Dr. P. Bahadur

Er. Shalabh Saxena

श्री BalaJi

NUMERICAL

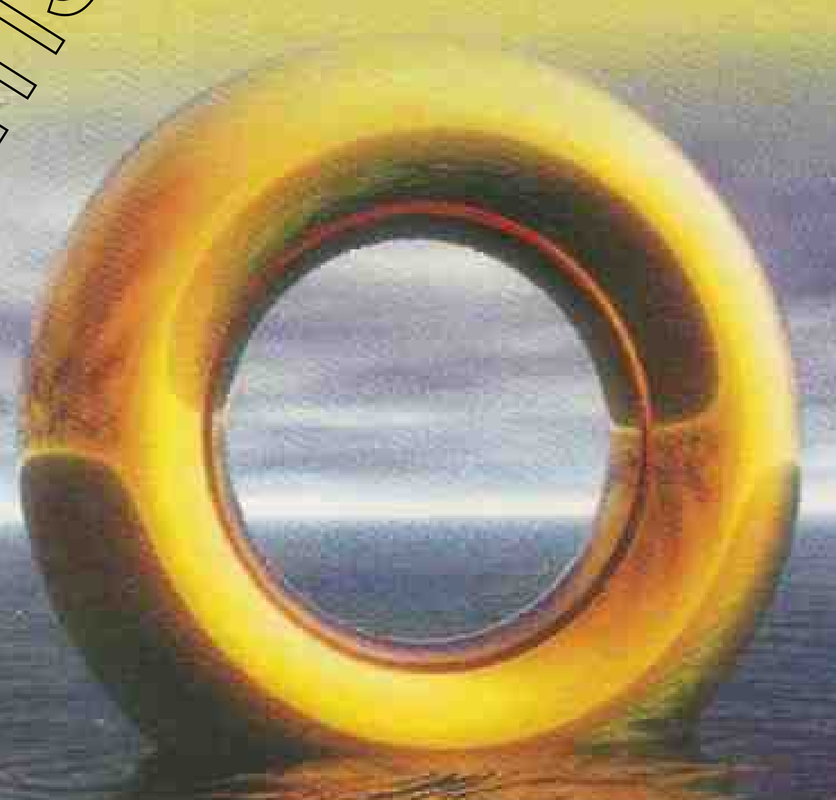
Problems in

PHYSICAL CHEMISTRY

for

IIT-JEE

AND ALL OTHER ENGINEERING ENTRANCE EXAMINATIONS



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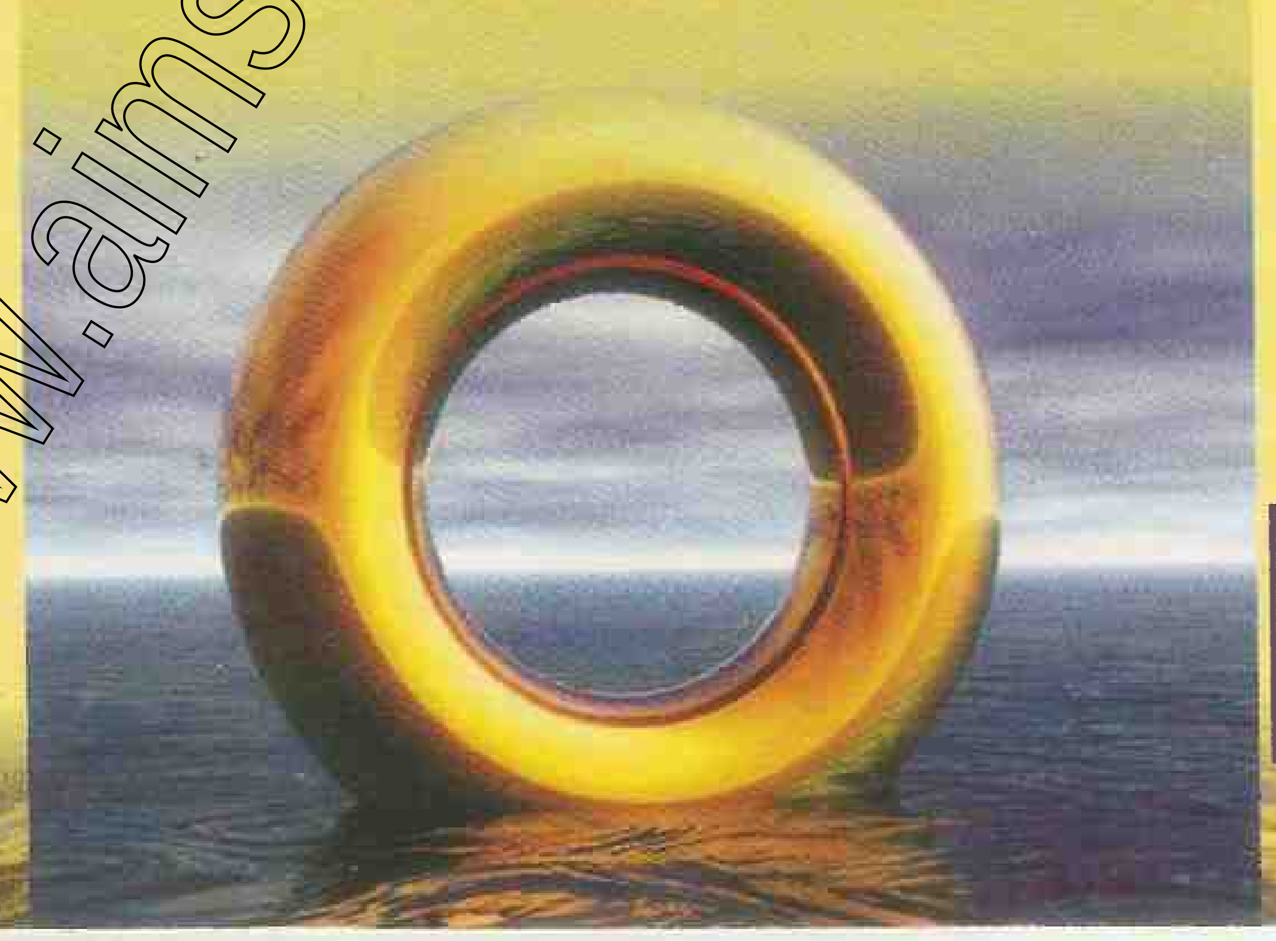

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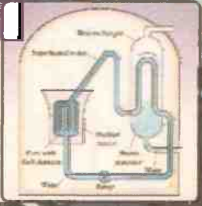
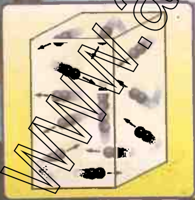
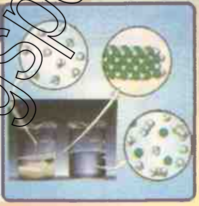
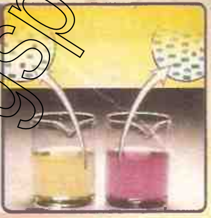








1

Gaseous State

Chapter at a Glance

1. Boyles' law:

$PV = \text{constant}$ (at constant T and n)

2. Charle's law:

$V/T = \text{constant}$ (at constant P and n)

3. Gay Lussac-Charles's law:

$P/T = \text{constant}$ (at constant V and n)

4. Avogadro's hypothesis:

$V \propto$ No. of molecules (at constant pressure and temperature)

5. Gas equalion:

$PV = nRT$

or $PV = (w/m)RT$ or $P = \frac{d}{m}RT$ (where d is density of gas)

6. Graham's law of diffusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{(at constant } P \text{ and } T\text{)}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \quad \text{(at constant } T\text{)}$$

7. Dalton's law of partial pressure:

$$P_T = P'_A + P'_B + P'_C + \ldots\ldots$$

and $P'_A = P_T \times$ mole fraction of A

8. Absolute density:

$d = \frac{\text{mass}}{\text{volume}}$; expressed usually in g litre^{-1}

9. Vapour density:

Molecular weight = Vapour density × 2 (For gases only)

10. Different speed terms for molecular motion:

$u_{AV} = \sqrt{\frac{8RT}{\pi M}}$, where u_{AV} is average speed

$u_{rms} = \sqrt{\frac{3RT}{M}}$; where u_{rms} is root mean square speed

$u_{MP} = \sqrt{\frac{2RT}{M}}$; where u_{MP} is most probable speed

$u_{MP} : u_{AV} : u_{rms} :: 1 : 1.128 : 1.224$

11. Kinetic equation:

$$PV = (1/3)m.n.u_{rms}^2 \quad (m \text{ is mass of one molecule and } n \text{ is number of molecule})$$

12. Kinetic energy:

$$\text{K.E./mol} = \frac{3}{2}RT$$

$$\text{Average K.E. or K.E./molecule} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT \qquad (k \text{ is Boltzman constant})$$

13. Van der Waals' Equation:

$$\left[P + \frac{a}{V^2}\right][V - b] = RT \qquad \text{(for 1 mole)}$$

$$\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT \qquad \text{(for } n \text{ mole)}$$

a is van der Waals' constant for attraction ; b is van der Waals' constant for volume. Also $b = 4 \cdot N \cdot v$

14. Boyle's temperature (T_b):

$$T_b = \frac{a}{Rb}$$

15. Critical constants :

$$T_c = \frac{8a}{27\,Rb}; \qquad P_c = \frac{a}{27b^2}; \qquad V_c = 3b$$

T_c, P_c and V_c are critical temperature, critical pressure and critical volume respectively.

16. Inversion temperature (T_i):

$$T_i = \frac{2a}{Rb}$$

17. Law of corresponding state:

$$\left[P_r + \frac{3}{V_r^2}\right][3V_r - 1] = 8T_r$$

P_r, V_r and T_r are reduced pressure, reduced volume and reduced temperature respectively.

18. Mean free path (λ):

$$\lambda = \eta\sqrt{\frac{3}{P.d.}} = \frac{1}{\sqrt{2}\,\pi\sigma^2 N} \qquad (\sigma \text{ is molecular diameter})$$

19. Collision frequency (c.f.):

$$\text{c.f.} = \frac{u_{rms}}{\lambda}$$

20. Specific heat and molar heat capacities:

$$c_p - c_v = \frac{R}{M}$$

$$C_p - C_v = R$$

$$\frac{c_p}{c_v} = \frac{C_p}{C_v} = \gamma$$

c_p and c_v are specific heat at constant pressure and constant volume respectively, C_p and C_v are molar heat capacities at constant P and V respectively.

The Basic Problems with Solutions

➤ **Problem 1.** A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure?

➤ **Problem 2.** What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30°C?

➤ **Problem 3.** A gas occupies 300 mL at 127°C and 730 mm pressure. What would be its volume at STP?

➤ **Problem 4.** Calculate the volume occupied by 7g CO at 27°C and 750 mm Hg.

➤ **Problem 5.** Calculate the temperature of 4.0 moles of a gas occupying 5 dm^3 at 3.32 bar. ($R = 0.083$ bar dm^3 K^{-1} mol^{-1}).

➤ **Problem 6.** Calculate the weight of CH_4 in a 9 dm^3 cylinder at 16 bar and 27°C. ($R = 0.083$ bar dm^3 K^{-1})

➤ **Problem 7.** A desiccator of internal volume one litre containing N_2 at 1 atm is partially evacuated to final pressure of 78 mm of Hg, while T remains constant. What is the volume of gas at this stage?

➤ **Problem 8.** In a certain region of space, there are only 5 molecules per cm^3 of an average. The temperature is 3 K. What is the average pressure of this gas.

➤ **Problem 9.** Using the equation of state $PV = nRT$, show that at a given temperature density of a gas is proportional to gas pressure P.

➤ **Problem 10.** Calculate the density of CO_2 at 100°C and 800 mm Hg pressure.

➤ **Problem 11.** At 0°C, the density of a gaseous oxide at 2 bar is same as that of nitrogen at 5 bar. What is the molecular mass of the oxide?

➤ **Problem 12.** The density of helium is 0.1784 kg/m^3 at STP. If a given mass of helium at STP is allowed to expand to 1.400 times of its initial volume by changing P and T, compute its resultant density.

➤ **Problem 13.** Density of a gas is found to be 5.46 g/dm^3 at 27°C at 2 bar pressure. What will be its density at STP?

➤ **Problem 14.** Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083$ bar litre K^{-1} mol^{-1}.

➤ **Problem 15.** 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of hydrogen at 17°C, at same pressure. What is the molar mass of the gas?

➤ **Problem 16.** Assuming the same pressure in each case, calculate the mass of hydrogen required to inflate a balloon to a certain volume V at 100°C if 3.5 g helium is required to inflate the balloon to half the volume V at 25°C.

➤ **Problem 17.** The densities of an unknown gas and O_2 were find 0.2579 kg/m^3 and 0.2749 kg/m^3 at the same P and T. Calculate the mol. weight of unkown gas.

➤ **Problem 18.** A manometer is connected to a gas containing bulb. The open arm reads 43.7 cm where as the arm connected to the bulb reads 15.6 cm. If the barometric pressure is 743 mm mercury. What is the pressure of gas in bar?

➤ **Problem 19.** 0.75 mole solid A_4 and 2 mole O_2 are heated in a sealed bulb to react completely and producing are compound. If product formed is also in gaseous state, predict the ratio of final pressure at 600 K to initial pressure at 300 K.

➤ **Problem 20.** What will be the pressure of the gas mixture when 0.5 litre of H_2 at 0.8 bar and 2.0 litre of oxygen at 0.7 bar are introduced in a 1 litre vessel at 27°C?

➤ **Problem 21.** What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C?

➤ **Problem 22.** A closed container of volume 0.02 m^3 contains a mixture of neon and argon gases at a temperature 27°C and pressure 1×10^5 Nm^{-2}. The total mass of mixture is 28 g. If the gram molecular weight of neon and argon are 20 and 40 respectively, find the masses of individual gases in the container, assuming them to be ideal.

➤ **Problem 23.** A jar contains a gas and a few drops of water at T K. The pressure in the jar is 830 mm of Hg. The temperature of the jar is reduced by 1%. The vapour pressure of water at two temperature are 30 and 25 mm of Hg. Calculate the new pressure in the jar.

➤ **Problem 24.** Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar when 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

➤ **Problem 25.** The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce hydrogen. What volume of hydrogen at 20°C and one bar will be released when 0.15 g of aluminium reacts?

➤ **Problem 26.** 4 litre $C_2H_4(g)$ burns in oxygen at 27°C and 1 atm to produce $CO_2(g)$ and $H_2O(g)$. Calculate the volume of CO_2 formed at (a) 27°C and 1 atm, (b) 127°C and 1 atm, (c) 27°C and 2 atm.

➤ **Problem 27.** How many gram of $CaCO_3$ be decomposed to produce 20 litre of CO_2 at 750 torr and 27°C.

➤ **Problem 28.** 34.05 mL of phosphorus vapour weighs 0.0625 g at 546°C and 1 bar pressure. What is the molar mass of phosphorus?

➤ **Problem 29.** The total pressure of a sample of methane collected over water is 735 torr at 29°C. The aqueous tension at 29°C is 30 torr. What is the pressure exerted by dry methane?

➤ **Problem 30.** A mixture of gases at 760 mm pressure contains 65% nitrogen, 15% oxygen and 20% carbon dioxide by volume. What is partial pressure of each in mm?

➤ **Problem 31.** A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Calculate the partial pressure of hydrogen.

➤ **Problem 32.** Calculate the total pressure in a mixture of 8 g of oxygen and 4 g of hydrogen confined in a vessel of 1 dm^3 at 27°C. $R = 0.083$ bar $dm^3\ K^{-1}\ mol^{-1}$.

➤ **Problem 33.** A student forgot to add the reaction mixture to the round bottomed open flask at 27°C and put it on the flame. After a lapse of time, he realized his mistake, using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out?

➤ **Problem 34.** Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and $R = 0.083$ bar $dm^3\ K^{-1}\ mol^{-1}$).

➤ **Problem 35.** Calculate the total number of electrons present in 1.4 g of nitrogen gas.

➤ **Problem 36.** For 10 minutes each, at 27°C, from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3 litre capacity. The resulting pressure is 4.18 bar and the mixture contains 0.4 mole of nitrogen. What is the molar mass of the unknown gas?

➤ **Problem 37.** Through the two ends of a glass tube of length 200 cm hydrogen chloride gas and ammonia are allowed to enter. At what distance ammonium chloride will first appear?

➤ **Problem 38.** Calculate the relative rates of diffusion for $^{235}UF_6$ and $^{238}UF_6$.

