta t} \text{ or } \frac{\Delta P}{\Delta t} = k[A][B][C] \quad \text{(For } A + B + C \rightarrow \text{product)}$$

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

$$\begin{array}{lccccr} & A & + B & + C & \longrightarrow \text{Product} & \\ & a & a & a & 0 & \text{(initially)} \\ & (a-x) & (a-x) & (a-x) & x & \text{(after time } t) \end{array}$$

The rate constant, k for the reaction is given by

$$k = \frac{1}{t}\cdot\frac{x(2a-x)}{2a^2(a-x)^2}$$

The units of rate constant for third order reaction are $L^2\ mol^{-2}\ time^{-1}$

Reactions of **third** and **higher orders** are rare, but some examples of 3rd order reactions are definitely seen. This is due to the fact that the chances of three molecules of coming to a single point simultaneously, *i.e.*, probability of trimolecular collisions is much less as compared to unimolecular or bimolecular collisions.

Examples of third order reactions are

(i) $2NO + O_2 \longrightarrow 2NO_2$
(ii) $2NO + Cl_2 \longrightarrow 2NOCl$
(iii) $2NO + Br_2 \longrightarrow 2NOBr$
(iv) Reaction between silver acetate and sodium formate i.e.,

$$2CH_3COOAg + HCOONa \longrightarrow 2Ag + CO_2 + CH_3COOH + CH_3COO^-Na^+$$

Negative Order Reactions

Sometimes the rate of reaction decreases as the concentration of one of the constituent is increased, *e.g.*, transformation of ozone into oxygen, *i.e.*, $2O_3 \longrightarrow 3O_2$

$$\text{rate} = -\frac{1}{2}\frac{d}{dt}[O_3] = K\frac{[O_3]^2}{[O_2]} = K[O_3]^2[O_2]^{-1}$$

Because the reaction involves two steps as

$$O_2 + O \xrightarrow{\text{Fast}} O_3 \quad \text{...(i)}$$

$$O_3 + O \xrightarrow{\text{Slow}} 2O_2 \quad \text{...(ii)}$$

Reaction (ii) gives the rate law as it is the slow step.

$$\text{Rate} = k[O_3][O] \quad \text{...(iii)}$$

Since [O] is an intermediate species and takes part in the fast reaction, so

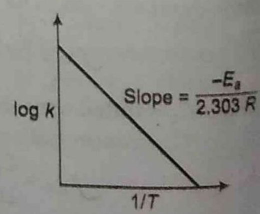
$$K' = \frac{[O_3]}{[O_2][O]} \text{ or } [O] = \frac{O_3}{K'[O_2]}$$

On putting the value of [O] in rate law, we get,

$$\text{Rate} = \frac{k[O_3][O_3]}{k'[O_2]} = k_1[O_3]^2[O_2]^{-1} \quad [\text{where}, k_1 = k \cdot K']$$

Effect of Temperature on Rate of Reactions

It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled. The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius Equation**



$$k = Ae^{-E_a/RT} \quad \text{...(i)}$$

Here,

k = rate constant
A = Arrhenius constant or frequency factor
E_a = activation energy

On taking log on both sides in Eq. (i), we get

$$\log_{10} k = \frac{-E_a}{2.303RT} + \log_{10} A; \log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

- *Photosensitisers are the substances which when added to a reaction mixture helps to initiate the photochemical reaction without undergoing any chemical change.*
- *Arrhenius equation is based on two theories of reaction rates, collision theory and transition state theory. Since, $k = Ae^{-E_a/RT}$ and E_a is always positive, thus, k always increases with temperature. Due to this rate always increases with temperature whether the reaction is exothermic or endothermic.*
- *When $T \longrightarrow \infty$, $k = Ae^0$ or rate constant becomes equal to Arrhenius or frequency factor. (For free radical reaction $E_a = 0$, thus $k = A$ and k becomes independent of temperature).*

Temperature Coefficient

(i) It is the ratio of two rate constants differing by a temperature of 10 K.

(ii) For most of the reactions, if temperature rises from 298 K to 308 K, the rate constant almost gets doubled.

(iii) The value of temperature coefficient for most of the reactions lies between 2 to 3.

Molecularity

Molecularity is defined as the number of ions or molecules or atoms taking part in an elementary process of the reaction mechanism.

In case of simple reactions, known as elementary reactions, the molecularity is simply the sum of molecules of different reactants as represented by balanced equation, *e.g.*,

(i) **Unimolecular reaction** $N_2O_4(g) \longrightarrow 2NO_2(g)$

(ii) **Bimolecular reaction** $2HI(g) \longrightarrow H_2(g) + I_2(g)$

(iii) **Trimolecular reaction** $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

In case of complex reactions, *i.e.*, the reactions involving more than one step the rate determining step is slowest step. The atoms, molecules or ions participating in this step decide the molecularity, *e.g.*, $HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2$

This reaction takes place through following steps

$$HBrO_3 + HI \xrightarrow{\text{Slow}} HBrO_2 + HIO$$
(rate determining step)

$$HBrO_2 + 4HI \xrightarrow{\text{Fast}} HBr + 2H_2O + 2I_2$$

$$HIO + HI \xrightarrow{\text{Fast}} H_2O + I_2$$

Hence, two molecules participate in slowest step, the reaction is bimolecular type.

- *Molecularity is always a whole number. It can never be zero, negative or fraction whereas order of a reaction may be whole number, fractional, zero or even negative.*
- *Order of reaction may change with the condition such as pressure, temperature etc., whereas molecularity does not change.*

Pseudo Unimolecular Reaction

When one of the reactants is present in large excess, the second order reaction confirms to the first order and is called pseudo unimolecular reaction, *e.g.*, hydrolysis of ester in acidic medium

$$CH_3COOC_2H_5 \xrightarrow{H^+/H_2O} CH_3COOH + C_2H_5OH$$

This is also known as pseudo first order reaction.

Rate $= k[\text{ester}]$

Collision Theory

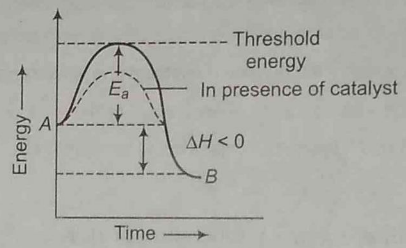
- The collisions among the reacting species which result in the products are known as the effective collisions.
- The species taking part in the chemical reaction must have a certain minimum energy known as threshold energy ($E°$).

Threshold energy = activation energy (E_a) + average energy of molecules.

Activation Energy

Activation energy is represented by E_a. It is constant for a particular reaction. Activation energy does not depend on temperature, volume, pressure etc., but gets affected by the presence of catalyst.