➤ **Problem 39.** Equal volumes of two gases *A* and *B* diffuse through a porous pot in 20 and 10 seconds respectively. If the molar mass of *A* be 80, find the molar mass of *B*.

➤ **Problem 40.** Calculate the total and average kinetic energy of 32 g methane molecules at 27°C. $R = 8.314\ JK^{-1}\ mol^{-1}$.

➤ **Problem 41.** Calculate the root mean square speed, total and average translational kinetic energy in joule of the molecules in 8 g methane at 27°C.

➤ **Problem 42.** Assuming a nitrogen molecule spherical in shape and occupying the radius 200 pm, calculate :

(a) the volume of single molecule of gas,

(b) the percentage of empty space in one mole of N_2 gas at NTP.

➤ **Problem 43.** Calculate the average volume available to a molecule in a sample of N_2 at NTP. Also report the average distance between two neighbouring molecules if a nitrogen molecule is assumed to be spherical. Comment on the result if the radius of one N_2 molecule = $2 \times 10^{-8}\ cm^3$.

➤ **Problem 44.** Calculate the compressibility factor for SO_2, if 1 mole of it occupies 0.35 litre at 300 K and 50 atm pressure. Comment on the result.

➤ **Problem 45.** Calculate root mean square speed, most probable speed and average speed of :

(a) SO_2 at STP.

(b) Ethane at 27°C and 760 mm of Hg.

(c) O_2 if its density is 0.0081 g mL^{-1} at 1 atm.

(d) O_2 if 6.431 g of it occupies 5 litre at 750 mm.

(e) O_3 at 92 cm and 20°C.

➤ **Problem 46.** The average speed of an ideal gas molecule at 27°C is 0.3 m sec^{-1}. Calculate average speed at 927°C.

➤ **Problem 47.** 6.0 g He and 12.0 g Ne molecules both having average velocity 4×10^2 ms^{-1} are mixed. Calculate kinetic energy per mole of the mixture.

Answers

1. 0.8 bar;
2. 2.5 bar;
3. 196.9 mL;
4. 6.23 litre;
5. 50 K;
6. 92.5 g;
7. 1 litre
8. 2.04×10^{-21} atm
9. See Solution;
10. 1.5124 g litre^{-1};
11. 70 g/mol;
12. 0.1274 g/litre;
13. 3 g/dm^3;
14. 5.05 litre;
15. 40 g mol^{-1};
16. 2.8 g;
17. 30.02;
18. 1.347 atm or 1.36 bar;
19. 1;
20. 1.8 bar;
21. 8.31×10^4 Pa;
22. $m_{Ne} = 4$ g ; $m_{Ar} = 24$ g
23. 817 mm
24. 1/4;
25. 202.9 mL;
26. (a) 8 litre, (b) 10.67 litre, (c) 16 litre;
27. 80 g;
28. 124.77;
29. 705 torr;
30. N_2 = 494 mm, O_2 = 114 mm, CO_2 = 152 mm;
31. 0.8 bar;
32. 56.025 bar;
33. 3/5;
34. 3811 kg;
35. 4.216×10^{23} electron;
36. 448 g mol^{-1};
37. 81.1 cm from HCl end;
38. 1.0043;
39. 20 g mol^{-1};
40. 7482.6 J; 6.21×10^{-21} J;
41. 6.84×10^4 cm sec^{-1}, 1871.42 J, 62.14×10^{-22} J
42. (a) 3.35×10^{-23} cm^3 per molecule; (b) 99.9%;
43. 3.72×10^{-20} cm^3, 41.4×10^{-8} cm;
44. 0.711;
45. (a) 3.26×10^4 cm sec^{-1}, 2.66×10^4 cm sec^{-1}, 3.00×10^4 cm sec^{-1};
    (b) 4.99×10^4 cm sec^{-1}, 4.07×10^4 cm sec^{-1}, 4.60×10^4 cm sec^{-1};
    (c) 1.94×10^4 cm sec^{-1}, 1.58×10^4 cm sec^{-1}, 1.78×10^4 cm sec^{-1};
    (d) 4.83×10^4 cm sec^{-1}, 3.94×10^4 cm sec^{-1}, 4.45×10^4 cm sec^{-1};
    (e) 3.9×10^4 cm sec^{-1}, 3.18×10^4 cm sec^{-1}, 3.59×10^4 cm sec^{-1};
46. 0.6 m sec^{-1}
47. 808.16 J/mol

Solution

Solution 1. Given, $V_1 = 120$ mL ; $P_1 = 1.2$ bar ;

$V_2 = 180$ mL ; $P_2 = ?$

$\because \quad P_1V_1 = P_2V_2$ (at constant T)

$\therefore \quad 1.2 \times 120 = P_2 \times 180$

$\therefore \quad \mathbf{P_2 = 0.8\ bar}$

Solution 2. Given, $V_1 = 500\ \text{dm}^3$; $P_1 = 1$ bar ; $T_1 = 30 + 273 = 303$ K

$V_2 = 200\ \text{dm}^3$; $P_2 = ?$; $T_2 = T_1$

$$\because \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$\therefore \quad 1 \times 500 = P_2 \times 200$ or $\mathbf{P_2 = 2.5\ bar}$

Solution 3. Given : at $T_1 = 400$ K, $T_2 = 273$ K (STP)

$V_1 = 300$ mL = (300/1000) litre, $V_2 = ?$

$P_1 = (730/760)$ atm, $P_2 = 1$ atm.

$$\because \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore \quad \frac{730 \times 300}{760 \times 1000 \times 400} = \frac{1 \times V_2}{273}$$

$\therefore \quad V_2 = 0.1969$ litre = **196.9 mL**

Solution 4. Given : $w_{CO} = 7$g ; $P = (750/760)$ atm ; $m_{CO} = 28$; $T = 300$ K

$PV = (w/m)\,RT$

$$\because \quad \frac{750}{760} \times V = \frac{7}{28} \times 0.0821 \times 300$$

$\therefore \quad \mathbf{V = 6.23\ litre}$

Solution 5. Given : $n = 4$, $V = 5\ \text{dm}^3$, $P = 3.32$ bar,

$R = 0.083\ \text{dm}^3\ \text{bar}\ \text{K}^{-1}\ \text{mol}^{-1}$

$\because \quad PV = nRT$

$\therefore \quad 3.32 \times 5 = 4 \times 0.083 \times T$

$\therefore \quad \mathbf{T = 50\ K}$

Solution 6. Given : $P = 16$ bar ; $V = 9\ \text{dm}^3$; $T = 300$ K; $m_{CH_4} = 16$;

$R = 0.083\ \text{bar}\ \text{dm}^3\ \text{K}^{-1}$

$\because \quad PV = (w/m)\,RT$

$\therefore \quad 16 \times 9 = (w/16) \times 0.083 \times 300$

$\mathbf{w = 92.5\ g}$

Solution 7. The volume of vessel remains constant and some moles are given out. Thus volume of gas = 1 litre.

Solution 8. Given $n = \frac{5}{6.023 \times 10^{23}}$; $V = 1\ \text{cm}^3 = 10^{-3}$ litre, $T = 3$ K

$$\therefore \quad P \times 10^{-3} = \frac{5 \times 0.0821 \times 3}{6.023 \times 10^{23}}$$

$$\therefore \quad \mathbf{P - 2.04 \times 10^{-21}\ atm}$$

Solution 9.

$$PV = nRT \qquad ...(1)$$

$$PV = \frac{w}{m} RT \qquad \left(\because \ n = \frac{w}{m}\right)$$

$$\therefore \quad \frac{w}{V} = \frac{Pm}{RT} \quad \text{or} \quad d = \frac{Pm}{RT} \qquad ...(2)$$

By eq. (2) at constant temperature for a given gas $\boldsymbol{d \propto P}$

Solution 10. Given : $P = (800/760)$ atm ; $T = 100 + 273 = 373$ K; $m_{CO_2} = 44$

$$\because \quad PV = (w/m)\ RT$$

$$w/V = \text{density } (d)$$

$$\therefore \quad w/V = d = (Pm/RT) \qquad (R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1})$$

$$\therefore \quad d = \frac{800 \times 44}{760 \times 0.0821 \times 373} = \mathbf{1.5124\ g\ litre^{-1}}$$

Solution 11.

$$d = \frac{Pm}{RT}$$

$$\therefore \quad \frac{P_{N_2} \times m_{N_2}}{RT} = \frac{P_{\text{oxide}} \times m_{\text{oxide}}}{RT}$$

$$\therefore \quad \frac{5 \times 28}{RT} = \frac{2 \times \text{mol. mass of oxide}}{RT}$$

Molecular mass of gaseous oxide = **70 g/mol**

Solution 12. Given $\frac{w}{V} = 0.1784\ \text{kg/m}^3 = 0.1784$ g/litre at STP

It means 1 litre of gas at STP occupies 0.1784 g weight

Now by changing P the V becomes 1.4 × 1 litre, where weight remains same.

Thus, $$d = \frac{w}{V} = \frac{0.1784}{1.4} = 0.1274\ \text{kg/m}^3 = \mathbf{0.1274\ g/litre}$$

Solution 13. $d_{(g)} = 5.46\ \text{g/dm}^3$, $T = 300$ K, $P = 2$ bar

$d_{(g)} = ?$. $T - 273$ K, $P = 1$ bar

$$\because \quad \frac{d_1}{d_2} = \frac{P_1 m_1}{RT_1} \times \frac{RT_2}{P_2 m_2} \qquad (m_1 = m_2 \text{ for same gas})$$

$$\therefore \quad \frac{5.46}{d} = \frac{2 \times 273}{1 \times 300}$$

$$\therefore \quad d = \mathbf{3\ g/dm^3}$$

Solution 14. Given : $P = 1$ bar, $w = 8.8$ g, $m = 44$,
$T = 304.1$ K, $R = 0.083$ bar litre K^{-1} mol^{-1}

$$PV = \frac{w}{m} RT$$

$$\therefore \quad V = \frac{8.8 \times 0.083 \times 304.1}{44 \times 1} = \mathbf{5.05\ litre}$$

Solution 15. **For gas :** $w = 2.9$ g $\qquad T = 95 + 273 = 368$ K,
For H_2 : $w = 0.184$ g $\qquad T = 17 + 273 = 290$ K,
Since, $V_{H_2} = V_g$, $P_{H_2} = P_g$

$$n_g T_g = n_{H_2} T_{H_2}$$

$$\frac{2.9}{m} \times 368 = \frac{0.184}{2} \times 290$$

$$\therefore \quad m = \mathbf{40\ g\ mol^{-1}}$$

Solution 16. **For H_2 :** $\qquad P \times V = \frac{w}{2} \times R \times 373 \qquad$ (V is volume of balloon)

For He : $\qquad P \times \frac{V}{2} = \frac{3.5}{4} \times R \times 298$

$$w_{H_2} = \mathbf{2.8\ g}$$

Solution 17.

$$P \times V = \frac{w}{m} RT = \frac{d}{m} RT$$

or $\qquad P = \frac{w}{V \times m} RT = \frac{d}{m} RT$

For gas : $\qquad P = \frac{0.2579}{m} RT \qquad (\because\ 0.2579\ \text{kg/m}^3 = 0.2579\ \text{g/litre})$

For O_2 : $\qquad P = \frac{0.2749}{32} RT$

$$\therefore \quad m = \mathbf{30.02}$$

Solution 18. The height developed due to pressure of gas = 43.7 – 15.6 = 28.1 cm

$$\therefore \quad h.d.g. = 28.1 \times 13.6 \times 980 = 374516.8\ \text{dyne/cm}^2$$

$$\therefore \quad = \frac{374516.8}{76 \times 13.6 \times 980}\ \text{atm} = 0.37\ \text{atm}$$

$$P_{gas} = P_{atm} + h\,d\,g$$

$$\therefore \quad P_{gas} = \frac{743}{760} + 0.37 = \mathbf{1.347\ atm} \quad \left(P_{atm} = \frac{743}{760}\ \text{atm}\right)$$

$$= \frac{1.347}{0.987} = \mathbf{1.36\ bar}$$

Solution 19.

$$\begin{array}{ccccc} A_{4(s)} & + & O_{2(g)} & \longrightarrow & A_xO_{y(g)} \\ 0.75 & & 2 & & 0 \\ 0 & & 0 & & 1 \end{array}$$

g-atoms of $A = 0.75 \times 4 = 3$

g-atoms of $O = 2 \times 2 = 4$

Thus compound formed is A_3O_4

Initially only O_2 was there $\therefore \quad P_i \times V = 2 \times R \times 300$

Finally only A_3O_4 is there $\therefore \quad P_f \times V = 1 \times R \times 600$

or $$\frac{P_f}{P_i} = 1$$

Solution 20. **For H_2 :** $$n = \frac{PV}{RT} = \frac{0.8 \times 0.5}{RT} = \frac{0.4}{RT}$$

For O_2 : $$n = \frac{0.7 \times 2.0}{RT} = \frac{1.4}{RT}$$

$\therefore$ Total moles in mixture $= \dfrac{0.4}{RT} + \dfrac{1.4}{RT} = \dfrac{1.8}{RT}$

Using, $PV = nRT$ for 1 litre container

Now, $$P_{mixture} \times 1 = \frac{1.8}{RT} \times RT = \mathbf{1.8\ bar}$$

Solution 21. $$PV = nRT$$

$$n = n_{CH_4} + n_{CO_2} = \frac{3.2}{16} + \frac{4.4}{44} = 0.3\ ;\ V = 9\ \text{dm}^3 = 9\ \text{litre},$$

$$\therefore \quad P \times 9 = 0.3 \times 0.082 \times 300$$

$$\therefore \quad P = 0.82\ \text{atm} = 0.82 \times 1.013 \times 10^5\ \text{Pa}$$

$$= \mathbf{8.31 \times 10^4\ Pa}$$

Solution 22. Given $V = 0.02\ \text{m}^3$, $T = 300$ K, $P = 1 \times 10^5\ \text{Nm}^{-2}$, $R = 8.314$ J

Let a and b g be mass of Ne and Ar respectively.

Thus $$a + b = 28 \quad \text{...(i)}$$

Also total mole of Ne and Ar $= \dfrac{a}{20} + \dfrac{b}{40}$

Thus from $PV = nRT$

$$\therefore \quad 1 \times 10^5 \times 0.02 = \left[\frac{a}{20} + \frac{b}{40}\right] \times 8.314 \times 300$$

$$2a + b = 32.0 \qquad \text{...(ii)}$$

By eq. (i) and (ii) $\boldsymbol{a = 21\ g}$

$\boldsymbol{b = 24\ g}$

Solution 23. At T K, $P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}}$

$$\therefore \quad P_{\text{dry gas}} = 830 - 30 = 800 \text{ mm}$$

Now at new temperature $T_1 = T - \frac{T}{100} - 0.99\,T$

Since $V_1 = V_2$; $\frac{P}{T} = \text{constt.}$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\therefore \quad P_{\text{dry gas}} = \frac{800 \times 0.99T}{T} = 792 \text{ mm}$$

$$\therefore \quad P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}}$$

$$= 792 + 25 = \mathbf{817\ mm\ of\ Hg}$$

Solution 24. Given for gas A : $w = 1$ g, $T = 300$ K, $P = 2$ bar

For gas B : $w = 2$g, $T = 300$ K; $P = 3 - 2 = 1$ bar

(gas B + gas A) mixture shows a pressure = 3 bar

For A : $P_A V = \frac{w_A}{m_A} RT$; **For B :** $P_B V = \frac{w_B}{m_B} RT$

$$\therefore \quad \frac{P_A}{P_B} = \frac{w_A}{w_B} \times \frac{m_B}{m_A}$$

$$\therefore \quad \frac{2}{1} = \frac{1}{2} \times \frac{m_B}{m_A}$$

$$\therefore \quad \frac{m_A}{m_B} = \frac{1}{4} \qquad \therefore \quad \mathbf{m_B = 4\,m_A}$$

Solution 25.

	$2Al$	$+ 2NaOH$	$+ 2H_2O$	$\longrightarrow NaAlO_2$	$+ 3H_2$
Initial moles	$\frac{0.15}{27}$	—		—	—
Final moles	—	—		—	$\frac{3}{2} \times \frac{015}{27}$

$$\therefore \quad \text{Moles of } H_2 = \frac{0.15 \times 3}{2 \times 27} = 8.33 \times 10^{-3}$$

By $PV = nRT$ $P = 1$ bar $= 0.987$ atm ;

$T = 20 + 273 = 293$ K

$$0.987 \times V = 8.33 \times 10^{-3} \times 0.082 \times 293$$

$$\mathbf{V = 0.2029\ litre = 202.9\ ml.}$$

Solution 26. $C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(g)}$

(a) Under same conditions of P and T, volume of gases react in their mole ratio and produce the products in the same molar ratio. Thus, at 27°C and 1 atm.

1 vol. or 1 mole of C_2H_4 gives = 2 volume CO_2

$\therefore$ 4 vol. of C_2H_4 gives = 2 × 4 volume CO_2 = **8 litre CO_2**

(b) Now, at 127°C and 1 atm . $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ or $\frac{1 \times 8}{300} = \frac{1 \times V}{400}$

$\therefore$ V = **10.67 litre**

(c) Similarly at 27°C and 2 atm :

$\therefore$ V = **16 litre**

Solution 27. $CaCO_3 \longrightarrow CaO + CO_2$

It is thus evident that 1 mole of CO_2 is obtained by decomposition of 1 mole of $CaCO_3$.

$$\text{Also moles of } CO_2 = \frac{PV}{RT} = \frac{750 \times 20}{760 \times 0.0821 \times 300} = 0.80$$

Thus, mole of $CaCO_3$ required = 0.80

Also amount of $CaCO_3$ required = 0.8 × 100 = **80 g**

Solution 28. Given : $V = 34.05$ mL, $w = 0.0625$ g; $T = 546 + 273 = 819$ K, $P = 1$ bar.

$\because$ $PV = \frac{w}{m}RT$ ($R = 0.083$ bar dm^3 K^{-1} mol^{-1})

$$\therefore \quad 1 \times \frac{34.05}{1000} = \frac{0.0625}{m} \times 0.083 \times 819$$

m = **124.77**

Solution 29. $P_{\text{total}} = P_{\text{dry methane}} + P_{\text{water}}$

$735 = P_{\text{dry methane}} + 30$

$\therefore$ $P_{\text{dry methane}}$ = **705 torr**

Solution 30. Since, $P' = P_M \times$ Mole fraction

$\therefore$ $P'_{N_2} = 760 \times \frac{65}{100}$ = **494 mm**

$\therefore$ $P'_{O_2} = 760 \times \frac{15}{100}$ = **114 mm**

$\therefore$ $P'_{CO_2} = 760 \times \frac{20}{100}$ = **152 mm**

Solution 31. Weight of H_2 = 20 g in 100 g mixture ; Weight of O_2 = 80 g

$\therefore$ Moles of $H_2 = \frac{20}{2} = 10$

$$\therefore \quad \text{Moles of } O_2 = \frac{80}{32} = \frac{5}{2}$$

$$\therefore \quad \text{Total moles} = 10 + \frac{5}{2} = \frac{25}{2}$$

$$\therefore \quad P'_{H_2} = P_T \times \text{mole fraction of } H_2 = 1 \times \frac{10}{25/2}$$

$$= \mathbf{0.8\ bar}$$

Solution 32. Moles of $O_2 = \frac{8}{32} = \frac{1}{4}$; Moles of $H_2 = \frac{4}{2} = 2$

$$\therefore \quad \text{Total moles of both gas } (n) = \frac{1}{4} + 2 = \frac{9}{4}$$

$V = 1\ dm^3$, $T = 300\ K$, $R = 0.083\ bar\ dm^3\ K^{-1}\ mol^{-1}$

$$\therefore \quad PV = nRT$$

$$\therefore \quad P = \frac{9 \times 0.083 \times 300}{4 \times 1} = \mathbf{56.025\ bar}$$

Solution 33. Initial mole of air in flask $= n_1$ Temperature = 27 + 273 = 300 K

Final mole of air in flask $= n_2$ Temperature = 477 + 273 = 750 K

The volume and pressure remains constant, thus, $n_1T_1 = n_2T_2$

$$\therefore \quad n_2 = \frac{n_1 \times 300}{750} = \frac{2}{5} n_1$$

Thus, air expelled out on heating $= n_1 - n_2 = n_1 - (2/5)n_1 = \mathbf{3/5\ n_1}$

or fraction of air expelled = **3/5**

Solution 34. Weight of balloon = 100 kg = 100×10^3 g = 10^5 g

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10 \times 100)^3\ cm^3$$

$$\therefore \quad = 4190 \times 10^6\ cm^3 = 4190 \times 10^3\ \text{litre}$$

$$\text{Weight of the gas filled in balloon} = \frac{PVm}{RT} = \frac{1.66 \times 4190 \times 10^3 \times 4}{0.083 \times 300}$$

$$= \mathbf{1.117 \times 10^6\ g}$$

Total weight of (gas + balloon) = $11.17 \times 10^5 + 10^5 = 12.17 \times 10^5$ g

Weight of air displaced (Volume × density) by balloon

$$= \frac{1.2 \times 4190 \times 10^6}{10^3} = 5.028 \times 10^6\ g$$

$$\therefore \quad \text{Pay load} = 50.25 \times 10^5 - 12.17 \times 10^5 = \mathbf{38.11 \times 10^5\ g}$$

$$= \mathbf{3811\ kg}$$

Solution 35.

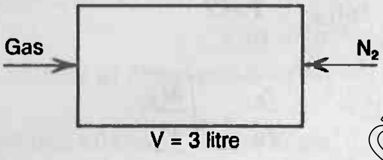
$$N_2 = 1.4\text{ g} = \frac{1.4}{28}\text{ mole}$$

$\because$ 1 mole N_2 has 14 N_A electron ($N_A = 6.022 \times 10^{23}$)

$$\therefore \frac{1.4}{28}\text{ mole } N_2 \text{ has } \frac{14 \times 1.4 \times N_A}{28} \text{ electron} = \mathbf{0.7\ N_A\ electron}$$

$$= \mathbf{4.216 \times 10^{23}\ electron}$$

Solution 36.



For the diffusion of both gases for 10 minutes under identical conditions

$$\frac{r_g}{r_{N_2}} = \sqrt{\frac{M_{N_2}}{M_g}}$$

$$\therefore \frac{n_g}{10} \times \frac{10}{n_{N_2}} = \sqrt{\frac{28}{M_g}} \quad (\because r = n/t) \qquad ...(1)$$

For mixture in vessel :

$$PV = nRT$$

$$\therefore 4.18 \times 3 = n \times 0.083 \times 300$$

$$\therefore n_{mix} = 0.50 \text{ mole}$$

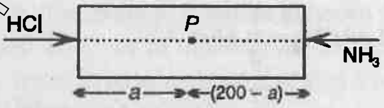
$$n_g = n_{mix} - n_N = 0.50 - 0.40 = 0.10 \qquad ...(2)$$

By eq. (2) and (1),

$$\frac{0.10}{0.4} = \sqrt{\frac{28}{M_g}}$$

$$\therefore M_g = \frac{28 \times 0.4 \times 0.4}{0.10 \times 0.10} = \mathbf{448\ g\ mol^{-1}}$$

Solution 37.



Let *a* cm from HCl end white fumes of NH_4Cl are noticed.
From Graham's law :

$$\frac{r_{HCl}}{r_{NH_3}} = \sqrt{\frac{M_{NH_3}}{M_{HCl}}} \quad \text{or} \quad \frac{a}{t} \times \frac{t}{(200 - a)} = \sqrt{\frac{17}{36.5}}$$

(time of diffusion in tube for both is same)

$\therefore$ $\mathbf{a = 81.1\ cm}$ from HCl end.

Solution 38. According to Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Since M.wt. of $^{235}UF_6 = 349$ M.wt. of $^{238}UF_6 = 352$

$$\therefore \quad \frac{r_{^{235}UF_6}}{r_{^{238}UF_6}} = \sqrt{\frac{352}{349}} = \mathbf{1.0043}$$

Solution 39.

$$\because \quad \frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\therefore \quad \frac{V}{20} \times \frac{10}{V} = \sqrt{\frac{M_B}{80}} \qquad \left(\because r = \frac{\text{volume diffused}}{\text{time}}\right)$$

$$\therefore \quad M_B = \frac{10 \times 10 \times 80}{20 \times 20} = \mathbf{20\ g\ mol^{-1}}$$

Solution 40.

$$\text{Total kinetic energy} = \frac{3}{2} nRT = \frac{3}{2} \times \frac{32}{16} \times 8.314 \times 300$$

$$= \mathbf{7482.6\ J}$$

$$\text{Average kinetic energy} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2} \times \frac{8.314 \times 300}{6.023 \times 10^{23}}$$

$$= \mathbf{6.21 \times 10^{-21}\ J}$$

Solution 41.

$$T = 27 + 273 = 300\ K$$

$$R = 8.314 \times 10^7\ erg$$

$$u_{rms} \text{ for } CH_4 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 300}{16}\right)}$$

$$= \mathbf{6.84 \times 10^4\ cm\ sec^{-1}}$$

$$\text{Now} \quad KE/mol \text{ of } CH_4 = \frac{1}{2} Mu^2$$

$$= \frac{1}{2} \times 16 \times (6.84 \times 10^4)^2$$

$$= 374.28 \times 10^8\ erg\ mol^{-1}$$

$$\therefore \quad KE \text{ for } \frac{1}{2} \text{ mole } CH_4 = \frac{374.28 \times 10^8}{2}\ erg = \frac{374.28 \times 10^8}{2 \times 10^7}\ joule$$

$$= \mathbf{1871.42\ Joule}$$

$$\text{Average kinetic energy} = \frac{\text{K.E./mol}}{\text{Av. No.}} = \frac{374.28 \times 10^{8}}{6.023 \times 10^{23}}$$

$$\therefore \quad = 62.14 \times 10^{-15} \text{ erg}$$

$$= \mathbf{62.14 \times 10^{-22} \text{ joule}}$$

Solution 42. **(a)** Volume of 1 molecule $= \frac{4}{3}\pi r^3$ (spherical shape)

$$(\because\ 200 \text{ pm} = 2 \times 10^{-8} \text{ cm}) = \frac{4}{3} \times \frac{22}{7} \times [2 \times 10^{-8}]^3$$

$$= \mathbf{3.35 \times 10^{-23} \text{ cm}^3 \text{ per molecule}}$$

(b) Now volume of N molecules of $N_2 = 3.35 \times 10^{-23} \times 6.02 \times 10^{23}$

$$= 20.177 = 20.20 \text{ cm}^3 \text{ per mol}$$

At NTP, volume of 1 mole $= 22400 \text{ cm}^3$

Thus, empty space $= 22400 - 20.20 = 22379.8 \text{ cm}^3$

$$\text{Thus,} \quad \%\text{ empty space} = \frac{\text{Empty volume}}{\text{Available volume}} \times 100$$

$$= \frac{22379.8}{22400} \times 100$$

$$= \mathbf{99.9\%}$$

Solution 43. Volume occupied by N molecules of $N_2 = 22400 \text{ cm}^3$

$$\therefore \text{ Volume occupied by 1 molecule of } N_2 = \frac{22400}{6.02 \times 10^{23}}$$

$$= \mathbf{3.72 \times 10^{-20} \text{ cm}^3}$$

$$\text{Also volume of 1 molecule of } N_2 = \frac{4}{3}\pi r^3$$

$$\therefore \quad \frac{4}{3} \times \frac{22}{7} \times r^3 = 3.72 \times 10^{-20}$$

$$\therefore \quad r = 20.7 \times 10^{-8} \text{ cm}$$

Thus, average distance in between two N_2 molecules $= 2 \times r$

$$= \mathbf{41.4 \times 10^{-8} \text{ cm}}$$

Given radius of $N_2 = 2 \times 10^{-8}$ cm; obtained radius is 20.7×10^{-8}. Thus, it means that average distance between two molecules is gaseous state is almost 10 times of the diameter of each molecule. This confirms the empty space in gaseous state and also a reasonable justification for their compression.

Solution 44. Given : $P = 50$ atm, $T = 300$ K, $V = 0.35$ litre, $m = 64$.

$$\therefore \quad Z = \frac{PV}{nRT} = \frac{50 \times 0.35}{1 \times 0.0821 \times 300} = \mathbf{0.711}$$

The Z values are lesser than 1 and thus, $nRT > PV$. This means to attain $Z = 1$, volume must have been more at same P and T or we can say that SO_2 is more compressible than ideal gas.

Solution 45. (a) Given : $T = 273$ K

$$u_{\text{rms}} \text{ of } SO_2 = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 273}{64}}$$

$$= \mathbf{3.26 \times 10^4 \text{ cm sec}^{-1}}$$

Now

$$u_{MP} = u_{\text{rms}} \times 0.816 = \mathbf{2.66 \times 10^4 \text{ cm sec}^{-1}}$$

$$u_{AV} = u_{\text{rms}} \times 0.9213 = \mathbf{3.00 \times 10^4 \text{ cm sec}^{-1}}$$

(b) $$u_{\text{rms}} \text{ of } C_2H_6 = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{30}}$$

$$= \mathbf{4.99 \times 10^4 \text{ cm sec}^{-1}}$$

($\because$ Given $T = 273 + 27 = 300$ K)

Note : If T is given, always use $u_{\text{rms}} = \sqrt{(3RT/M)}$

Calculate u_{MP} and u_{AV} as above

$$u_{MP} \text{ for } C_2H_6 = \mathbf{4.07 \times 10^4 \text{ cm sec}^{-1}}$$

$$u_{AV} \text{ for } C_2H_6 = \mathbf{4.60 \times 10^4 \text{ cm sec}^{-1}}$$

(c) Given density (d) of $O_2 = 0.0081$ g mL^{-1}, $P = 1$ atm

$$\therefore \quad u_{\text{rms}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 1 \times 76 \times 13.6 \times 981}{0.0081}}$$

$$= \mathbf{1.94 \times 10^4 \text{ cm sec}^{-1}}$$

Calculate u_{MP} and u_{AV} as above

$$u_{MP} = \mathbf{1.58 \times 10^4 \text{ cm sec}^{-1}}$$

$$u_{AV} = \mathbf{1.78 \times 10^4 \text{ cm sec}^{-1}}$$

(d) Given for O_2 : $w = 6.431$ g, $V = 5$ litre, $P = 750$ mm.

Using $PV = (w/m)\, RT$

$$\frac{750}{760} \times 5 = \frac{6.431}{32} \times 0.0821 \times T$$

$$\therefore \quad T = 299.05 \text{ K}$$

$$u_{\text{rms}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 299.05}{32}}$$

$$= \mathbf{4.83 \times 10^4 \text{ cm sec}^{-1}}$$

$$u_{MP} = \mathbf{3.94 \times 10^4 \text{ cm sec}^{-1}}$$

$$u_{AV} = \mathbf{4.45 \times 10^4 \text{ cm sec}^{-1}}$$

(e) Given for O_3 : $T = 293$ K, $P = (92/76)$ atm

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 293}{48}}$$

$$= \mathbf{3.9 \times 10^4 \text{ cm sec}^{-1}}$$

$$\therefore \quad u_{MP} = 3.18 \times 10^4 \text{ cm sec}^{-1}$$

$$u_{AV} = 3.59 \times 10^4 \text{ cm sec}^{-1}$$

Solution 46. Average speed $u_{AV} = \sqrt{[(8RT)/(\pi M)]}$ at temperature T_1 ;

d_2 $$u_{AV_1} = \sqrt{\frac{8RT_1}{\pi M}} \text{ at temperature } T_2 \text{ ;}$$

$$u_{AV_2} = \sqrt{\frac{8RT_2}{\pi M}}$$

$$\therefore \quad \frac{u_{AV_1}}{u_{AV_2}} = \sqrt{\frac{T_1}{T_2}}$$

$$\therefore \quad \frac{0.3}{u_{AV_2}} = \sqrt{\frac{300}{1200}} \qquad [\because T_1 = 300 \text{ K}, \ T_2 = 1200 \text{ K}]$$

$$\therefore \quad u_{AV_2} = 0.6 \text{ m sec}^{-1}$$

Solution 47. $$u_{AV} = \sqrt{\frac{8RT}{\pi M}}$$

For He : $$4 \times 10^2 = \sqrt{\frac{8RT}{\pi \times 4 \times 10^{-3}}} \qquad (M \text{ in kg})$$

$$\therefore \quad RT = \frac{16 \times 10^4 \times \pi \times 4 \times 10^{-3}}{8} = 80\,\pi$$

For Ne : $$4 \times 10^2 = \sqrt{\frac{8RT}{\pi \times 20 \times 10^{-3}}} \qquad (M \text{ in kg})$$

$$\therefore \quad RT = \frac{16 \times 10^4 \times \pi \times 20 \times 10^{-3}}{8} = 400\,\pi$$

$$\because \quad KE = \frac{3}{2}nRT$$

$$\therefore \quad \text{Total KE of He} = \frac{3}{2} \times \frac{6}{4} \times 80\,\pi = 565.71 \text{ J/mol}$$

$$\text{Total KE of Ne} = \frac{3}{2} \times \frac{12}{20} \times 400\,\pi = 1131.42 \text{ J/mol}$$

$$\therefore \text{Total KE of mixture} = 565.71 + 1131.42 \text{ J} = 1697.14 \text{ J/mol}$$

$$\text{Total mole in mixture} = \frac{6}{4} + \frac{12}{20} = 1.5 + 0.6 = 2.1$$

$$\text{KE/mole of mixture} = \frac{1697.14}{2.1} = 808.16 \text{ J/mol}$$

Selected Problems with Solutions

➤ **Problem 1.** An evacuated bulb of unknown volume is filled with a sample of H_2 gas at a temperature *T*. The pressure of the gas in the bulb is 756 mm Hg. A portion of the H_2 gas is transferred to a different flask and found to occupy a volume of 40.0 mL at 1.00 atm and the same temperature *T*. The pressure of the H_2 gas remaining in the original bulb drops to 625 mm Hg at the same temperature *T*. Assuming H_2 is an ideal gas, what is the volume of the bulb?