Catalyst increases the rate of reaction by providing alternative path of lower activation energy to the reactants. $A \longrightarrow B$ $\Delta H < 0$, i.e., exothermic reaction



- Enzyme catalysed reaction are faster than the metal catalysed reaction because they have lower activation energy.
- Threshold energy is independent of temperature but E_a shows temperature dependence.

Calculation of Activation Energy

Activation energy can be calculated by knowing the rate constants at two different temperatures, assuming that E_a and A remains constant.

Taking log of both the sides in Arrhenius equation, we get

$$\ln k = \ln A - \frac{E_a}{RT}$$

Now, if the values of rate constant at temperatures T_1 and T_2 are k_1 and k_2 respectively then

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \ldots \text{(i)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \ldots \text{(ii)}$$

Subtracting the Eq. (i) from (ii), we get

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right) = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \quad [\text{Here, } T_2 > T_1]$$

This relation is used when rate constants at two different temperatures are given.

This reaction is also written as $\frac{d \log k}{dT} = \frac{E}{RT^2}$

Arrhenius equation is purely an empirical equation that gives a reasonably good representation of temperature dependence of the rate constant.

When $\log k$ is plotted against $1/T$, we get a straight line which is represented by Arrhenius equation as

$$k = Ae^{-E_a/RT}$$

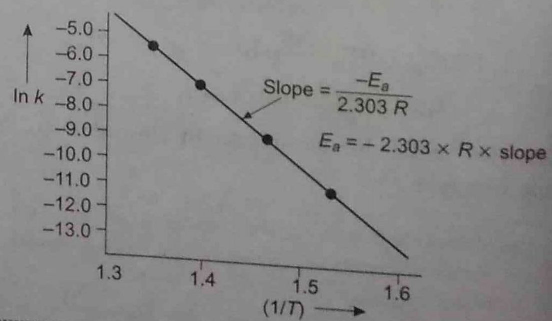
$$\ln k = \ln A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

The intercept of this line is equal to $\log A$ and slope is equal to $-\frac{E_a}{2.303R}$.

Therefore,

$$E_a = -2.303R \times \text{slope}$$



Practice Zone

DAY 14

1. The role of a catalyst is to change .... **[NCERT Exemplar]**

(a) Gibbs energy of reaction
(b) enthalpy of reaction
(c) activation energy of reaction
(d) equilibrium constant

2. The rate law for the reaction,
$RCl + NaOH(aq) \longrightarrow ROH + NaCl$ is given by,
rate $= k[RCl]$. 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) decreased on increasing the temperature of the reaction
(d) unaffected by increasing the temperature of the reaction

3. The chemical reaction, $2O_3 \longrightarrow 3O_2$, proceeds as follows

$$O_3 \rightleftharpoons O_2 + O \text{ (fast)}$$
$$O + O_3 \longrightarrow 2O_2 \quad \text{(slow)}$$

The rate law expression should be

(a) $r = k'[O_3]^2$
(b) $r = k'[O_3]^2[O_2]^{-1}$
(c) $r = k'[O_3][O_2]$
(d) Unpredictable

4. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be

(a) less than ΔH
(b) zero
(c) more than ΔH
(d) equal to ΔH

5. The rate of reaction is doubled for every 10°C rise in temperature. The increase in the reaction rate as a result of temperature rise from 10°C to 100°C is

(a) equal to the ener y of activation of products
(b) 112 times
(c) 512 times
(d) 614 times

6. The rate for the decomposition of NH_3 on platinum surface is zero order. What are the rate of production of N_2 and H_2 respectively, if $k = 2.5 \times 10^{-4}$ mol $L^{-1}s^{-1}$?

(a) 1.25×10^{-4} mol L^{-1} s^{-1}; 3.75×10^{-4}mol $L^{-1}s^{-1}$
(b) 3.75×10^{-4} mol L^{-1} s^{-1}; 1.25×10^{-4}mol $L^{-1}s^{-1}$
(c) 2.5×10^{-4} mol L^{-1} s^{-1}; 3.75×10^{-4}mol $L^{-1}s^{-1}$
(d) 1.25×10^{-4} mol L^{-1} s^{-1}; 2.5×10^{-4}mol $L^{-1}s^{-1}$

7. The rate of chemical reaction is doubled for every 10°C rise in temperature because of

(a) increase in the activation energy
(b) decrease in the activation energy
(c) increase in the number of molecular collisions
(d) increase in the number of activated molecules

8. In a reversible reaction,

$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

the rate of disappearance of NO_2 is equal to

(a) $\frac{2k_1}{k_2}[NO_2]^2$
(b) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$
(c) $2k_1[NO_2]^2 - k_2[N_2O_4]$
(d) $(2k_1 - k_2)[NO_2]$

9. The half-life period for first order reaction having activation energy 39.3 kcal mol^{-1} at 300°C and frequency constant $1.11 \times 10^{11} s^{-1}$ will be

(a) 1 h
(b) 1.68 h
(c) 1.28 h
(d) 1.11 h

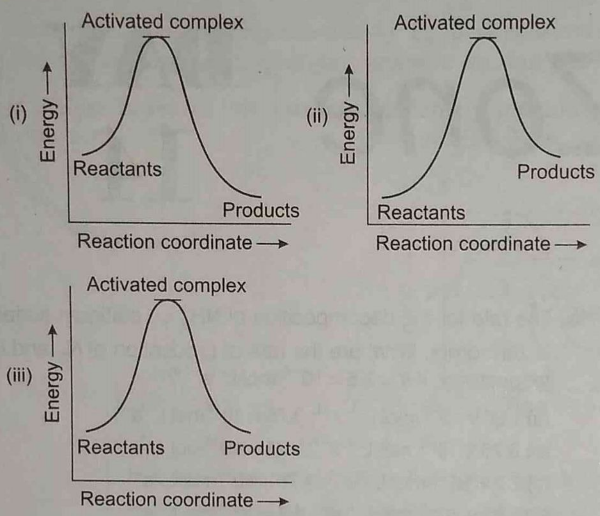
10. Half-life of a hypothetical reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is

(a) 4
(b) 3
(c) 5
(d) 2

11. The half-life for the reaction, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ is 24 h at 30°C. Starting with 10 g of N_2O_5, how many grams of N_2O_5 will remain after a period of 96 h ?