➤ **Problem 2.** Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 27°C and contain 0.70 mole of H_2 at 0.5 atm. One of the flask is then immersed into a bath kept at 127°C, while the other remains at 27°C. Calculate the final pressure and the number of mole of H_2 in each flask.

➤ **Problem 3.** An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that,

(a) $\frac{1}{3}$rd of air measured at 27°C escapes out.

(b) $\frac{1}{3}$rd of air measured at final temperature escapes out.

➤ **Problem 4.** A bulb of three litre capacity filled with air is heated from 27°C to *t*°C. The air thus, expelled measured 1.45 litre at 17°C. Considering the pressure to be 1 atm throughout the experiment and ignoring the expansion of bulb, calculate *t*.

➤ **Problem 5.** The density of helium is 0.1784 kg/m^3 at STP. If a given mass of helium at STP is allowed to expand 1.40 times of its initial volume by changing the temperature and pressure, compute its resultant density.

➤ **Problem 6.** A spherical balloon of 21 cm diameter is to be filled up with H_2 at NTP from a cylinder containing the gas at 20 atm 27°C. The cylinder can hold 2.82 litre of water at NTP. Calculate the number of balloons that can be filled up.

➤ **Problem 7.** A 2 litre vessel is filled with air at 50°C and a pressure of 3 atm. The temperature is now raised to 200°C. A valve is now opened so that the pressure inside drops to one atm. What fraction of the total number of moles, inside, escaped on opening the valve? Assume no change in the volume of the container.

➤ **Problem 8.** In a basal metabolism measurements timed at 6.0 minute, a patient exhaled 52.5 litre of air, measured over water at 20°C. The vapour pressure of water at 20°C is 17.5 torr. The barometric pressure was 750 torr. The exhaled air analysed 16.75 volume per cent of oxygen and the inhaled air 20.32 volume per cent of oxygen, both on a dry basis. Neglecting any solubility of the gases in water and any difference in the total volume of inhaled and exhaled air, calculate rate of oxygen consumption by the patient in mL (STP) per minute.

► **Problem 9.** 5.0 litre water is placed in a closed room of volume 2.5×10^1 litre having temperature 300 K. If vapour pressure of water is 27.0 mm and density is 0.990 g/cm^3 at this temperature, how much water is left in liquid state.

► **Problem 10.** How much water vapour is contained in a cubic room of 4 m along an edge if the relative humidity is 50% and the temperature is 27°C? The vapour pressure of water at 27°C is 26.7 torr. (The relative humidity expresses the partial pressure of water as a per cent of water vapour pressure).

► **Problem 11.** A closed container of volume 0.02 m^3 contains a mixture of neon and argon gases at a temperature of 27°C and pressure of 1×10^5 N/m^2. The total mass of the mixture is 28 g. If molar masses of neon and argon are 20 and 40 g mol^{-1} respectively, find the masses of individual gases in the container, assuming than to be ideal. ($R = 8.314$ J/mol-K)

► **Problem 12.** 44 g dry ice is placed in a bottle of 1 litre capacity and tightly corked. Calculate the total pressure in bottle after complete evaporation of dry ice at 300 K.

► **Problem 13.** A tightly sealed 25.0 litre acetone drum was found to have 15.4 litre acetone (l) at 780 mm Hg pressure and 18°C. Suddenly during transportation the drum was dented and its internal volume was found to decrease by 4.6 litre. If vapour pressure of acetone at 18°C is 400 mm of Hg, calculate the pressure inside the drum after denting.

► **Problem 14.** 100 g of an ideal gas (mol. wt. 40) is present in a cylinder at 27°C and 2 atm pressure. During transportation, cylinder fell and a dent was developed in cylinder. The valve attached to cylinder cannot keep the pressure greater than 2 atm and therefore 10 g of gas leaked out through cylinder. Calculate :

(i) the volume of cylinder before and after dent.

(ii) the pressure developed after dent if valve can withstand any pressure inside the cylinder.

► **Problem 15.** The vapour pressure of water at 80°C is 355 torr. A 100 mL vessel contained water saturated oxygen at 80°C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 mL vessel at the same temperature. What were the partial pressures of oxygen and water vapour, what was the total pressure in the first equilibrated state? Neglect volume of any water which might condense.

► **Problem 16.** A certain container has 5×10^{22} molecules of a gas *A* at a pressure of 900 torr. By a photo-chemical combination allowing light to fall on the molecules, the pressure drops to 500 torr due to dimerization. If the temperature and volume remain the same, how many monomer, dimer and total molecules are present after exposure to light?

► **Problem 17.** A container holds 3 litre of $N_2(g)$ and $H_2O(l)$ at 29°C. The pressure is found to be 1 atm. The water in container is instantaneously electrolysed to give H_2 and O_2 following the reaction, $H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$. At the end of electrolysis the pressure was found to be 1.86 atm.

Calculate the amount of water present in the container if the aqueous tension of water at 29°C is 0.04 atm.

➤ **Problem 18.** Three hollow metallic boxes *A*, *B* and *C* are connected to one another through narrow tube of negligible volume and are filled with Argon gas. If the internal volume of these boxes are in the ratio 1 : 2 : 4, find out

(a) The molar ratio of Argon in these boxes.

(b) The mole ratio of Argon if boxes *A*, *B* and *C* are immersed in different temperatures bath having 27°C, 127°C and 327°C respectively.

➤ **Problem 19.** A 10 cm column of air is trapped by a column of Hg, 8 cm long is capillary tube horizontally fixed as shown below at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature,

(a) Vertically with open end up,

(b) Vertically with open end down,

(c) At 45° from horizontal with open end up.

➤ **Problem 20.** A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.

➤ **Problem 21.** A mixture of 0.5 mole of CO and 0.5 mole of CO_2 is taken in a vessel and allowed to effuse out through a pinhole into another vessel which has vacuum. If a total of *A* mole has effused out in time *t*, show that $M_1A + M_2(1 - A) = 36$, where M_1 and M_2 are mean molar masses of the mixture that has effused out and the mixture still remaining in vessel respectively.

➤ **Problem 22.** One molecule of haemoglobin will combine with four O_2 molecules. If 1.0 g of haemoglobin combines with 1.53 mL of oxygen at body temperature (37°C) and a pressure of 743 torr, what is the molar mass of haemoglobin?

➤ **Problem 23.** A closed bulb contains 0.01 mole of inert helium gas and a sample of solid white NH_4Cl. The pressure of the He is measured at 27°C and is found to be 114 mm Hg. The bulb is then heated to 327°C. All the NH_4Cl decomposes according to the equation:

$$NH_4Cl(s) = NH_3(g) + HCl(g)$$

The final total pressure in the bulb after complete decomposition of solid is 908 mm Hg. Assume all the gases are ideal.

(a) What is the partial pressure of HCl(g) in the bulb at 327°C when reaction is complete?

(b) How many grams of $NH_4Cl(s)$ were in the bulb at 27°C?

► Problem 24. A man weighs 72.15 kg and want to fly in the sky with the aid of balloons itself weighing 20 kg and each containing 50 moles of H_2 gas at 0.05 atm and 27°C. If the density of air at the given conditions is 1.25 g/litre, how many such types of balloons he is needed to fly in the sky.

► Problem 25. The rate of diffusion of a sample of ozonised oxygen is 0.98 times more than that of pure oxygen. Find the percentage (by volume) of ozone in the ozonised sample. Also report percentage by weight.

► Problem 26. Calculate the temperatures at which the molecules of the first two members of the homologous series C_nH_{2n+2} will have the same RMS speed as CO_2 gas has 770 K.

► Problem 27. The ratio rate of diffusion of gases *A* and *B* is 1 : 4. If the ratio of their masses present in the initial mixture is 2 : 3, calculate the ratio of their mole fraction.

► Problem 28. At 20°C, two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg of H_2. The N_2 balloon leaks to a pressure of 1/2 atm in 1 hr. How long will it take for H_2 balloon to reach a pressure of 1/2 atm?

► Problem 29. The pressure in bulb dropped from 2000 to 1500 mm of Hg in 47 minutes when the contained O_2 leaked through a small hole. The bulb was then completely evacuated. A mixture of O_2 and another gas of mol. wt. 79 in the molar ratio 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the mole ratio of two gases remaining in the bulb after a period of 74 minutes.

► Problem 30. Calculate the rms speed of hydrogen molecule which occupies 22.4 dm^3 at S.T.P.

► Problem 31. It has been considered that during the formation of earth, H_2 gas was available on our planet. Due to excessively high temperature during the formation of earth, H_2 gas escaped out of the planet. If average escaping velocity of H_2 is 1.1×10^6 cm/sec, what was the temperature at the time of earth formation.

► Problem 32. The critical temperature and pressure of CO_2 gas are 304.2 K and 72.9 atm respectively. Calculate the radius of CO_2 molecule assuming it to behave van der Waals' gas.

► Problem 33. 400 moles of van der Waals' gas having $b = 0.02$ L mol^{-1} are contained in a 1000 litre vessel. The temperature and pressure of the gas are 400 K and 90 atm respectively. Calculate the pressure of the gas at 700 K.

► Problem 34. Calculate the % of the free volume available in 1 mole gaseous water at 1.00 atm and 100°C. Density of liquid water at 100°C is 0.958 g/cm^3.

► Problem 35. If the rate of change of rms speed of a gas is twice the rate of change of absolute temperature, calculate the rms speed of Ne.
(At. Wt. of Ne = 20).

➤ **Problem 36.** The density of vapours at 1.0 atm and 500 K is $0.35\ \text{kg/m}^3$. The vapours effuse through a small hole at a rate of 1.33 times faster than oxygen under similar conditions. Calculate :

(a) molecular weight
(b) molar volume
(c) compressibility factor and which forces predominates
(d) if vapours behaves ideally at 1000 K, the average translational kinetic energy.

➤ **Problem 37.** One litre of a gas at 300 atm and 473 K is compressed to a pressure of 600 atm and 273 K. The compressibility factors found to be 1.072 and 1.375 respectively at the initial and finally conditions. Calculate the final volume.

Answers

1. 232.1 mL ;
2. 0.5714 atm ;
3. (a) 177°C, (b) 127°C ;
4. 327°C
5. 0.1274 kg/m^3
6. 10
7. 0.77 ;
8. 280 mL/minute ;
9. 4.344 litre ;
10. 824.4 g ;
11. Neon = 4 g, Argon = 24 g ;
12. 25.63 atm
13. 1129.6 mm ;
14. 30.79 litre, 27.71 litre, 2.22 atm
15. 910 torr, 355 torr, 1265 torr ;
16. $\frac{5}{9} \times 10^{23}$, $\frac{20}{9} \times 10^{23}$, $\frac{25}{9} \times 10^{23}$;
17. 1.24 g ;
18. (a) 1 : 2 : 4 ; (b) 2 : 3 : 4 ;
19. (a) 9.05 cm, (b) 11.18 cm, (c) 9.3 cm ;
20. 337.5 K ;
21. See solution ;
22. 6.8×10^4 ;
23. (a) 0.447 atm , (b) 0.797 g ;
24. 3 ;
25. 8.25% by volume of O_3, 11.88% by weight of O_3 ;
26. 280 K, 525 K ;
27. 0.347 ;
28. 16 minute ;
29. 1 : 1.236 ;
30. 1.84×10^3 m/sec ;
31. 11425 K ;
32. 1.62×10^{-8} cm ;
33. 99.93 atm ;
34. 99.9386% ;
35. 311.775 ms^{-1}
36. (a) 18.1, (b) 51.71 litre, (c) 1.26, (d) 2.07×10^{-20} J
37. 0.37 litre

Problems for self Assessment

1. A 1.5 litre sample of a gas having density 1.25 kg/m^3 at 1.0 atm and 0°C was compressed to 575 atm resulting a gas volume of 3.92 cm^3 in violation of Boyle's Law. What is the final density of this gas?

2. An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find out
   (a) The temperature at which vessel was heated.
   (b) The air escaped out if vessel is heated to 900 K.
   (c) The temperature at which half of the air escapes out.

3. A bulb was heated from 27°C to 227°C at constant pressure. Calculate the volume of bulb if,
   (a) 200 mL of air measured at 227°C was expelled during process.
   (b) 200 mL of air measured at 27°C was expelled during process.

4. A 100.0 m^3 tank is constructed to store LNG (liquefied natural gas, CH_4) at −164°C and 1 atm pressure, under which its density is 415 kg/m^3. Calculate the volume of storage tank capable of holding the same mass of LNG as a gas at 20°C and 1.0 atm pressure.

5. In order to economize on the oxygen supply in space ships, it has been suggested that the oxygen in exhaled CO_2 be converted to water by a reduction with hydrogen. The CO_2 output per astronaut has been estimated as 1.00 kg per 24 hr day. An experimental catalytic converter reduces CO_2 at a rate of 600 mL (STP) per minute. What fraction of the time would such a converter have to operate in order to keep up with the CO_2 output of one astronaut.

6. The respiration of a suspension of yeast cells was measured by observing the decrease in pressure of gas above the cell suspension. The apparatus was arranged so that the gas was confined to a constant volume, 16.0 cm^3, and the entire pressure change caused by uptake of oxygen by the cells. The pressure was measured in a manometer, the fluid of which has a density of 1.034 g/cm^3. The entire apparatus was immersed in a thermostat at 37°C. In a 30 minute observation period the fluid in the open side of the manometer dropped 37 mm. Neglecting the solubility of oxygen in the yeast suspension, compare the rate of oxygen consumption by the cells in mm^3 of O_2 (STP) per hour.

7. An air bubble starts rising from the bottom of a lake. Its diameter is 3.6 mm at the bottom and 4 mm at the surface. The depth of the lake is 250 cm and temperature at the surface is 40°C. What is the temperature at the bottom of the lake? Given atmospheric pressure = 76 cm of Hg and $g = 980$ cm sec^{-2}. Neglect surface tension effect.

8. [illegible] g of CO_2 gas was injected into a bulb of internal volume 8 litre at pressure P and temperature T K. When the bulb was then placed in a thermostat maintained at $(T + 115$ K$)$, 0.6 g of the gas was let off to keep the original pressure. Find the value of P and T.

9. Two glass bulbs of equal volumes are connected by a narrow tube and are filled with a gas at 0°C and a pressure of 76 cm of Hg. One of the bulb is then placed in melting ice and the other is placed in a water bath at 62°C. What is the new value of pressure inside the bulbs. The volume of connecting tube is negligible.

10. The compressibility factor for N_2 at 223 K and 81.06 MPa is 1.95 and at 373 K and 20.265 MPa is 1.10. If a certain mass of N_2 occupies 1 litre at 223 K and 81.06 MPa, what would be its volume at 373 K and 20.265 MPa.

11. A mixture of H_2O_v, CO_2 and N_2 was trapped in a glass apparatus with a volume of 0.731 mL. The pressure of total mixture was 1.74 mm of Hg at 23°C. The sample was transferred to a bulb in contact with dry ice (–75°C) so that H_2O_v are frozen out. When the sample returned to normal value of temperature, pressure was 1.32 mm of Hg. The sample was then transferred to a bulb in contact with liquid N_2 (–95°C) to freeze out CO_2. In the measured volume, pressure was 0.53 mm of Hg at original temperature. How many moles of each constituent are in mixture?