(a) 1.25 g
(b) 0.63 g
(c) 1.77 g
(d) 0.5 g

12. Which of the following graphs represents exothermic reaction? **[NCERT Exemplar]**



(a) Only (i) (b) Only (ii)
(c) Only (iii) (d) (i) and (ii)

13. The units of second order rate constant are
(a) mol $dm^{-3}s^{-1}$ (b) s^{-1}
(c) $dm^3mol^{-1}s^{-1}$ (d) None of these

14. In the sequence of reactions,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

$k_3 > k_2 > k_1$, then the rate determining step of the reaction is
(a) $A \to B$ (b) $B \to C$ (c) $C \to D$ (d) $A \to D$

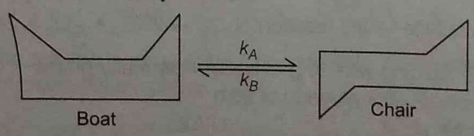
15. The hydrolysis of methyl formate in acid solution has rate expression : rate $= k\,[HCOOCH_3][H^+]$

The balanced equation being

$$HCOOCH_3 + H_2O \longrightarrow HCOOH + CH_3OH$$

The rate law contains $[H^+]$ though the balanced equation does not contain $[H^+]$ because
(a) H^+ ion is a catalyst
(b) H^+ is an important constituent of any reaction
(c) more for convenience to express the rate law
(d) all acids contain H^+ ions

16. Consider the interconversion of the 'boat' and 'chair conformations of cyclohexane.



The reaction is first-order in each direction with an equilibrium constant of 10^4. The activation energy for the conversion of the chair conformer to the boat conformer is 42 kJ mol^{-1}. Assuming an Arrhenius pre-exponential factor of $10^{12}\,s^{-1}$, what is the expected observed reaction rate constant at 298 K if one were to initiate this reaction starting with only the boat conformer?
(a) $8.01 \times 10^5\ s^{-1}$ (b) $4.34 \times 10^8\ s^{-1}$
(c) $2.56 \times 10^7 s^{-1}$ (d) $3.63 \times 10^7\ s^{-1}$

17. Consider the Arrhenius equation given below and mark the correct option.

$$K = Ae^{-Ea/RT}$$ **[NCERT Exemplar]**

(a) Rate constant increases exponentially with increasing activation energy and decreasing temperature
(b) Rate constant decreases exponentially with increasing activation energy
(c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature
(d) Rate constant increases exponentially with decreasing activation energy and increasing temperature

18. A first order reaction is half-completed in 45 min. How long does it need for 99.9% of the reaction to be completed?
(a) 20 h (b) 10 h
(c) $7\frac{1}{2}$ h (d) 5 h

19. Rate constant k varies with temperature as given by equation

$$\log k\,(\text{min}^{-1}) = 5 - \frac{2000\text{ K}}{T}$$

Consider the following about this equation
I. Preexponential factor is 10^5
II. E_a is 9.212 kcal
III. Variation of log K with $\frac{1}{T}$ is linear

Select the correct statement.
(a) I, II, III (b) I, III
(c) II, III (d) I, II

20. Velocity constant of a reaction at 290 K was found to be 3.2×10^{-3}. At 300 K it will be
(a) 1.28×10^{-2} (b) 32 times
(c) 6.4×10^{-3} (d) 3.2×10^{-4}

21. H_2O and O atom react in upper atmosphere bimolecularly to form two OH radicals. ΔH for the reaction is 72 kJ at 500 K and energy of activation is 77 kJ mol^{-1}. E_a for bimolecular recombination of two OH radicals to form H_2O and O atom will be
(a) 5 kJ mol^{-1} (b) 72 kJ mol^{-1}
(c) 77 kJ mol^{-1} (d) 149 kJ mol^{-1}

22. The half-life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 h and at 10 mm, it is 2 h. The order of reaction is
(a) 3 (b) 1
(c) 2 (d) 0

23. For the reaction following data is given

$A \longrightarrow B;\ k_1 = 10^{15}\exp\left(\frac{-2000}{T}\right)$

$C \longrightarrow D;\ k_2 = 10^{14}\exp\left(\frac{-1000}{T}\right)$

At what temperature, k_1 and k_2 will be same?

(a) 434.22 K (b) 868.43 K (c) 217.10 K (d) 130.26 K

24. The rate constant for a zero order reaction is

(a) $k = \frac{C_0}{2t}$ (b) $k = \frac{C_0 - C_t}{t}$

(c) $k = \ln\frac{C_0 - C_t}{t}$ (d) $k = \frac{C_0}{C_t}$

25. Calculate the half-life of the first order reaction,

$C_2H_4O(g) \longrightarrow CH_4(g) + CO(g)$

if the initial pressure of C_2H_4O (g) is 80 mm and the total pressure at the end of 20 min is 120 mm.

(a) 40 min (b) 120 min (c) 20 min (d) 80 min

26. For a first order reaction, the time required for 99.9% of the reaction to take place is nearly

(a) 10 times that required for half of the reaction
(b) 100 times that required for two third of the reaction
(c) 10 times that required for one fourth of the reaction
(d) 20 times that required for half of the reaction

27. A drop of a solution (volume=0.05 mL) contains 6×10^{-7} mol of H^+. If the rate of disappearance of H^+ is 6.0×10^5 mol $L^{-1}s^{-1}$, how long will it take for the H^+ in the drop to disappear?

(a) 8.0×10^{-8} s (b) 2.0×10^{-8} s

(c) 6.0×10^{-6} s (d) 2.0×10^{-2} s

Directions (Q. Nos. 28 to 30) *The following reaction was studied at 25°C in benzene solution containing 0.1 M pyridine.*

$$\underset{(A)}{CH_3OH} + \underset{(B)}{(C_6H_5)_3CCl} \longrightarrow \underset{(C)}{(C_6H_5)_3C\cdot OCH_3} + HCl$$

The following sets of data were observed

Set	Initial concentration $[A]_0$	Initial concentration $[B]_0$	Time, Δt	Final concentration [C]
I.	0.10 M	0.05 M	25 min	0.0033 M
II.	0.10 M	0.10 M	15 min	0.0039 M
III.	0.20 M	0.10 M	7.5 min	0.0077 M

28. Rates, $\frac{d[C]}{dt}$ in sets I,II and III are respectively (in M min^{-1})

	I	II	III
(a)	1.30×10^{-4}	2.6×10^{-4}	1.02×10^{-3}
(b)	0.033	0.0039	0.0077
(c)	0.02×10^{-4}	0.04×10^{-4}	0.017

(d) None of the above

29. Rate law of the above experiment is

(a) $k[A][B]$ (b) $k[A]^2[B]$

(c) $k[A][B]^2$ (d) $k[A]^2[B]^0$

30. Rate constant of the above experiments is (in $M^{-2}\ \text{min}^{-1}$)

(a) 1.3×10^{-1} (b) 2.6×10^{-2}

(c) 2.6×10^{-1} (d) 1.3×10^{-2}

Directions (Q. Nos. 31 to 33) *For the overall reaction between A and B to yield C and D, two mechanisms are proposed*

I. $A + B \rightarrow AB^* \rightarrow C + D,\quad k_1' = 1 \times 10^{-5}\ M^{-1}s^{-1}$

II. $A \rightarrow A^* \rightarrow E,\quad k_1 = 1 \times 10^{-4}\ s^{-1}$

$E + B \rightarrow C + D,\quad k_2 = 1 \times 10^{10}\ M^{-1}s^{-1}$

(species with * are short-lived)