12. Assume that dry air contains 79% N_2 and 21% O_2 by volume. Calculate the density of dry air and moist air at 25°C and 1 atmospheric pressure when relative humidity is 60%. The vapour pressure of water at 25°C is 23.76 mm.

[Relative humidity is given by percentage relative humidity

$$= \frac{100 \times \text{partial pressure of water}}{\text{vapour pressure of water at that temperature}}]$$

13. Three vessels *X*, *Y* and *Z* are of 1.5, 2.5 and 4.0 litre capacity respectively. Vessel *X* contains 0.5 g of N_2 gas at 740 mm pressure. Vessel *Y* contains 1 g argon gas at 480 mm pressure and vessel *Z* contains neon at 160 mm. What will be the pressure in vessel *Z* if gases of *X* and *Y* are transferred to Z. The temperature during whole systems remains constant.

14. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mm Hg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume the temperature to be 50°C. Aqueous tension at 50°C = 93 mm Hg.

15. The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure in two bulbs if the temperature remains same?

16. A vessel contains 7.1 g chlorine gas at pressure *P* and temperature *T* K. On heating the vessel to 30° higher temperature, 246 mL of chlorine at 1 atm and 27°C is taken out to maintain same pressure in vessel. Calculate,

(a) The original temperature.

(b) If the gas is not allowed to escape out, the pressure increases by 0.11 atm. Calculate the volume of vessel and initial pressure.

17. A thin tube of uniform cross-section is sealed at both ends. It lies horizontally. The middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0. When the tube is held at an angle 60° with the vertical, the length of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate the pressure P_0 in cm of Hg. (Temperature of the system is kept at 30°C)

18. A jar contains a gas and few drops of water at T K. The pressure in the jar is 830 mm of Hg. The temperature of the jar is reduced to 99%. The vapour pressure of water at two temperatures are 30 and 25 mm of Hg respectively. Calculate the pressure in jar.

19. A sample of SF$_5$OF(g) was contained in a glass vessel of one litre at 25°C and a pressure of 80 mm. A quantity of N$_2$F$_4$(g) was added to bring in the pressure to 160 mm. The reaction using SF$_5$OF(g) and N$_2$F$_4$(g) completely produced a variety of products such as NF$_3$, NO, SiF$_4$ (by reaction with glass) and SF$_6$, SO$_2$F$_2$, SOF$_4$, SF$_5$ONF$_2$, and NO$_2$. The mixture contained SF$_5$ONF$_2$ 40% mole with respect to reactant SF$_5$OF(g). Calculate the mass of SF$_5$ONF$_2$. Assume atomic weight of F = 19.

20. There are 201 equidistant rows of spectators sitting in a hall. A magician releases laughing gas N$_2$O from the front and the tear gas (mol. wt. 176) from the rear of the hall spontaneously. Which row spectators will have a tendency to smile and weep simultaneously?

21. The rate of diffusion of a sample of ozonised oxygen is 0.98 times more than that of pure oxygen. Find the percentage (by volume) of ozone in the ozonised sample. Also report percentage by weight.

22. A mixture of H$_2$ and O$_2$ in the 2 : 1 volume ratio is allowed to diffuse through a porous diaphragm. Calculate the composition of the gases coming out initially.

23. N$_2$ and He gases are contained in a container, the density of the gaseous mixture is found to be 1.35 lit^{-1} at 2.1 atmosphere and 320K temperature. If both the gases are effusing through the constant area of orifice of the container at the 320K, then find out the composition of the mixture effusing out initially.

24. Find the temperature at which 3 mole of SO$_2$ obeying van der Waals' equation occupies a volume of 10 litre at a pressure of 15 atm. (a = 6.71 atm lit^2 mol^{-2}, b = 0.0564 lit mol^{-1}).

25. van der Waals' constant b for a gas is 4.2 × 10^{-2} litre mol^{-1}. How close the nuclei of the two molecules come together?

26. Radius of a spherical molecule of a gas is 2 × 10^{-8} cm. Calculate:
    (a) Co-volume per molecule,
    (b) Co-volume per mole,
    (c) Critical volume.

27. Reduced temperature for benzene is 0.7277 and its reduced volume is 0.40. Calculate the reduced pressure of benzene.

Answers

1. 478.3 kg/m^3 ;
2. (a) 477°C, (b) $\frac{2}{3}n$, (c) 327°C ;
3. (a) 300 mL, (b) 500 mL ;
4. 6.240×10^3 m^3 ;
5. 58.8% ;
6. 1.0×10^2 mm^3/hr ;
7. 10.4°C ;
8. $P = 0.48$ atm , $T = 575$ K ;
9. 83.8 cm of Hg ;
10. 3.774 litre ;
11. $n_{H_2} = 2.1 \times 10^{-8}$, $n_{CO_2} = 3.1 \times 10^{8}$, $n_{H_2O} = 1.7 \times 10^{-8}$;
12. 1.171 g litre^{-1} ;
13. 737.5 mm ;
14. 146.5 mm ;
15. 7 atm ;
16. (a) 270 K, (b) $V = 2.239$ litre, $P = 0.99$ atm ;
17. 75.4 cm of Hg ;
18. 817 mm ;
19. 0.348 g ;
20. 134th row ;
21. 8.25% by volume ;
22. 8 : 1 ;
23. 0.438 ;
24. 349.80°C ;
25. 3.2×10^{-8} cm ;
26. (a) 1.34×10^{-22} cm^3, (b) 80.71 cm^3, (c) 242.13 cm^3 ;
27. $P_r = 10.358$.

2

Mole and Equivalent Concept

Chapter at a Glance

For Elements:

1. **1 g atom** = N atoms = g atomic weight

For Compounds:

2. 1 mole = N molecule = g molecular weight

Dulong Petits law:

3. Atomic weight × specific heat ≈ 6.4 (for metals only)

Equivalent weight:

4. **Equivalent weight of element** = $\dfrac{\text{Atomic weight}}{\text{Valence}}$

5. **Equivalent weight of compound** = $\dfrac{\text{Molecular weight (Mol. wt.)}}{\text{Total charge on cation or anion}}$

6. **Equivalent weight of acid** = $\dfrac{\text{Mol. wt.}}{\text{Basicity}}$

7. **Equivalent weight of base** = $\dfrac{\text{Mol. wt.}}{\text{Acidity}}$

8. **Equivalent weight of acid salt** = $\dfrac{\text{Mol. wt.}}{\text{Replaceable H atom in acid salt}}$

9. **Equivalent weight of an ion** = $\dfrac{\text{Formula weight}}{\text{Charge on ion}}$

Methods for expressing concentrations:

10. **Normality** = $\dfrac{\text{Equivalent of solute}}{\text{Volume in litre}}$

11. **Equivalent** = $N \times V_{(\text{in } l)} = \dfrac{\text{wt.}}{\text{Eq. wt.}}$

12. **Milli-equivalent** = $N \times V_{(\text{in mL})} = \dfrac{\text{wt.}}{\text{Eq. wt.}} \times 1000$

13. **Molarity** = $\dfrac{\text{Moles of solute}}{\text{Volume in litre}}$

14. **Moles** = $M \times V_{(\text{in } l)} = \dfrac{\text{wt.}}{\text{Mol. wt.}}$

15. **Milli-moles** = $M \times V_{(\text{in mL})} = \dfrac{\text{wt.}}{\text{Mol. wt.}} \times 1000$

16. **Molality** = $\dfrac{\text{Moles of solute}}{\text{wt. of solvent (in kg)}}$

17. **Strength (S)** = $N \times \text{Eq. wt.}$

18. **% by weight** $= \dfrac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$

19. **% by volume** $= \dfrac{\text{wt. of solute}}{\text{Volume of solution}} \times 100$

20. **% by strength** $= \dfrac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$

21. **Mole fraction of solute** $= \dfrac{\text{Moles of solute}}{\text{Moles of solute + Moles of solvent}}$

22. **Mole fraction of solvent** $= \dfrac{\text{Moles of solvent}}{\text{Moles of solute + Moles of solvent}}$

23. **Specific gravity** $= \dfrac{\text{wt. of solution}}{\text{Volume of solution}}$ *i.e.*, wt. of 1 mL solution

24. **Formality** $= \dfrac{\text{wt. of ionic solute}}{\text{Formula wt. of solute} \times \text{volume (in litre)}}$

25. **Molecular wt.** = Vapour density × 2 (for gases only)

Note:

1. Molality, mole fraction, % by wt. are temperature independent.
2. Moles, milli-moles, equivalent, milli-equivalent of solute does not change on dilution.
3. Equal equivalents or Meq. of reactants react to give same no. of eq. or Meq of products.
4. Moles and millimoles react according to stoichiometry of equation.
5. One mole of gas at STP occupies 22.4 litre volume.

The Basic Problems with Solutions

➤ **Problem 1.** (a) When 4.2 g $NaHCO_3$ is added to a solution of CH_3COOH weighing 10.0 g, it is observed that 2.2 g CO_2 is released into atmosphere. The residue is found to weigh 12.0 g. Show that these observations are in agreement with the low of conservation of weigh.

(b) If 6.3 g of $NaHCO_3$ are added to 15.0 g CH_3COOH solution. The residue is found to weigh 18.0 g. What is the mass of CO_2 released in this reaction.

➤ **Problem 2.** 1.7 g of silver nitrate dissolved in 100 g of water is taken. 0.585 g of sodium chloride dissolved in 100 g of water is added to it and chemical reaction occurs. 1.435 g of silver chloride and 0.85 g of sodium nitrate are formed. Justify that the data obey law of conservation of mass.

➤ **Problem 3.** 1.08 g of copper wire was allowed to react with nitric acid. The resulting solution was dried and ignited when 1.35 g of copper oxide was obtained. In another experiment 2.30 g of copper oxide was heated in presence of hydrogen yielding 1.84 g of copper. Show that the above data are in accordance with law of constant proportion.

➤ **Problem 4.** Carbon and oxygen are known to form two compounds. The carbon content in one of these is 42.9% while in the other it is 27.3%. Show that this data is in agreement with the law of multiple proportions.

➤ **Problem 5.** 8 litre of H_2 and 6 litre of Cl_2 are allowed to react to maximum possible extent. Find out the final volume of reaction mixture. Suppose *P* and *T* remains constant throughout the course of reaction.

➤ **Problem 6.** Calculate the mass in g of :

(a) 2 g-atom of Mg (b) 3 *N* atoms of Mg.

➤ **Problem 7.** What is the weight of one atom of H in g (at.wt. of H = 1.008)?

➤ **Problem 8.** How many g-atoms and no. of atoms are there in 120 g carbon?

➤ **Problem 9.** Calculate the mass in g of :

(a) 2 mole of CO_2 (b) 2 *N* molecules of CO_2.

➤ **Problem 10.** How many molecules are in 5.23 g of glucose ($C_6H_{12}O_6$)?

➤ **Problem 11.** How many carbon atoms are present in 0.35 mole of $C_6H_{12}O_6$?

➤ **Problem 12.** How many nitrogen atoms are in 0.25 mole of $Ca(NO_3)_2$?

➤ **Problem 13.** How many molecules of water are present in the one mL of water?

➤ **Problem 14.** How many molecules are present in one mL of water vapours of STP?

➤ **Problem 15.** What is the weight of 3.01×10^{23} molecules of ammonia?

➤ **Problem 16.** If it requires one second to count four wheat grains, calculate the time in years to count one mole of wheat grains.

➤ **Problem 17.** How many years it would take to spend Avogadro's number of rupees at the rate of 1 million rupees in one second ?

➤ **Problem 18.** How many g of S are required to produce 10 moles and 10 g of H_2SO_4 respectively?

➤ **Problem 19.** How many g atoms of S are present in 4.9 g H_2SO_4?

➤ **Problem 20.** Calculate the number of Cl^- and Ca^{2+} ions in 333 g anhydrous $CaCl_2$.

➤ **Problem 21.** Calculate the number of mole of water in 366 g $BaCl_2 \cdot 2H_2O$.

➤ **Problem 22.** Calculate the number of molecules of methane and atoms of C and H in 24 g methane.

➤ **Problem 23.** Which of the following will weigh maximum amount?

(a) 20 g iron, (b) 1.2 g atom of N,

(c) 1×10^{23} atoms of carbon, (d) 1.12 litre of O_2 at STP.

➤ **Problem 24.** For a precious stone, 'carat' is used for specifying its mass. If 1 carat = 3.168 grains (a unit of mass) and 1 gram = 15.4 grains, find the total mass in kilogram of the ring that contains a 0.500 carat diamond and 7.00 gram gold.

➤ **Problem 25.** Vanadium metal is added to steel to impart strength. The density of vanadium is 5.96 g/cm^3. Express this in SI unit (kg/m^3).

➤ **Problem 26.** Naturally occurring chlorine is 75.53% Cl ^{35} which has an atomic mass of 34.969 amu and 24.47% Cl ^{37}, which has a mass of 36.966 amu. Calculate the average atomic mass of chlorine.

➤ **Problem 27.** Use the data given in the following table to calculate the molar mass of naturally occuring argon :

Isotope	**Isotopic molar mass**	**Abundance**
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

➤ **Problem 28.** The specific heat of metal is 1 Jg^{-1} K^{-1}. If equivalent weight of metal is 9, calculate its exact at.wt.

➤ **Problem 29.** 1 g of a metal (specific heat = 0.06 cal/g), combines with oxygen to form 1.08 g of oxide. What is the atomic mass of metal? Also report its valency.

➤ **Problem 30.** For the dissolution of 1.08 g of a metal, 0.49 g of H_2SO_4 was required. If specific heat of metal is 0.06 cal/g, what is its atomic mass?

➤ **Problem 31.** Determine the equivalent weight of each given below, if formula weight of these compounds are *X*, *Y* and *Z* respectively :

(i) Na_2SO_4 (ii) $Na_3PO_4.12H_2O$ (iii) $Ca_3(PO_4)_2$

➤ **Problem 32.** Calculate equivalent weight of Cu in CuO and Cu_2O. At.wt. of Cu = 63.6.

➤ Problem 33. The vapour density of a metal chloride is 85. If equivalent weight of metal is 7.01, calculate the at.wt. of metal.

➤ Problem 34. Potassium chromate is isomorphous to potassium sulphate (K_2SO_4) and it is found to have 26.78% Cr. Calculate the at.wt. of Cr if at.wt. of potassium is 39.10.

➤ Problem 35. From 280 mg of CO, 10^{21} molecules are removed. How many g and mole of CO are left?

➤ Problem 36. What is the molecular weight of a substance, each molecule of which contains 9 carbon atoms, 13 hydrogen atoms and 2.33×10^{-23} g of other component?

➤ Problem 37. A hydrate of iron (III) thiocyanate $Fe(SCN)_3$, was found to contain 19% H_2O. What is the formula of the hydrate.

➤ Problem 38. A plant virus was examined by the electron microscope and was found to consists of uniform cylindrical particles 150 Å in diameter and 5000 Å long. The virus has a specific volume of 0.75 cm^3/g. Assuming virus particles as one molecule, calculate molecular weight of virus.

➤ Problem 39. Calculate the mass of $BaCO_3$ produced when excess CO_2 is bubbled through a solution containing 0.205 moles of $Ba(OH)_2$.

➤ Problem 40. What weight of AgCl would be precipitated if 10 mL HCl gas at 12°C and 750 mm pressure were passed into excess of solution of silver nitrate?

➤ Problem 41. The density of O_2 at NTP is 1.429 g $litre^{-1}$. Calculate the standard molar volume of gas.

➤ Problem 42. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the mole of NO_2 in 100 g mixture.

➤ Problem 43. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the mole of NO_2 in 100 mole mixture.

➤ Problem 44. Insulin contains 3.4% sulphur. Calculate minimum mol. wt. of insulin.

➤ Problem 45. Haemoglobin contains 0.25% iron by weight. The molecular weight of haemoglobin is 89600. Calculate the number of iron atoms per molecule of haemoglobin.

➤ Problem 46. P and Q are two elements which form P_2Q_3, PQ_2 molecules. If 0.15 mole of P_2Q_3 and PQ_2 weighs 15.9 g and 9.3 g, respectively, what are atomic weighs of P and Q?

➤ Problem 47. Sugar reacts with oxygen as :

$C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$. How many g of CO_2 is produced per g of sucrose (sugar) used. How many mole of oxygen are needed to react with 1.0 g sugar.

➤ Problem 48. 4 g of an impure sample of $CaCO_3$ on treatment with excess HCl produces 0.88 g CO_2. What is per cent purity of $CaCO_3$ sample.