31. Rate law for mechanism I when concentration of each is 1 M, is

(a) $1 \times 10^{-7}\ Ms^{-1}$ (b) $1 \times 10^{-6}\ Ms^{-1}$

(c) $1 \times 10^{-5}\ Ms^{-1}$ (d) $1 \times 10^{-4}\ Ms^{-1}$

32. Rate law for mechanism II, when concentration of each 1 M is

(a) $1 \times 10^{-4}\ Ms^{-1}$ (b) $1 \times 10^{10}\ Ms^{-1}$

(c) $1 \times 10^{-6}\ Ms^{-1}$ (d) $1 \times 10^{-10}\ Ms^{-1}$

33. At what concentration of B, rates of two mechanism are equal ?

(a) 1 M (b) 5 M (c) 7 M (d) 10 M

Directions (Q. Nos. 34 to 37) *Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

34. Statement I Rate of hydrolysis of methyl chloride to methanol is higher in DMF than in water.

Statement II Hydrolysis of methyl chloride follows second order kinetics.

35. Statement I Every collision of reactant molecule is not successful.

Statement II Every collision of reactant molecule with proper orientation is successful one.

36. Statement I Order of the reaction can be zero or fractional

Statement II We cannot determine order from balanced chemical equation **[NCERT Exemplar]**

37. **Statement I** Activation energy always increases the potential energy of reaction system.

Statement II The minimum kinetic energy that molecule must possess in order to react on collision is called its activation energy.

38. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 yr. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 yr and 60 yr if it is not lost metabolically?

[Nuclear explosions follow first order kinetics].

(a) 0.7814 μg and 0.227 μg (b) 0.227 μg and 0.7814 μg
(c) 0.9338 μg and 0.3323 μg (d) 0.500 μg and 0.300 μg

39. The hydrolysis of sucrose into glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows first order kinetics. In a neutral solution, if at 27°C, rate constant is $2.1 \times 10^{-11}\ s^{-1}$ and at 37°C, rate constant is $8.5 \times 10^{-11}\ s^{-1}$. The rate constant at 47°C will be

(a) 4.04 (b) 3.155×10^{-10}
(c) 8.5×10^{-11} (d) 1.785×10^{-21}

40. The gas phase decomposition of dimethyl ether follows first order kinetics $CH_3OCH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$

The reaction is carried out at constant volume container at 500°C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.4 atmosphere. What is the total pressure of the system after 12 min?

(a) 0.564 atm (b) 0.1744 atm (c) 0.693 atm (d) 0.249 atm

41. 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. What will be the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1}?

(a) 120 kJ mol^{-1} (b) 80 kJ mol^{-1}
(c) 100 kJ mol^{-1} (d) 20 kJ mol^{-1}

42. The vapour pressure of two miscible liquids *A* and *B* are 300 and 500 mm of Hg respectively. In a flask, 10 moles of *A* is mixed with 12 moles of *B*. However, as soon as *B* is added, *A* starts polymerising into a completely insoluble solid. The polymerisation follws first order kinetics. After 100 min 0.525 mol 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.

(a) $1.005 \times 10^{-4}\ min^{-1}$ (b) $0.78 \times 10^{-4}\ min^{-1}$
(c) $8.003 \times 10^{-4}\ min^{-1}$ (d) $10.05 \times 10^{-4}\ min^{-1}$

AIEEE & JEE Main Archive

43. The rate constant of a zero order reaction is $2.0 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$. If the concentration of the reactant after 25 s is 0.5 M, what is the initial concentration? **[JEE Main Online 2013]**

(a) 0.5 M (b) 1.25 M
(c) 12.5 M (d) 1.0 M

44. The reaction, $X \longrightarrow Y$ is an exothermic reaction. Activation energy of the reaction for conversion of *X* into *Y* is 150 kJ mol^{-1}. Enthalpy is 135 kJ mol^{-1}. The activation energy for the reverse reaction, $Y \longrightarrow X$ will be **[JEE Main Online 2013]**

(a) 280 kJ mol^{-1} (b) 285 kJ mol^{-1}
(c) 270 kJ mol^{-1} (d) 15 kJ mol^{-1}

45. The instantaneous rate of disappearance of MnO_4^- ion in the following reaction is $4.56 \times 10^{-3}\ Ms^{-1}$

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

The rate of appearance I_2 is **[JEE Main Online 2013]**

(a) $4.56 \times 10^{-4}\ Ms^{-1}$
(b) $1.14 \times 10^{-2}\ Ms^{-1}$
(c) $1.14 \times 10^{-3}\ Ms^{-1}$
(d) $5.7 \times 10^{-3}\ Ms^{-1}$

46. Which one of the following is the wrong assumption of kinetic theory of gases? **[JEE Main Online 2013]**

(a) Momentum and energy always remain conserved
(b) Pressure is the result of elastic collision of molecules with the container's wall
(c) Molecules are separated by great distances compared to their sizes
(d) All the molecules move in straight line between collision and with same velocity

47. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be [$R = 8.314\ JK^{-1}\ mol^{-1}, \log 2 = 0.301$] **[IIT JEE Main 2013]**

(a) 48.6 kJ mol^{-1} (b) 58.5 kJ mol^{-1}
(c) 60.5 kJ mol^{-1} (d) 53.6 kJ mol^{-1}

48. 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 $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? ($\log_{10} 2 = 0.3$) **[IIT JEE Main 2012]**

(a) 2 (b) 3 (c) 6 (d) 9

49. For a first order reaction, $(A) \longrightarrow$ products the concentration of *A* changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of *A* is 0.01 M is **[AIEEE 2012]**

(a) 1.73×10^{-5} M/min (b) 3.47×10^{-4} M/min
(c) 3.47×10^{-5} M/min (d) 1.73×10^{-4} M/min

50. The rate of a chemical reaction doubles for every 10° C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about **[AIEEE 2011]**

(a) 10 times (b) 24 times
(c) 32 times (d) 64 times

51. The time for half-life period of a certain reaction, $A \rightarrow$ products is 1 h. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1}, if it is a zero order reaction? **[AIEEE 2010]**

(a) 4 h (b) 0.5 h
(c) 0.25 h (d) 1 h

52. Consider the reaction,

$$Cl_2(aq) + H_2S\,(aq) \longrightarrow S\,(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is,

$$\text{rate} = k[Cl_2][H_2S]$$

Which of these mechanisms is/are consistent with this rate equation? **[AIEEE 2010]**

(A) $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)
$Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

(B) $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)
$Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

(a) (B) only
(b) Both (A) and (B)
(c) Neither (A) nor (B)
(d) (A) only

53. The half-life period of a first order chemical reaction is 6.93 min. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) **[AIEEE 2009]**