➤ **Problem 49.** How much CO is produced by the reaction of 1.0 kg octane and 1.0 kg oxygen. Also report the limiting reagent for this reaction.

➤ **Problem 50.** (i) Butyric acid contains only C, H and O. A 4.24 mg sample of butyric acid is completely burned. It gives 8.45 mg of carbon dioxide (CO_2) and 3.46 mg of water. What is the mass percentage of each element in butyric acid?

(ii) If the elemental composition of butyric acid is found to be 54.2% C, 9.2% H and 36.6% O, determine the empirical formula.

(iii) The molecular mass of butyric acid was determined by experiment to be 88. What is the molecular formula?

➤ **Problem 51.** $Fe_2(SO_4)_3$ is emprical formula of a crystalline compound of iron. It is used in water and sewage treatment to aid in the removal of suspended impurities. Calculate the mass percentage of iron, sulphur and oxygen in this compound.

➤ **Problem 52.** A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 litre (Measured at STP) of this welding gas is found to weigh 11.6 g. Calculate : (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

➤ **Problem 53.** 5.325 g sample of methyl benzoate, a compound used in the manufacture of perfumes is found to contain 3.758 g of carbon, 0.316 g hydrogen and 1.251 g of oxygen. What is empirical formula of compound. If mol. weight of methyl benzoate is 136.0, calculate its molecular formula.

➤ **Problem 54.** Calculate the moles of H_2O vapours formed if 1.57 mole of O_2 are used in presence of excess of H_2 for the given change,

$$2H_2 + O_2 \longrightarrow 2H_2O$$

➤ **Problem 55.** Potassium bromide KBr contains 32.9% by mass potassium. If 6.40 g of bromine reacts with 3.60 g of potassium, calculate the number of moles of potassium which combine with bromine to form KBr.

➤ **Problem 56.** Zinc and hydrochloric acid react according to the reaction :

$$Zn(s) + 2HCl(aq.) \longrightarrow ZnCl_2(aq.) + H_2(g)$$

If 0.30 mole of Zn are added to hydrochloric acid containing 0.52 mole HCl, how many moles of H_2 are produced?

➤ **Problem 57.** A mixture of 1.0 mole of Al and 3.0 mole of Cl_2 are allowed to react as:

$$2Al_{(s)} + 3Cl_2 \longrightarrow 2AlCl_{3(s)}$$

(a) Which is limiting reagent?

(b) How many moles of $AlCl_3$ are formed?

(c) Moles of excess reagent left unreacted.

➤ **Problem 58.** 23 g sodium metal reacts with water. Calculate the :

(a) volume of H_2 liberated at NTP,

(b) moles of H_2 liberated,

(c) weight of H_2 liberated.

➤ **Problem 59.** How many moles of potassium chlorate to be heated to produce 5.6 litre oxygen?

➤ **Problem 60.** For the reaction ;

$$2Na_3PO_{4(aq)} + 3Ba(NO_3)_{2(aq)} \longrightarrow Ba_3(PO_4)_{2(s)} + 6NaNO_{3(aq)}$$

Suppose that a solution containing 32.8 g of Na_3PO_4 and 26.1 g of $Ba(NO_3)_2$ is mixed. How many g of $Ba_3(PO_4)_2$ are formed?

➤ **Problem 61.** Calculate the weight of lime (CaO) obtained by heating 300 kg of 90% pure limestone ($CaCO_3$).

➤ **Problem 62.** Calculate the weight of FeO produced from 2 g VO and 5.75 g of Fe_2O_3. Also report the limiting reagent.

Given : $VO + Fe_2O_3 \longrightarrow FeO + V_2O_5$

➤ **Problem 63.** A mixture of FeO and Fe_3O_4 when heated in air to constant weight gains 5% in its weight. Find out composition of mixture.

➤ **Problem 64.** A mixture of Al and Zn weighing 1.67 g was completely dissolved in acid and evolved 1.69 litre of H_2 at NTP. What was the weight of Al in original mixture?

➤ **Problem 65.** Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction;

$$4HCl(aq.) + MnO_2(s) \longrightarrow 2H_2O(l) + MnCl_2(aq.) + Cl_2(g)$$

How many gram of HCl react with 5.0 g of manganese dioxide?

➤ **Problem 66.** Chlorophyll, the green colouring matter of plants responsible for photosynthesis, contains 2.68% of magnesium by mass. Calculate the number of magnesium atoms in 2.00 g of chlorophyll.

➤ **Problem 67.** How much $CaCl_2.6H_2O$ and water must be weighed to prepare 100 g of a solution that is 5.0% $CaCl_2$.

➤ **Problem 68.** Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 g of a 25% and 400 g of a 40% solution by mass.

➤ **Problem 69.** When dissolved in dilute H_2SO_4 , 0.275 g of metal evolved 119.7 mL of H_2 at 20°C and 780.4 mm pressure. H_2 was collected over water. Aqueous tension is 17.4 mm at 20°C. Calculate equivalent weight of metal.

➤ **Problem 70.** A gaseous alkane on complete combustion gives CO_2 and H_2O. If the ratio of moles of O_2 needed for combustion and moles of CO_2 formed is 5 : 3 find out the formula of alkane.

➤ Problem 71. Find the milli-equivalent of :

(a) $Ca(OH)_2$ in 111 g, (b) NaOH in 30 g, (c) H_2SO_4 in 4.9 g.

➤ Problem 72. Find the weight of NaOH in its 60 milli-equivalents.

➤ Problem 73. Find the normality of H_2SO_4 having 50 milli-equivalents in 3 litre.

➤ Problem 74. Find the weight of H_2SO_4 in 1200 mL of a solution of 0.4 *N* strength.

➤ Problem 75. Calculate normality of mixture obtained by mixing :

(a) 100 mL of 0.1 *N* H_2SO_4 + 50 mL of 0.25 *N* NaOH.

(b) 100 mL of 0.2 *M* H_2SO_4 + 200 mL of 0.2 *M* HCl.

(c) 100 mL of 0.2 *M* H_2SO_4 + 100 mL of 0.2 *M* NaOH.

(d) 1 g equivalent of NaOH + 100 mL of 0.1 *N* HCl.

➤ Problem 76. What volume of water is required to make 0.20 *N* solution from 1600 mL of 0.2050 *N* solution?

➤ Problem 77. How many mL of 2.0 *M* $Pb(NO_3)_2$ contains 600 mg Pb^{2+}.

➤ Problem 78. How would you prepare exactly 3.0 litre of 1.0 *M* NaOH by mixing proportions of stock solutions of 2.50 *M* NaOH and 0.40 *M* NaOH. No water is to be used.

➤ Problem 79. What weight of Na_2CO_3 of 95% purity would be required to neutralize 45.6 mL of 0.235 *N* acid?

➤ Problem 80. Calculate normality of NH_4OH when 2 g is present in 800 mL solution. Also calculate its molarity.

➤ Problem 81. What is the strength in g per litre of a solution of H_2SO_4, 12 mL of which neutralized 15 mL of *N*/10 NaOH solution?

➤ Problem 82. Calculate the concentration of a solution obtained by mixing 300 g 25% by weight solution of NH_4Cl and 150 g of 40% by weight solution of NH_4Cl.

➤ Problem 83. A sample of NaOH weighing 0.38 g is dissolved in water and the solution is made to 50.0 mL in a volumetric flask. What is the molarity of the resulting solution?

➤ Problem 84. How many moles of NaOH are contained in 27 mL of 0.15 *M* NaOH?

➤ Problem 85. A sample of $NaNO_3$ weighing 0.38 g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck. What is the molarity of the solution?

➤ Problem 86. In a reaction vessel 0.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.150 *M* NaOH solution should be added for this requirement.

➤ Problem 87. Commercially available concentrated hydrochloric acid contains 38% HCl by mass.

(a) What is the molarity of this solution? The density is 1.19 g mL^{-1}.

(b) What volume of concentrated HCl is required to make 1.00 litre of 0.10 *M* HCl?

➤ **Problem 88.** Concentrated nitric acid used in the laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of solution is 1.504 g mL^{-1}?

➤ **Problem 89.** A solution of glucose in water is labelled as 10 per cent *w/w*, what would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2 g mL^{-1}, then what shall be the molarity of the solution?

➤ **Problem 90.** An antifreeze solution is prepared from 222.6 g of ethylene glycol $[C_2H_4(OH)_2]$ and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} then what shall be the molarity of the solution?

➤ **Problem 91.** Calculate the amount of oxalic acid ($H_2C_2O_4.2H_2O$) required to obtain 250 mL of deci-molar solution.

➤ **Problem 92.** 4 g of NaOH are present in 0.1 dm^3 solution have specific gravity 1.038 g/mL. Calculate :

(a) mole fraction of NaOH; (b) molality of NaOH solution;

(c) molarity of NaOH solution; (d) normality of NaOH solution.

➤ **Problem 93.** Suppose 5 g of acetic acid are dissolved in one litre of ethanol. Assume no reaction in between them. Calculate molality of resulting solution if density of ethanol is 0.789 g/mL.

➤ **Problem 94.** Find the molality of H_2SO_4 solution whose specific gravity is 1.98 g mL^{-1} and 90% by volume H_2SO_4.

➤ **Problem 95.** A sample of H_2SO_4 (density 1.787 g mL^{-1}) is labelled as 80% by weight. What is molarity of acid? What volume of acid has to be used to make 1 litre of 0.2 *M* H_2SO_4?

➤ **Problem 96.** 30 mL of 0.2 *N* $BaCl_2$ is mixed with 40 mL of 0.3 *N* $Al_2(SO_4)_3$. How many g of $BaSO_4$ are formed?

➤ **Problem 97.** 20 mL of 0.2 *M* $Al_2(SO_4)_3$ mixed with 20 mL of 0.6 *M* $BaCl_2$. Calculate the concentration of each ion in solution.

➤ **Problem 98.** What are the final concentrations of all the ions when following are mixed?

50 mL of 0.12 *M* $Fe(NO_3)_3$, 100 mL of 0.10*M* $FeCl_3$ and 100 mL of 0.26*M* $Mg(NO_3)_2$.

➤ **Problem 99.** 30 mL of 0.1 *M* $BaCl_2$ is mixed with 40 mL of 0.2 *M* $Al_2(SO_4)_3$. What is the weight of $BaSO_4$ formed?

$$BaCl_2 + Al_2(SO_4)_3 \longrightarrow BaSO_4 + AlCl_3$$

➤ **Problem 100.** Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction;

$$CaCO_3(s) + 2HCl(aq.) \longrightarrow CaCl_2(aq.) + CO_2(g) + H_2O(l)$$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 *M* HCl?

➤Problem 101. Calculate the volume of 1.00 mol L^{-1} aqueous sodium hydroxide that is neutralized by 200 mL of 2.00 mol L^{-1} aqueous hydrochloric acid and the mass of sodium chloride produced. Neutralization reaction is:

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

➤Problem 102. How many mL of a 0.1 *M* HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two?

➤Problem 103. A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogen. The level of contamination was 15 ppm (by mass).

(i) Express this in per cent by mass.

(ii) Determine the molality of chloroform in the water sample.

➤Problem 104. An aqueous solution of sodium chloride is marked 10% (*w/w*) on the bottle. The density of the solution is 1.071 g mL^{-1}. What is its molality and molarity? Also, what is the mole fraction of each component in the solution?

Answers

1. (a) See solution, (b) 3.3 g;
2. See solution;
3. See solution;
4. See solution;
5. 14 litre;
6. (a) 48 g, (b) 72 g;
7. 1.67×10^{-24} g;
8. 10, 10 N;
9. (a) 88 g, (b) 88 g;
10. 1.75×10^{22} molecules;
11. 1.26×10^{24} carbon atoms;
12. 3.0×10^{23};
13. 3.34×10^{22} molecules;
14. 2.69×10^{19} molecules;
15. 8.50 g;
16. 4.77×10^{15} yr;
17. 19.098×10^{9} year;
18. 320 g, 3.265 g;
19. 0.05 g atom;
20. 3 N ions of Ca^{2+}, 6 N ions of Cl^-;
21. 3 mole;
22. 9.03×10^{23} molecules, 9.03×10^{23} atoms of C, 3.612×10^{24} atoms of H;
23. (a) 20 g, (b) 16.8 g, (c) 1.99 g, (d) 1.6 g;
24. 7.10×10^{-3} kg;
25. $5.96 \times 10^{3+}$ kg/m^3;
26. 35.46 amu;
27. 39.947;
28. 27;
29. 100, 1
30. 108
31. $\frac{x}{2}, \frac{y}{3}, \frac{z}{6}$
32. 31.8, 63.6;
33. 28.04;
34. 52.0;
35. 8.34×10^{-3};
36. 135.04;
37. $Fe(SCN)_3.3H_2O$;
38. 7.10×10^{7};
39. 40.5 g;
40. 0.0605 g ;
41. 22.39 litre mol^{-1};
42. 0.437;
43. 33.48 mole;
44. 941.176;
45. 4 atom of Fe;
46. $P = 26, Q = 18$;
47. 1.54 g CO_2, 3.5×10^{-2} mole;
48. 50%;
49. 823.48 g;
50. (i) C = 54.35%, H = 9.06%, O = 36.59%, (ii) C_2H_4O, (iii) $C_4H_8O_2$;
51. Fe = 28%, S = 24%, O = 48%
52. (i) CH, (ii) 25.98, (iii) C_2H_2;
53. C_4H_4O, $C_8H_8O_2$;
54. 3.14 mole;
55. 8.01×10^{-2} mole;
56. 0.26;
57. (a) Al, (b) 1.0, (c) 1.5;
58. (a) $\frac{1}{2}$, (b) 1 g, (c) 11200 mL;
59. 1/6 mole $KClO_3$;
60. 20.07 g;

61. 151.20 kg;
62. 5.18 g, Fe_2O_3;
63. $FeO = 21.06\%$, $Fe_3O_4 = 78.94\%$;
64. $Al = 1.25$ g, $Zn = 0.42$ g;
65. 8.39 g;
66. 1.345×10^{21} atoms of Mg;
67. $CaCl_2.6H_2O = 9.9$ g, $H_2O = 90.1$ g;
68. 33.57%;
69. 27.52 ;
70. C_3H_8
71. (a) 3000, (b) 750, (c) 100;
72. 2.4 g;
73. 0.0166 ;
74. 23.52 g;
75. (a) 0.0167, (b) 0.267, (c) 0.1, (d) 9.9;
76. 40 mL;
77. 1.44 mL;
78. 857.14 mL of 2.50 M × 2142.96 mL of 0.4 M;
79. 0.5968 g;
80. $N = 0.07$, $M = 0.07$;
81. 6.125 g/litre;
82. 30%;
83. 0.19;
84. 4.05×10^{-3};
85. 8.94×10^{-2};
86. 30.67 mL;
87. (a) 12.4, (b) 8.06 mL;
88. 16.23 M;
89. 0.617 m, 0.67 M, 0.011, 0.989;
90. 17.95 m, 9.11 M;
91. 3.15 g;
92. (a) 0.018, (b) 1.002 m (c) 1 M, (d) 1 N;
93. 0.1056;
94. 8.50;
95. 14.59, 13.71 mL;
96. 0.70 g;
97. $Al^{3+} = 0.2\ M$, $Cl^- = 0.6\ M$;
98. $[Fe^{3+}] = 0.064M$; $[NO_3^-] = 0.28M$; $[Cl^-] = 0.12\ M$; $[Mg^{2+}] = 0.104M$
99. 0.699 g;
100. 0.94 g;
101. 400 mL, 23.4 g;
102. 157.8 mL;
103. (i) 1.5×10^{-3}, (ii) $1.25 \times 10^{-4}\ m$
104. $M = 1.83$, $m = 1.90$, $m.f._{NaCl} = 0.03$, $m.f._{H_2O} = 0.97$

Solution

Solution 1. (a) $NaHCO_3 + CH_3COOH \longrightarrow CH_3COONa + H_2O + CO_2$

Initial mass = 4.2 + 10 = **14.2**

Final mass = 12 + 2.2 = **14.2**

Thus, during the course of reaction law of conservation of mass is obeyed.

(b) $NaHCO_3 + CH_3COOH \longrightarrow CH_3COONa + H_2O + CO_2$

Initial mass = 6.3 + 15 = **21.3**

Final mass = 18.0 + mass of CO_2

According to law of conservation of mass : 21.3 = 18.0 + mass of CO_2

∴ Mass of CO_2 = **3.3 g**

Solution 2. Total mass before the chemical change

= mass of $AgNO_3$ + mass of NaCl + mass of water

= 1.7 + 0.585 + 200

= 202.285 g

Total mass after the chemical reaction

= mass of AgCl + mass of $NaNO_3$ + mass of water

= 1.435 + 0.85 + 200

= 202.285 g

Thus total mass before reaction = total mass after reaction. This confirms the law of conservation of mass.