(a) 230.3 min (b) 23.03 min (c) 46.06 min (d) 460.6 min

54. For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[AIEEE 2008]**

(a) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (b) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$
(c) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

55. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is **(IIT JEE Main 2008)**

(a) 0.5 $mol^{-1}dm^3$ (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 $mol^{-1}dm^3$

56. Consider a reaction $aG + bH \rightarrow$ products, when concentration of both the reactants G and H is doubled, the rate increases by eight 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 JEE Main 2007]**

(a) 0 (b) 1 (c) 2 (d) 3

57. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 $kJmol^{-1}$ respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction $(A_2 + B_2 \longrightarrow 2AB)$ in the presence of catalyst will be (in kJ mol^{-1}) **[AIEEE 2007]**

(a) 300 (b) 120 (c) 280 (d) 20

58. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr

$$NO\,(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$
$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[AIEEE 2006]**

(a) 1 (b) 0
(c) 3 (d) 2

59. A reaction involving two different reactants can never be **[AIEEE 2005]**

(a) bimolecular reaction
(b) second order reaction
(c) first order reaction
(d) unimolecular reaction

60. (A) follows first order reaction, (A) $\longrightarrow$ Product

Concentration of A, changes from 0.1 M to 0.025 M in 40 min. Find the rate of reactions of A, when concentration of A is 0.01 M. **[IIT JEE Main 2004]**

(a) 3.47×10^{-4}M min^{-1} (b) 3.47×10^{-5}M min^{-1}
(c) 1.73×10^{-4}M min^{-1} (d) 1.73×10^{-5}M min^{-1}

61. In a first order reaction, the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 s. The rate constant of reaction in s^{-1} is **[IIT JEE 2003]**

(a) 2×10^4 (b) 3.45×10^{-5}
(c) 1.386×10^{-4} (d) 2×10^{-4}

62. For the reaction system,

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO; the rate of reaction will **[AIEEE 2003]**

(a) diminish to one fourth of its initial value
(b) diminish to one eighth of its initial value
(c) increase to eight times of its initial value
(d) increase to four times of its initial value

Answers

1. (c)	2. (b)	3. (b)	4. (c)	5. (c)	6. (a)	7. (d)	8. (b)	9. (b)	10. (a)
11. (b)	12. (a)	13. (c)	14. (a)	15. (a)	16. (b)	17. (d)	18. (c)	19. (a)	20. (c)
21. (a)	22. (c)	23. (a)	24. (b)	25. (c)	26. (a)	27. (b)	28. (a)	29. (b)	30. (c)
31. (a)	32. (a)	33. (d)	34. (a)	35. (c)	36. (b)	37. (b)	38. (a)	39. (b)	40. (b)
41. (c)	42. (a)	43. (d)	44. (b)	45. (b)	46. (d)	47. (d)	48. (d)	49. (b)	50. (c)
51. (c)	52. (d)	53. (c)	54. (d)	55. (a)	56. (d)	57. (d)	58. (d)	59. (b)	60. (a)
61. (c)	62. (b)								

Hints & Solutions

1. A catalyst lower the activation energy of reaction.

2. As rate $= k\,[R\,Cl]$, on decreasing the concentration of RCl to half, the rate will also be halved.

3. From the step (ii),

$$\text{Rate, } r = k\,[O][O_3] \quad \text{...(i)}$$

For fast reaction,

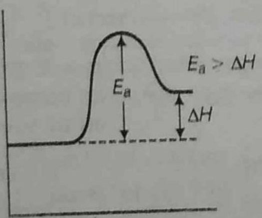
$$K_c = \frac{[O_2][O]}{[O_3]} \quad \text{or} \quad [O] = \frac{K_c[O_3]}{[O_2]}$$

On putting the value of [O] in Eq. (i), we get

$$\text{Rate, } r = k \cdot \frac{K_c[O_3]}{[O_2]}[O_3]$$

or
$$= k \cdot K_c [O_3]^2 [O_2]^{-1} = k'[O_3]^2 [O_2]^{-1}$$

4.



5. Increase in steps of 10°C has been made 9 times, hence rate of reaction should, increase 2^9 times, *i.e.*, 512 times.

6. $2NH_3 \longrightarrow N_2 + 3H_2$

$$-\frac{1}{2}\frac{d\,[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\text{Rate} = k[NH_3]^0$$

or
$$\frac{d[NH_3]}{dt} = 2.5 \times 10^{-4}\ \text{mol L}^{-1}\,\text{s}^{-1}$$

$$\frac{d[N_2]}{dt} = \frac{1}{2} \times 2.5 \times 10^{-4}$$
$$= 1.25 \times 10^{-4}\ \text{mol L}^{-1}\,\text{s}^{-1}$$

$$\frac{d[H_2]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$
$$= 3.75 \times 10^{-4}\text{mol L}^{-1}\,\text{s}^{-1}$$

7. Rate of reaction increase due to increase in number of activated molecules.

8.
$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

$$\text{Rate} = -\frac{1}{2}\frac{d\,[NO_2]}{dt} = k_1[NO_2]^2 - k_2[N_2O_4]$$

$\therefore$ Rate of disappearance of NO_2

i.e.,
$$-\frac{d[NO_2]}{dt} = 2k\,[NO_2]^2 - 2k_2[N_2O_4]$$

9. Given $A = 1.11 \times 10^{11}\text{s}^{-1}$; $E_a = 39.3 \times 10^3$ cal mol^{-1}

$R = 1.987$ cal; $T = 573$ K

$\because$
$$k = Ae^{-E_a/RT}$$

$\therefore$
$$\ln k = \ln A - \frac{E_a}{RT}$$

or
$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\,RT}$$

or
$$\log_{10} k = \log_{10} 1.11 \times 10^{11} - \left\{\frac{39.3 \times 10^3}{2.303 \times 1.987 \times 573}\right\}$$

or
$$k = 1.14 \times 10^{-4}\ \text{s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.14 \times 10^{-4}} = 6078\ \text{s} = 1.68\ \text{h}$$

10. $t_{1/2} \propto a^{n-1}$

Hence, $t_{1/2} \propto a^{1/3}$, only when $n = 4$

11.
$$k = \frac{0.693}{24}\text{h}^{-1} = \frac{2.303}{96}\log\frac{10}{a-x}$$

or
$$\log\frac{10}{a-x} = 1.2036$$

or
$$1 - \log\,(a-x) = 1.2036$$

or
$$\log(a-x) = -\,0.2036$$
$$= +\ 1.7964 - 2$$

or
$$(a-x) = \text{antilog}\,(1.7964 - 2)$$
$$= 0.6258 = 0.63\ \text{g}$$

Alternatively, 96 h = four half-lives.

12. Graph (i) only represents exothermic reaction because products have lesser energy than reactants ($\Delta H < 0$).

13. For second order, $\frac{dx}{dt} = k(\text{conc.})^2$

Hence, $k = \frac{\text{conc.}}{\text{time}} \times \frac{1}{(\text{conc.})^2} = (\text{conc.})^{-1} \cdot \text{time}^{-1}$

$= \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}$

14. $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$

$\because \quad k_3 > k_2 > k_1$

As k_1 is smallest (slowest), hence $A \longrightarrow B$ is the rate determining step of the reaction.

15. H^+ ions act as catalyst for the given reaction.

16. $k_B = Ae^{-E_a/RT} = 10^{12}\, e^{-42000/8.314 \times 298} = 4.34 \times 10^4\ \text{s}^{-1}$

Also, $K_c = 10^4$

and $K_c = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}}$

$10^4 = \frac{k_A}{k_B}$

$\therefore \quad k_A = 10^4\, k_B = 4.34 \times 10^8\ \text{s}^{-1}$

Expected observed reaction rate constant $= k_A + k_B$
$= 4.34 \times 10^8\ \text{s}^{-1}$

17. Rate constant increases exponentially with decreasing activation energy and increasing temperature.

18. $k = \frac{0.693}{45}\text{min}^{-1} = \frac{2.303}{t_{99.9\%}} \log \frac{a}{a - 0.999a} \qquad [\because a = 1]$

or $\quad t_{99.9\%} = \frac{2.303 \times 45}{0.693} \log 10^3 = 448 \text{ min} \approx 7\frac{1}{2}\text{h}$

19. $\log k\ (\text{min}^{-1}) = 5 - \frac{2000\ \text{K}}{T}$

$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\, RT}$

I. $\log A = 5$, $A = 10^5$ true

II. $\frac{E_a}{2.303\, R} = 2000$

$E_a = 2000 \times 2.303 \times 0.002$ kcal
$= 9.212$ kcal, true

III. Equation represents straight line, hence, true.

20. For 10°C rise, the velocity constant becomes nearly double.

21. $H_2O + O \xrightarrow{E_a} 2OH;\ \Delta H = 72\,\text{kJ}$

$2OH \xrightarrow{E_b} H_2O + O;\ \Delta H = -72\,\text{kJ}$

Also $\quad E_a - E_b = \Delta H$

or $\quad 77 - E_b = 72$

$\therefore \quad E_b = 5\,\text{kJ mol}^{-1}$

22. $t_{1/2} \propto \frac{1}{C_0}$. Hence, it is a reaction of second order.

23. $k_1 = k_2$

$10^{15} e^{\left(\frac{-2000}{T}\right)} = 10^{14} e^{\left(\frac{-1000}{T}\right)}$

or $\quad 15 - \frac{2000}{T \times 2.303} = 14 - \frac{1000}{T \times 2.303}$

or $\quad \frac{1000}{T \times 2.303} = 1$

$\therefore \quad T = 434.22\,\text{K}$

24. For a zero order reaction,

$-\frac{d[A]}{dt} = k$

$\int_{C_0}^{C_t} d[A] = k \int_{t=0}^{t=0} dt$

$C_0 - C_t = kt \Rightarrow k = \frac{C_0 - C_t}{t}$

25. $C_2H_4O(g) \longrightarrow CH_4(g) + CO(g)$

	$C_2H_4O(g)$	$CH_4(g)$	$CO(g)$
At t_0:	p_0	0	0
At t_{20}:	$p_0 - p$	p	p

Initial pressure, $p_0 = 80$ mm

Total pressure after 20 min,

$p_{\text{Total}} = p_0 - p + p + p$

$p_{\text{Total}} = p_0 + p$

$120 = 80 + p$

or $\quad p = 120 - 80 = 40$ mm

$k = \frac{2.303}{20} \log \frac{80}{40} = \frac{2.303}{20} \log 2$

$k = \frac{2.303 \times 0.3010}{20} = \frac{0.693}{20}$

We know that, $t_{1/2} = \frac{0.693}{k}$

By putting the value of k in this equation we get,

$t_{1/2} = \frac{0.693 \times 20}{0.693} = 20$ min

26. $k = \frac{1}{t} \ln \frac{100}{100 - 99.9} = \frac{1}{t} \ln \frac{100}{0.1}$

or $\quad \frac{\ln 2}{t_{1/2}} = \frac{1}{t} \ln 10^3$

or $\quad \frac{\log 2}{t_{1/2}} = \frac{1}{t} \times \log 10^3 = \frac{3}{t}$

$t_{1/2} = \frac{\log 2}{3} \times t = \frac{0.30103}{3} \times t \approx 0.10t$

27. $[H^+] = \frac{6 \times 10^{-7}\ \text{mol}}{0.05 \times 10^{-3}\text{L}} = 1.2 \times 10^{-2}$ M

or $\quad r = \frac{\Delta x}{\Delta t}$ or $\Delta t = \frac{\Delta x}{r} = \frac{1.2 \times 10^{-2}\ \text{M}}{6 \times 10^5\ \text{Ms}^{-1}}$

$\therefore \quad t = 2 \times 10^{-8}$ s

28. Concentration of the product has been given

$$\left(\frac{d[C]}{dt}\right)_{I} = \frac{0.0033}{25} = 1.32 \times 10^{-4}\ \text{M min}^{-1}$$

$$\left(\frac{d[C]}{dt}\right)_{II} = 2.6 \times 10^{-4}\ \text{M min}^{-1}$$

$$\left(\frac{d[C]}{dt}\right)_{III} = 1.02 \times 10^{-3}\ \text{M min}^{-1}$$

29. On comparing rates, order *wrt* $A = 2$ and *wrt* $B = 1$ Thus, rate law $= k[A]^2[B]$

30. $\left(\frac{dx}{dt}\right) = k[A]^2[B]$ and $k = \frac{\left(\frac{dx}{dt}\right)}{[A]^2[B]} = 0.26$

(Take values of any sets)

31. Rate law for mechanism I

$$= k_1'[A][B] = 1 \times 10^{-5} \times 0.1 \times 0.1 = 1 \times 10^{-7}\ \text{Ms}^{-1}$$

32. In mechanism II, step II is fast, thus rate law is

$$= k_1[A] = 1 \times 10^{-4} \times 1\ \text{Ms}^{-1} = 1 \times 10^{-4}\ \text{Ms}^{-1}$$

33. Rates are equal, $k_1'[A][B] = k_1[A]$

$$\therefore \quad [B] = \frac{k_1}{k_1'} = \frac{1 \times 10^{-4}}{1 \times 10^{-5}} = 10\ \text{M}$$

34. Primary alkyl halides undergo S_N2 mechanism and not S_N1 mechanism. Hence, hydrolysis of CH_3Cl is favoured by non-polar medium or polar non protic solvent in which proton is not generated (like DMF) whereas S_N1 mechanism are favoured by polar solvents like water.