Solution 3. **Case I :** $\underset{1.08\text{ g}}{Cu} \xrightarrow{HNO_3} Cu(NO_3)_2 \xrightarrow{\Delta} \underset{1.35\text{ g}}{CuO}$

∵ 1.35 g CuO contains 1.08 g Cu

∴ 100 g CuO contains (1.08 × 100)/1.35 g Cu = 80 g Cu

∴ % of Cu in CuO = **80**; % of O in CuO = **20**

Case II : $\underset{2.30\text{ g}}{CuO} + H_2 \longrightarrow \underset{1.84\text{ g}}{Cu} + H_2O$

∵ 2.30 g CuO has 1.84 g Cu

∴ 100 g CuO has (1.84 × 100)/2.30 = 80 g Cu

∴ % of Cu in CuO = **80**; % of O in CuO = **20**

Since the percentage of Cu and oxygen in CuO in both the cases is same and thus the data are in accordance with law of definite proportion.

Solution 4. In a compound of C and O

C = 42.9 O = 57.1

∴ Ratio of C : O : $\dfrac{42.9}{57.1}$ = 0.751

In other compound of C and O

C = 27.3, O = 72.7

Selected Problems with Solutions

➤ Problem 1. A sample of polystyrene prepared by heating styrene with tribromobenzoyl peroxide in the absence of air has the formula $Br_3\ C_6H_3(C_8H_8)_n$. The number n varies with the condition of preparation. One sample of polystyrene prepared in this manner was found to contain 10.46% bromine. What is the value of n?

➤ Problem 2. Calculate the % of free SO_3 in oleum (a solution of SO_3 in H_2SO_4) that is labelled 109% H_2SO_4 by weight.

➤ Problem 3. A mixture of $NH_3(g)$ and $N_2H_4(g)$ is placed in a sealed container at 300 K. The total pressure is 0.5 atm. The container is heated to 1200 K, at which time both substances decompose completely according to the equations:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

$$N_2H_4(g) \longrightarrow N_2(g) + 2H_2(g)$$

After decomposition is complete, the total pressure at 1200 K is found to be 4.5 atm. Find the amount (mole) per cent of $N_2H_4(g)$ in the original mixture?

➤ Problem 4. Chemical absorbers can be used to remove exhaled CO_2 of space travellers in short space flights. Li_2O is one of the most efficient in terms of absorbing capacity per unit weight. If the reaction is $Li_2O + CO_2 \rightarrow Li_2CO_3$, what is the absorption efficiency of pure Li_2O in litre CO_2 (STP) per kg? [atomic weight of Li = 7]

➤ Problem 5. Copper forms two oxides. For the same amount of copper, twice as much oxygen was used to form first oxide than to form second one. What is the ratio of the valencies of copper in first and second oxides?

➤ Problem 6. 105 mL of pure water at 4°C saturated with NH_3 gas yielded a solution of density 0.9 g mL^{-1} and containing 30% NH_3 by mass. Find out the volume of NH_3 solution resulting and the volume of NH_3 gas at 4°C and 775 mm of Hg which was used to saturate water.

➤ Problem 7. 50 mL of dry ammonia gas was sparked for a long time in an eudiometer tube over mercury. After sparking, the volume becomes 97 mL. After washing the gas with water and drying, the volume becomes 94 mL. This was mixed with 60.5 mL of oxygen and the mixture was burnt. After the completion of the combustion of H_2, the volume of the residual gas was 48.75 mL. Derive molecular formula of ammonia.

➤ Problem 8. The weight of one litre sample of ozonised oxygen at NTP was found to be 1.5 g. When 100 mL of this mixture at NTP were treated with terpentine oil, the volume was reduced to 90 mL. Hence calculate the molecular weight of ozone.

➤ Problem 9. A sample of gaseous hydrocarbon occupying 1.12 litre at NTP, when completely burnt in air produced 2.2 g CO_2 and 1.8 g H_2O. Calculate the weight of hydrocarbon taken and the volume of O_2 at NTP required for its combustion.

➤ **Problem 10.** A 5.0 g sample of a natural gas consisting of CH_4, C_2H_4 was burnt in excess of oxygen yielding 14.5 g CO_2 and some H_2O as product. What is weight percentage of CH_4 and C_2H_4 in mixture.

➤ **Problem 11.** Determine the formula of ammonia from the following data:

(i) Volume of ammonia = 25 mL.

(ii) Volume on addition of O_2 after explosion = 71.2 mL.

(iii) Volume after explosion and reaction with O_2 on cooling = 14.95 mL.

(iv) Volume after being absorbed by alkaline pyrogallol = 12.5 mL.

➤ **Problem 12.** 0.05 g of a commercial sample of $KClO_3$ on decomposition liberated just sufficient oxygen for complete oxidation of 20 mL CO at 27°C and 750 mm pressure. Calculate % of $KClO_3$ in sample.

➤ **Problem 13.** Igniting MnO_2 in air converts it quantitatively to Mn_3O_4. A sample of pyrolusite has MnO_2 80%, SiO_2 15% and rest having water. The sample is heated in air to constant mass. What is the % of Mn in ignited sample?

➤ **Problem 14.** A granulated sample of aircraft alloy (Al, Mg, Cu) weighing 8.72 g was first treated with alkali and then with very dilute HCl, leaving a residue. The residue after alkali boiling weighed 2.10 g and the acid insoluble residue weighed 0.69 g. What is the composition of the alloy?

➤ **Problem 15.** A hydrated sulphate of metal contained 8.1% metal and 43.2% SO_4^{2-} by weight. The specific heat of metal is 0.24 cal/g. What is hydrated sulphate?

➤ **Problem 16.** A saturated solution is prepared at 70°C containing 32.0 g $CuSO_4 \cdot 5H_2O$ per 100 g solution. A 335 g sample of this solution is then cooled to 0°C so that $CuSO_4 \cdot 5H_2O$ crystallises out. If the concentration of a saturated solution at 0°C is 12.5 g $CuSO_4 \cdot 5H_2O$ per 100.0 g solution, how much of $CuSO_4 \cdot 5H_2O$ is crystallised.

➤ **Problem 17.** In a gravimetric determination of P, an aqueous solution of dihydrogen phosphate ion $[H_2PO_4^-]$ is treated with a mixture of ammonium and magnesium ions to precipitate magnesium ammonium phosphate, $[Mg(NH_4)PO_4 \cdot 6H_2O]$. This is heated and decomposed to magnesium pyrophosphate $[Mg_2P_2O_7]$, which is weighed. A solution of $H_2PO_4^-$ yielded 1.054 g of $Mg_2P_2O_7$. What weight of NaH_2PO_4 was present originally? (Na = 23, H = 1, P = 31, O = 16, Mg = 24)

➤ **Problem 18.** A mixture contains NaCl and unknown chloride *M*Cl.

(a) 1 g of this is dissolved in water, excess of acidified $AgNO_3$ solution is added to it, so that 2.567 g of white ppt. is obtained.

(b) 1 g of original mixture is heated to 300°C. Some vapours come out which are absorbed in $AgNO_3$ (acidified) solution. 1.341 g of white precipitate is obtained. Find the mol. wt. of unknown chloride.

➤ Problem 19. A precipitate of AgCl and AgBr weighs 0.4066 g. On heating in a current of chlorine, the AgBr is converted to AgCl and the mixture loses 0.0725 g in weight. Find the % of Cl in original mixture.

➤ Problem 20. What weight of Na_2CO_3 of 95% purity would be required to neutralize 45.6 mL of 0.235 *N* acid?

➤ Problem 21. What volume of water is required to make 0.20 *N* solution from 1600 mL of 0.2050 *N* solution?

➤ Problem 22. How much $BaCl_2 \cdot 2H_2O$ and pure water are to be mixed to prepare 50 g of 12.0% (by wt.) $BaCl_2$ solution.

➤ Problem 23. A piece of Al weighing 2.7 g is titrated with 75.0 mL of H_2SO_4 (sp. gr. 1.18 g mL^{-1} and 24.7% H_2SO_4 by weight). After the metal is completely dissolved, the solution is diluted to 400 mL. Calculate molarity of free H_2SO_4 in solution.

➤ Problem 24. To 50 litre of 0.2 *N* NaOH, 5 litre of 1 *N* HCl and 15 litre of 0.1 *N* $FeCl_3$ solution are added. What weight of Fe_2O_3 can be obtained from the precipitate? Also report the normality of NaOH left in the resultant solution.

➤ Problem 25. Chloride samples are prepared for analysis by using NaCl, KCl and NH_4Cl separately or as mixture. What minimum volume of 5% by weight $AgNO_3$ solution (sp. gr. 1.04 g mL^{-1}) must be added to a sample of 0.3 g in order to ensure complete precipitation of chloride in every possible case?

➤ Problem 26. A sample of water has its hardness due to only $CaSO_4$. When this water is passed through on anion exchange resin, SO_4^{2-} ions are replaced by OH^-. A 25.0 mL sample of water so treated requires 21.58 mL of 10^{-3} *M* H_2SO_4 for its titration. What is the hardness of water expressed in terms of $CaCO_3$ in ppm. Assume density of water 1.0 g/mL.

➤ Problem 27. 250 mL of xM solution and 500 mL of yM solution of a solute *A* are mixed and diluted to 2 litre to produce a final concentration of 1.6 *M*. If $x : y = 5 : 4$, calculate x and y.

➤ Problem 28. The cupric salt (*i.e.*, Cu^{2+}) of a monobasic acid contains 3 molecules of water of hydration per atom of Cu. One g of hydrated salt yielding on strong heating 0.3306 g of CuO. What is the equivalent weight of anhydrous acid?

➤ Problem 29. 25 mL of 0.107 H_3PO_4 was titrated with 0.115 *M* solution of NaOH to the end point identified by indicator bromocresol green. This required 23.1 mL. The titration was repeated using phenolphthalein as indicator. This time 25 mL of 0.107 *M* H_3PO_4 required 46.2 mL of the 0.115 *M* NaOH. What is the coefficient of *n* in this equation for each reaction?

$$H_3PO_4 + nOH^- \longrightarrow nH_2O + [H_{3-n}PO_4]^{n-}$$

➤ **Problem 30.** How many mL of 0.1 *N* HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two?

➤ **Problem 31.** A solution of specific gravity 1.6 g mL^{-1} is 67% by weight. What will be the % by weight of the solution of same acid if it is diluted to specific gravity 1.2 g mL^{-1}?

➤ **Problem 32.** 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 mL of 0.4 *N* NaOH for complete neutralization. Find the % of free SO_3 in the sample of oleum.

➤ **Problem 33.** A sample of Mg metal containing some MgO as impurity was dissolved in 125 mL of 0.1*N* H_2SO_4. The volume of H_2 evolved at 27.5°C and 1 atm was 120.0 mL. The resulting solution was found to be 0.02*N* with respect to H_2SO_4. Calculate the weight of sample dissolved and the % by weight of pure Mg metal in sample. Neglect any change in volume.

➤ **Problem 34.** Manganese trifluoride can be prepared by the reaction :

$$MnI_{2(S)} + {}^{13}\!/\!_2F_{2(g)} \longrightarrow MnF_3 + 2IF_5$$

What is the minimum amount of F_2 that must be used to react with 12g of MnI_2 if only 75%. F_2 is utilized to convert all of MnI_2 to MnF_3.

➤ **Problem 35.** A natural gas sample contains 84% (by volume) of CH_4. 10% of C_2H_6, 3% of C_3H_8 and 3% N_2. If a series of catalytic reactions could be used for converting all the carbon atoms into butadiene, C_4H_6, with 100% efficiency, how much butadiene could be prepared from 100 g of the natural gas?

➤ **Problem 36.** 1.5 g sample of P_2O_3 and some impurity was dissolved in water and warmed gentally till P_2O_3 disproportionates quantitatively to PH_3 and H_3PO_4. The solution was then boiled to get rid off $PH_{3(g)}$ and then cooled finally to room temperature and diluted to 100 mL. 10 mL of this solution was mixed with 20 mL of 0.3*M* NaOH. Now 10 mL of this solution required 3.6 mL of 0.05 *M* H_2SO_4 for back titration. Determine % by weight of P_2O_3 in sample.

➤ **Problem 37.** In presence of fluoride ion Mn^{2+} can be titrated with MnO_4^- both reactants being converted to a complex of Mn (III) inpresence of F^- ions. A 0.545 g of sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+}. The titration in presence of fluoride ion consumed 31.1 mL of $KMnO_4$ that was 0.117 *N* against oxalate.

(a) Write balanced chemical equation for the titration assuming that the complex is MnF_4^-.

(b) What was the % of Mn_3O_4 in sample.

➤ **Problem 38.** What volume of 0.20 *M* H_2SO_4 is required to produce 34.0 g of H_2S by the reaction: $8KI + 5H_2SO_4 \longrightarrow 4K_2SO_4 + 4I_2 + H_2S + 4H_2O$

➤ **Problem 39.** A drop (0.05 mL) of 12 *M* HCl is spread over a thin sheet of aluminium foil (thickness 0.10 mm and density of Al = 2.70 g/mL). Assuming whole of the HCl is used to dissolve Al, what will be the maximum area of hole produced in foil?

➤ Problem 40. A solution of palmitic acid in benzene contains 4.24 g of acid per litre. When this solution is dropped on water surface, benzene gets evaporated and palmitic acid forms a unimolecular film on surface. If we wish to cover an area of $500\ \text{cm}^2$ with unimolecular film, what volume of solution should be used. The area covered by one palmitic acid molecule may be taken as $0.21\ \text{nm}^2$. Mol. wt. of palmitic acid is 256.

➤ Problem 41. 11.2 g carbon reacts completely with 19.63 litre of O_2 at NTP. The cooled gases are passed through 2 litre of 2.5 N NaOH solution. Calculate concentration of remaining NaOH and Na_2CO_3 in solution. CO does not react with NaOH under these conditions.

➤ Problem 42. 20 litre of air containing CO_2 at STP passed through 100 mL of 0.12N solution of $Ca(OH)_2$. The filtrate obtained after the reaction required 50 mL of a solution of HCl of specific gravity 1.25 g mL^{-1} containing 0.35% by weight of acid. Find the amount of CO_2 present in the volume of air as well as the percentage by volume of CO_2 in air.

➤ Problem 43. 1.0 gallon pure octane (density 2.65 kg/gallon) on combustion produces 11.53 kg CO, CO_2 and H_2O. CO is formed partailly due to combustion of octane which is responsible to decrease the efficiency of engine. If complete combustion of octane to CO_2 and H_2O provide 100% efficiency to enzine, calculate efficiency of engine in the above case.

➤ Problem 44. 11.2 g of carbon reacts completely with 21.2 litre of oxygen at 18°C and 750 mm of Hg. The cooled gases are passed through 2 litre of 2.5 N NaOH solution. Determine the concentration of NaOH remaining in solution which is not converted to Na_2CO_3 (CO does not react with NaOH) under these conditions.

(i) What is the mole fraction of CO in the gases?

(ii) What is the molarity of NaOH which is not converted to Na_2CO_3 in the remaining solution?

➤ Problem 45. 5 mL of a gaseous hydrocarbon was exposed to 30 mL of O_2. The resultant gas, on cooling is found to measure 25 mL of which 10 mL are absorbed by NaOH and the remainder by pyrogallol. Determine molecular formula of hydrocarbon. All measurements are made at constant pressure and temperature.

➤ Problem 46. The gases produced when 18 g carbon reacts with 5 litre of oxygen at 18°C and 5 atm pressure are treated with 0.5 litre of 2 M NaOH. Calculate the concentration of sodium carbonate and sodium bicarbonate produced by the reaction of CO_2 with NaOH. CO has no reaction under these conditions.

➤ Problem 47. The molecular mass of an organic acid was determined by the study of its barium salt. 4.290 g of salt was quantitatively converted to free acid by the reaction with 21.64 mL of 0.477 M H_2SO_4. The barium salt was found to have two mole of water of hydration per Ba^{2+} ion and the acid is mono-basic. What is molecular weight of anhydrous acid?

➤ **Problem 48.** 1 g of a mixture containing equal no. of moles of carbonates of two alkali metals, required 44.4 mL of 0.5 *N* HCl for complete reaction. The atomic weight of one metal is 7, find the atomic weight of other metal. Also calculate amount of sulphate formed on quantitative conversion of 1.0 g of the mixture in two sulphates.