35. A successful collision leads to a chemical reaction, when the reactant molecules collide with proper orientation and attain threshold energy level.

36. The order of reaction can only be determined by experiments.

37. Statement I and statement II are true but both are the facts.

38. Since, nuclear explosion follow the first order kinetics

$\because \quad t_{1/2}$ of $^{90}Sr = 28.1\ \text{yr}$

$$\therefore \quad k = \frac{0.693}{28.1}\ \text{yr}^{-1}$$

Now, $\quad t = \frac{2.303}{k}\log\frac{a}{(a-x)}$ [Here $a = 1\ \mu g$]

At $t = 10$ yr; $10 = \frac{2.303 \times 28.1}{0.693}\log\frac{1}{(a-x)}$

$\therefore$ Amount of Sr left $= (a-x) = 0.7814\ \mu g$.

At $t = 60$ yr; $60 = \frac{2.303 \times 28.1}{0.693}\log\frac{1}{(a-x)}$

$\therefore \quad (a-x) = 0.227\ \mu g$.

39. $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

$$\log\frac{8.5 \times 10^{-11}}{2.1 \times 10^{-11}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{300 \times 310}\right]$$

$$\therefore \quad E_a = 108.1\ \text{kJ}$$

$$\log k = \log A - \frac{E_a}{2.303RT_1}$$

$$\log 2.1 \times 10^{-11} = \log A - \frac{108.1 \times 10^3}{2.303 \times 8.314 \times 300}$$

$$\therefore \quad A = 13.87 \times 10^7$$

$$\log(k)_{47^\circ C} = \log A - \frac{E_a}{2.303 \times R \times T}$$

$$= \log 13.87 \times 10^7 - \frac{108.1 \times 10^3}{2.303 \times 8.314 \times 320}$$

$$= 3.155 \times 10^{-10}\ \text{s}^{-1}$$

40.

	$CH_3OCH_3(g) \longrightarrow$	$CH_4(g)$ +	$H_2(g)$ +	$CO(g)$
At $t = 0$	p_0	0	0	0
At t	$p_0 - p$	p	p	p

Total pressure at $t = p^0 + 2p$

Rate expression for first order kinetics :

$$\log\frac{p_0 - p}{p_0} = -\left(\frac{k}{2.303}\right)t = -\left(\frac{0.693/t_{1/2}}{2.303}\right)t$$

$$= -\frac{0.93 / 14.5\ \text{min}}{2.303} \times 12\ \text{min}$$

or $\log\frac{p_0 - p}{p_0} = -0.249$ or $\frac{p_0 - p}{p_0} = 0.564$

or $p = p_0 - 0.564\,p_0 = p_0(1 - 0.564)$

$= (0.40\ \text{atm})\ (0.436) = 0.1744\ \text{atm}$

41. Let E_a = activation energy in presence of catalyst

$E_a{}'$ = activation energy in absence of catalyst

Then, $\quad k = Ae^{-E_a/RT}$

In presence of catalyst : $k_1 = Ae^{-E_a/(R \times 500)}$

In absence of catalyst : $k_2 = Ae^{-E_a^1/(R \times 400)}$

Given, the rates are same, *i.e.*, $r_1 = r_2$

$$\therefore \quad e^{-E_a/(R \times 500)} = e^{-E_a'/(R \times 400)}$$

or $\quad \frac{E_a}{R \times 500} = \frac{E_a'}{R \times 400}$

or $\quad \frac{E_a}{500} = \frac{E_a - 20}{400}$ $\quad [\because E_a - E_a' = 20]$

or $\quad E_a = 100\ \text{kJmol}^{-1}$

42. Let n_A moles of liquid A are polymerised so that final solution has

(i) $(10 - n_A)$ moles of A

(ii) 12 moles of B

(iii) 0.525 moles of solute added

$\therefore x_A$ (mole fraction of A after polymerisation)

$$= \frac{10 - n_A}{(10 - n_A) + 12 + 0.525}$$

$$x_A = \frac{10 - n_A}{(22.525 - n_A)} \text{ and } x_B = \frac{12}{22.525 - n_A}$$

$$\therefore \quad x_A p_A^\circ + x_B p_B^\circ = 400$$

$$\frac{(10-n_A)\,300+12\times 500}{22.525-n_A}=400$$

$$n_A = 0.10$$

Thus, number of moles of A after polymerisation

$$= 10 - 0.1 = 9.9$$

$$k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$k=\frac{2.303}{100}\log\frac{10}{9.9}=1.005\times 10^{-4}\ \text{min}^{-1}$$

43. For zero order reaction,

$$\text{rate }=\frac{dx}{dt}=k=\frac{x_1-x_2}{dt}=2.0\times 10^{-2}$$

$$\frac{x_1-0.5}{25}=2.0\times 10^{-2}$$

(Here, x_1 = initial concentration)

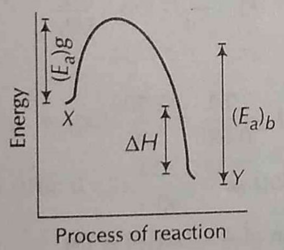
$$x_1-0.5=0.5=0.5+0.5=1.0\text{ M}$$

44. An exothermic reaction can be represented as

$$X \longrightarrow Y + \text{energy}$$

i.e., energy of $Y << X$

So, the energy profile diagram is



$$\therefore\quad (E_a)_f+\Delta H=(E_a)_b$$

$$150+135=(E_a)_b$$

$$(E_a)_b=285\text{ kJ mol}^{-1}$$

45. Rate of reaction $=-\frac{1}{2}[MnO_4]=\frac{1}{5}[I_2]$

$\therefore$ Given, Rate of disappearance of MnO_4^-

$$=\frac{d\,[MnO_4^-]}{dt}=4.56\times 10^{-3}$$

$\because$ Rate of appearance of $I_2=\frac{5}{2}\times 4.56\times 10^{-3}$

$$=11.4\times 10^{-3}=1.14\times 10^{-2}\,\text{Ms}^{-1}$$

46. According to kinetic theory of gases, the gaseous molecules are so far apart that the actual volume of the molecules is negligible as compared to the total volume of the gas.

The gaseous molecules move in straight lines with uniform speed and change direction on collision with other molecules or the walls of container.

All the collisions are perfectly elastic, hence there is no loss of kinetic energy during the collision. The pressure of the gas is caused by the hits recorded by molecules on the walls of the container.

47. As per Arrhenius equation

$$\ln\frac{K_2}{K_1}=\frac{-E_a}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

$$2.303\log 2=\frac{-E_a}{8.314}\left[\frac{1}{310}-\frac{1}{300}\right]\Rightarrow E_a=53.6\text{ kJ/mole}$$

48. For a first order process,

$$kt=\ln\frac{[A]_0}{[A]}$$

where, $[A]_0$ = initial concentration.

$[A]$ = concentration of reactant remaining at time t.

$$k\,t_{1/8}=\ln\frac{[A]_0}{[A]_0/8}=\ln 8 \qquad \ldots\text{(i)}$$

$$k\,t_{1/10}=\ln\frac{[A]_0}{[A]_0/10}=\ln 10 \qquad \ldots\text{(ii)}$$

Therefore, $\frac{t_{1/8}}{t_{1/10}}=\frac{\ln 8}{\ln 10}=\log 8=3\log 2$

$$\frac{t_{1/8}}{t_{1/10}}=3\times 0.3=0.9$$

$$\frac{t_{1/8}}{t_{1/10}}\times 10=0.9\times 10=9.0$$

49. By first order kinetic, rate constant

$$k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$a=0.1\text{ M}$$

$$(a-x)=0.025\text{ M}$$

$$t=40\text{ min}$$

$$\therefore\quad k=\frac{2.303}{40}\log\frac{0.1}{0.025\text{ M}}=0.0347\text{ min}^{-1}$$

$$\text{Rate}=\left(\frac{dx}{dt}\right)=k\,[A]^1=0.0347\times 0.01$$

$$=3.47\times 10^{-4}\text{ M min}^{-1}$$

50. For every 10°C rise of temperature, rate is doubled. Thus, temperature coefficient of the reaction = 2.

When temperature is increased by 50°, rate becomes

$$=2^{\left(\frac{50}{10}\right)}=2^5\text{ times}=32\text{ times}$$

51. For a zero order reaction,

$$k_0=\frac{[A]_0}{2t_{1/2}}$$

Since, $[A]_0=2\text{ M}, t_{1/2}=1\text{ h}$

So, $k_0=1$

and $k_0=\frac{\Delta X}{t}$

or $t=\frac{0.50-0.25}{1}=0.25\text{ h}$

52. Slowest step is the rate determining step. Thus, in case (A), rate law is given as rate $= k[Cl_2][H_2S]$

While for the reaction given in case (B), rate law is given as rate $= k[H_2S][Cl_2][H^+]^{-1}$.

Hence, only mechanism (A) is consistent with the given rate law.

53. Half-life $= 6.93$ min $k_1 = \frac{0.693}{6.93} = 0.1$

We know, k_1 for per cent completion

$$k_1 = \frac{2.303}{t}\log\left(\frac{100}{100x}\right)$$

$$0.1 = \frac{2.303}{t} \times \log\frac{100}{1} = \frac{2.303}{t}\log 10^2$$

$$t = \frac{2.303 \times 2}{0.1} = 46.06 \text{ min}$$

54. Rate of reaction $= -\frac{2d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

$$\therefore \quad \frac{-d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$$

55. First order kinetics,

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}\text{ s}^{-1}$$

Zero order kinetics, $k_1 = \frac{C_0}{2t_{1/2}} = \frac{1.386}{2 \times 20}$

Hence, $\quad \frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5$

56. $aG + bH \rightarrow$ Product

Suppose order of reaction $= n$

When concentration of both G and H is doubled, the rate increase by eight times.

$$\text{rate} = k\,(\text{reactants})^n$$

$$(8) = k\,(2)^n$$

$$(2)^3 = k\,(2)^n$$

$$\therefore \quad n = 3$$

when concentration of G is doubled keeping the concentration of H fixed, the rate is double.

$$\text{Rate} \propto [G]^1$$

then, $\quad \text{Rate} \propto [G]^1[H]^2$

57. $A_2 + B_2 \rightleftharpoons 2AB$

$$E_a \text{ (forward)} = 180 \text{ kJ mol}^{-1}$$

$$E_a \text{ (backward)} = 200 \text{kJ mol}^{-1}$$

In the presence of catalyst

$$E_a \text{ (forward)} = 180 - 100 = 80 \text{ kJ mol}^{-1}$$

$$E_a \text{ (backward)} = 200 - 100 = 100 \text{ kJ mol}^{-1}$$

$$\Delta H = E_a \text{ (forward)} - E_a \text{ (backward)}$$

$$= 80 - 100 = -20 \text{ kJ mol}^{-1}$$

58. Rate $= k\,[NOBr_2][NO]$ ...(i)

But $NOBr_2$ is in equilibrium

$$K_{eq} = \frac{[NOBr_2]}{[NO][Br_2]}$$

$$[NOBr_2] = K_{eq}[NO][Br_2] \quad \text{...(ii)}$$

Putting the $[NOBr_2]$ in Eq (i)

$$\text{Rate} = k \cdot K_{eq}[NO][Br_2][NO]$$

Hence, $\quad \text{Rate} = k \cdot K_{eq}[NO]^2[Br_2]$

$$\text{Rate} = k'[NO]^2[Br_2]$$

where, $\quad k' = k \cdot K_{eq}$

59. There are two different reactants (say A and B).

$$A + B \longrightarrow \text{Product}$$

Thus, it is a bimolecular reaction.

If $\quad \frac{dx}{dt} = k[A][B],$

It is second order reaction.

60. $A \longrightarrow$ Product (first order reaction)

For first order reaction,

Rate constant $\quad (k) = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$

At, $t = 40$ min,

$$= \frac{2.303}{40}\log_{10}\frac{0.1}{0.025} = \frac{2.303}{40}\log_{10}4$$

$$= \frac{2.303}{40} \times 2\log_{10}2 = \frac{2.303}{40} \times 2 \times 0.3010 = 0.0347 \text{min}^{-1}$$

At concentration of $A = 0.01\text{M} = [A]$

$$\text{Rate}\left(\frac{dx}{dt}\right) = k[A]$$

$$\frac{dx}{dt} = 0.0347 \times 0.01$$

$$= 3.47 \times 10^{-4} \text{mol L}^{-1}\text{min}^{-1}$$

61. For first order reaction,

$$k = \frac{2.303}{t}\log\frac{A_0}{A_t}$$

$$= \frac{2.303}{2 \times 10^4}\log\frac{800}{50}$$

$$= 1.386 \times 10^{-4}\text{ s}^{-1}$$

62.

$$\left(\frac{dx}{dt}\right) = k\,[NO]^2[O_2]$$

$$= k\left(\frac{n_{NO}}{V}\right)^2\left(\frac{n_{O_2}}{V}\right)$$

$$\left(\frac{dx}{dt}\right)' = \frac{k}{V^3}(n_{NO})^2(n_{O_2})$$

$$\left(\frac{dx}{dt}\right)' = \frac{k(n_{NO})^2(n_{O_2})}{\left(\frac{V}{2}\right)^3} = 8\left(\frac{dx}{dt}\right)$$