➤ **Problem 49.** What would be the molality of a solution obtained by mixing equal volumes of 30% by weight H_2SO_4 ($d = 1.218$ g mL^{-1}) and 70% by weight H_2SO_4 ($d = 1.610$ g mL^{-1})? If the resulting solution has density 1.425 g/mL, calculate its molarity.

➤ **Problem 50.** A sample of fuming sulphuric acid containing H_2SO_4, SO_3 and SO_2 weighing 1.0 g is found to require 23.47 mL of 1.0 *N* alkali for its neutralisation. A separate sample shows the presence of 1.5% SO_2. Find the percentage of free SO_3, H_2SO_4 and combined SO_3 in the sample.

➤ **Problem 51.** Calculate the ionic strength of a solution containing 0.2 *M* NaCl and 0.1 *M* Na_2SO_4.

➤ **Problem 52.** 200 mL of a solution of mixture of NaOH and Na_2CO_3 was first titrated with phenolphthalein and $N/10$ HCl. 17.5 mL of HCl was required for the end point. After this methyl orange was added and 2.5 mL of same HCl was again required for next end point. Find out amounts of NaOH and Na_2CO_3 in mixture.

➤ **Problem 53.** Two drops of phenolphthalein solution was added to 40.0 mL of an HCl solution. This solution was titrated with 0.10 *M* NaOH solution. When 30.0 mL of base had been added, part of the solution turned pink, but the colour disappeared upon mixing the solution. Addition of NaOH solution was continued dropwise until one drop addition produced a lasting pink colour. At this point, the volume of base added was 32.56 mL. Calculate:

(a) The concentration of HCl solution.

(b) Concentration of HCl in solution when 30.0 mL base had been added.

(c) pH of the solution when 30.0 mL base was added.

(d) pH of the solution when 32.56 mL base was added.

➤ **Problem 54.** A sample supposed to be pure $CaCO_3$ is used to standardise a solution of HCl. The substance really was a mixture of $MgCO_3$ and $BaCO_3$, but the standardisation of HCl was accurate. Find the percentage of $BaCO_3$ and $MgCO_3$ in mixture.

➤ **Problem 55.** 100 mL sample of hard water is passed through a column of the ion exchange resin RH_2. The water coming off the column requires 15.17 mL of 0.0265 *M* NaOH for its titration. What is the hardness of water as ppm of Ca^{2+}

➤ **Problem 56.** A sea water sample has a density of 1.03 g/cm^3 and 2.8% NaCl by mass. A saturated solution of NaCl in water is 5.45 *M* NaCl. How much water would have to be evaporated from 10^6 litre of sea water before NaCl would precipitate.

➤ **Problem 57.** One litre of a mixture containing BaF_2 and H_2SO_4 was taken for analysis. 25 mL of this mixture was treated with 20.0 mL of 0.1 *N* KOH for complete neutralisation. Another 25 mL of the mixture was added to 100 mL of 0.05 *N* K_2CO_3 solution and precipitate was filtered off. The filtrate required 12 mL of 0.025 *M* oxalic acid solution using phenolphthalein as indicator. Find the strength of BaF_2 and H_2SO_4 in mixture.

➤ **Problem 58.** 5 g of $CuSO_4\,5H_2O$ is intended to be prepared by using CuO and four times the stoichiometric amount of H_2SO_4. Assuming that 10% of the material is lost in crystallisation, what weight of oxide should be taken and how many litre or mL of a 5 *M* H_2SO_4.

➤ **Problem 59.** A mixture contains 20 g of caustic soda, 20 g of sodium carbonate and 20 g of sodium bicarbonate in one litre. What will be the titre value if 55 mL of this mixture is used for titration against 1 *N* HCl if:

(a) First titrated with phenolphthalein.
(b) Methyl orange added after first end point.
(c) Methyl orange added from the very begining.

➤ **Problem 60.** The reaction, $Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$ goes to completion. In one experiment, 10 g of metallic zinc was added to 200 mL $CuSO_4$ solution. After all the Cu was precipitated, it was found that not all the zinc had dissolved. After filtration, the total solid at the end of reaction was 9.81 g. Calculate the weight of Cu deposited and molarity of $CuSO_4$ in original solution.

➤ **Problem 61.** A sample of green crystals of nickel (II) sulphate heptahydrate was heated carefully to produce the bluish-green nickel (II) sulphate hexahydrate. What are the formulas of the hydrates? If 8.753 g of the heptahydrate produces 8.192 g of the hexahydrate, how many gram of anhydrous nickel (II) sulphate could be obtained?

➤ **Problem 62.** A sample of metallic elements *X*, weighing 3.177 g. Combines with 0.6015 litre of O_2 gas (at normal pressure and 20°C) to form the metal oxide with the formula *X*O. If the density of O_2 gas under these conditions is 1.330 g/litre, what is the mass of this oxygen? The atomic weight of oxygen is 15.9994 amu. What is the atomic weight of *X*? What is the identity of *X*?

➤ **Problem 63.** Copper sulphide reacts with nitric acid as $3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3S_{(s)} + 4H_2O_{(g)} + 2NO_{(g)}$. In an experiment, the volume of moist NO gas at 27°C and one atm pressure was collected in a chamber 1642 mm × 760 mm × 30 mm in dimensions. Calculate the amount of copper sulphide taken and the volume of 8 *M* nitric acid required for the reaction. The vapour pressure of pure water at 27°C is 27 mm of Hg. (Cu = 63.5, S = 32).

Answers

1. $n = 19$;
2. 40% ;
3. 25% ;
4. 746.66 litre / kg ;
5. 2 : 1 ;
6. 166.66 mL , 59.03 litre ;
7. NH_3 ;
8. 48.2 ;
9. 0.8 g, 2.24 litre O_2 ;
10. $C_2H_4 = 39.2\%$, $CH_4 = 60.8\%$;
11. NH_3 ;
12. 65.4% ;
13. 59.37% ;
14. Al = 75.9%, Mg = 16.2%, Cu = 7.9%;
15. $Al_2(SO_4)_3 \cdot 18H_2O$;
16. 74.47 g ;
17. 1.1395 g ;
18. 53.50 ;
19. 6.13% ;
20. 0.5978 g ;
21. 40 mL ;
22. $BaCl_2 \cdot 2H_2O = 7.038$ g , $H_2O = 42.962$ g ;
23. 0.183 ;
24. 40 g, 0.05 *N* ;
25. 18.33 mL ;
26. 86 ppm ;
27. $x = 4.92$, $y = 3.94$;
28. 62.58 ;
29. $n = 2$;
30. 157.8 mL ;
31. 29.78% ;
32. 20.78% ;
33. 122.16 g , Mg = 95.57% ;
34. 12.78 g ;
35. 82.08 g ;
36. 80% ;
37. (a) See solution, (b) 40.734% ;
38. 25 litre ;
39. 0.2 cm^2 ;
40. 2.386×10^{-5} litre ;
41. NaOH = 1.68 *N*, $Na_2CO_3 = 0.82$ *N* ;
42. 0.132 g , 0.0672 litre, 0.336% ;
43. 95.5% ;
44. (i) 0.122, (ii) 3.362, 1.345 ;
45. C_2H_4
46. $Na_2CO_3 = 0.816$ *M* , $NaHCO_3 = 0.368$ *M* ;
47. 122.31 ;
48. 23, 1.3998 g ;
49. 7.61, 11.22 ;
50. 65.3%, 33.2%, 27.10% ;
51. 9.2 g/litre, 7.1 g/litre, 9.6 g/litre ;
52. NaOH = 0.06 g per 200 mL, $Na_2CO_3 = 0.0265$ g per 200 mL ;
53. (a) 0.0814 , (b) 3.66×10^{-3}, (c) 2.4365, (d) 7 ;
54. $BaCO_3 = 27.89\%$, $MgCO_3 = 72.11\%$;
55. 80.40 ;
56. 90.9×10^4 litre ;
57. $BaF_2 = 6.372$ g/litre, $H_2SO_4 = 3.92$ g/litre ;
58. $w = 1.753$ g, 4.41 mL ;
59. (a) 31.34 mL, (b) 16.93 mL, (c) 48.26 mL ;
60. 8.001 g , 0.63 *M* ;
61. 4.826 g ;
62. 0.80 g, 63.54 ;
63. 210.29 g, 0.734 litre.

$$\therefore \quad \text{Ratio of C : O} :: \frac{27.3}{72.7} = 0.376$$

Thus, the ratio of amounts of C reacting with same mass of O

$$\therefore \quad = 0.751 : 0.376 = 2 : 1$$

This is in agreement with law of multiple proportions.

Solution 5.

	H_2 +	Cl_2 $\longrightarrow$	2HCl
Volume before reaction	8 litre	6 litre	
Volume after reaction	2	0	12 litre

$\therefore$ Volume after reaction = volume of H_2 left + volume of HCl formed = 2 + 12 = **14 litre**

Solution 6. (a) $\because$ 1 g-atom of Mg has mass = 24 g;

$\therefore$ 2 g-atom of Mg has mass = 24 × 2 = **48 g**

(b) $\because$ N atoms of Mg has mass = 24 g;

$$\therefore \quad 3N \text{ atoms of Mg has mass} = \frac{24 \times 3N}{N} \text{ g} = \mathbf{72\ g}$$

Solution 7. $\because$ N atoms of H has wt. = 1.008 g

$$\therefore \quad 1 \text{ atom of H has wt.} = \frac{1.008}{6.023 \times 10^{23}} = \mathbf{1.67 \times 10^{-24}\ g}$$

Solution 8.

$$\text{No. of g-atoms of Carbon} = \frac{\text{mass of carbon}}{\text{at. mass of carbon}} = \frac{120}{12} = 10$$

$\because$ 1 g-atom of carbon has no. of atoms = 6.023×10^{23}

$\therefore$ 10 g-atoms of carbon has no. of atoms = $10 \times 6.023 \times 10^{23}$ or **10*N***

Solution 9. (a) $\because$ 1 mole of CO_2 has molecular mass = 44

$\therefore$ 2 mole of CO_2 has molecular mass = 2 × 44 = **88 g**

(b) N molecules of CO_2 has molecular mass = 44

$\therefore$ $2N$ molecules of CO_2 has molecular mass = 44 × 2 = **88 g**

Solution 10. $\because$ 180 g glucose has = N molecules

$$\therefore \quad 5.23 \text{ g glucose has} = \frac{5.23 \times 6.023 \times 10^{23}}{180}$$

$$= \mathbf{1.75 \times 10^{22}\ molecules}$$

Solution 11. $\because$ 1 mole of $C_6H_{12}O_6$ has = 6 N atoms of C

$\therefore$ 0.35 mole of $C_6H_{12}O_6$ has = 6 × 0.35 N atoms of C = 2.1 N atoms

= $2.1 \times 6.023 \times 10^{23}$

= **1.26×10^{24} carbon atoms**

Solution 12. $\because$ 1 mole of $Ca(NO_3)_2$ has = 2 N atoms of nitrogen

$\therefore$ 0.25 mole of $Ca(NO_3)_2$ has = $2 \times 0.25 \times 6.023 \times 10^{23}$ atoms of N

= **3.0×10^{23}**

Solution 13. ∵ 1 mL water = 1 g water (density of water = 1 g/cm³)

Now 18 g water has 6.023×10^{23} molecules

∴ 1 g water has $\frac{6.023 \times 10^{23}}{18}$ molecules = $\mathbf{3.34 \times 10^{22}}$ **molecules**

Solution 14. ∵ 22.4 litre water vapour at STP has = 6.023×10^{23} molecules

∴ 1×10^{-3} litre water vapours at STP has = $\frac{6.023 \times 10^{23} \times 10^{-3}}{22.4}$

= $\mathbf{2.69 \times 10^{19}}$ **molecules**

Solution 15. ∵ 6.023×10^{23} molecules of NH_3 has weight = 17 g

∴ 3.01×10^{23} molecules of NH_3 has weight = $\frac{17 \times 3.01 \times 10^{23}}{6.023 \times 10^{23}}$

= **8.50 g**

Solution 16. 4 wheat grains are counted in 1 sec.

∴ 6.023×10^{23} wheat grains are counted in $\frac{6.023 \times 10^{23}}{4}$ sec.

$$= \frac{6.023 \times 10^{23}}{4 \times 60 \times 60 \times 24 \times 365} \text{ year}$$

= $\mathbf{4.77 \times 10^{15}}$ **year**

Solution 17. ∵ 10^6 rupees are spent in 1 sec.

∴ 6.023×10^{23} rupees are spent in $\frac{1 \times 6.023 \times 10^{23}}{10^6}$ sec

$$= \frac{1 \times 6.023 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365} \text{ year}$$

= $\mathbf{19.098 \times 10^{9}}$ **year**

Solution 18. ∵ 1 mole of H_2SO_4 has = 32 g S

∴ 10 mole of H_2SO_4 has = 32 × 10 = **320 g S**

Also, ∵ 98 g of H_2SO_4 has = 32 g S

∴ 10 g of H_2SO_4 has = (32 × 10)/98 = **3.265 g S**

Solution 19. ∵ 98 g H_2SO_4 has g-atom of S = 1

∴ 4.9 g H_2SO_4 has g-atom of S = $\frac{4.9}{98}$ = **0.05 g-atom of S**

Solution 20. Mol. wt. of $CaCl_2$ = 111 g

∵ 111 g $CaCl_2$ has = *N* ions of Ca^{2+}

∴ 333 g $CaCl_2$ has $\frac{N \times 333}{111}$ ions of Ca^{2+} = **3 *N* ions of** $\mathbf{Ca^{2+}}$

Also, $\because$ 111 g $CaCl_2$ has = $2N$ ions of Cl^-

$\therefore$ 333 g $CaCl_2$ has = $\frac{2N \times 333}{111}$ ions of Cl^-

= **$6N$ ions of Cl^-**

Solution 21. Mol. wt. of $BaCl_2 \cdot 2H_2O$ = 244 g,

$\because$ 244 g $BaCl_2 \cdot 2H_2O$ = 36 g H_2O = 2 mole of H_2O

$\therefore$ 366 g $BaCl_2 \cdot 2H_2O$ = $\frac{2 \times 366}{244}$ mole of H_2O = **3 mole of H_2O**

Solution 22. Mol. wt. of methane (CH_4) = 16,

$\because$ 16 g CH_4 has molecules = N

$\therefore$ 24 g CH_4 has molecules = $\frac{6.023 \times 10^{23} \times 24}{16}$

= **9.03×10^{23} molecules**

Also, 16 g CH_4 = N atoms of carbon

$\therefore$ 24 g CH_4 has = $\frac{6.023 \times 10^{23} \times 24}{16}$

= **9.03×10^{23} atoms of C**

and $\because$ 16 g CH_4 = $4N$ atoms of H

$\therefore$ 24 g CH_4 = $\frac{4 \times 6.023 \times 10^{23} \times 24}{16}$

= **3.612×10^{24} atoms of H**

Solution 23. **(a)** Mass of iron = **20 g**

(b) Mass of 1.2 g-atom of N = 14 × 1.2 = **16.8 g**

(c) Mass of 1×10^{23} atoms of C = $\frac{12 \times 1 \times 10^{23}}{6.023 \times 10^{23}}$ = **1.99 g**

(d) Mass of 1.12 litre of O_2 at STP = $\frac{32 \times 1.2}{22.4}$ = **1.6 g**

Thus **20 g iron** has maximum weight.

Solution 24. 1 carat = 3.168 grains = $\frac{3.168}{15.4}$ gram

$\therefore$ 0.500 carat diamond = $\frac{3.168 \times 0.5}{15.4}$ g = 0.10 g

Thus weight of ring = 0.10 + 7.0 = 7.10 g = **7.10×10^{-3} kg**

Solution 25. Density of Vanadium = 5.96 g/cm^3 = 5.96×10^{-3} kg/cm^3

= $\frac{5.96 \times 10^{-3}}{10^{-6}}$ kg/m^3 = **$5.96 \times 10^{+3}$ kg/m^3**

Solution 26. Average atomic mass $= \dfrac{75.53 \times 34.969 + 24.47 \times 36.966}{100} =$ **35.46 amu**

Solution 27. Molar mass of Ar

$$\therefore = \frac{0.337 \times 35.96755 + 0.063 \times 37.96272 + 99.600 \times 39.9624}{100}$$

$= \mathbf{39.947}$

Solution 28. Sp. heat $= 1\ \text{J g}^{-1}\ \text{K}^{-1} = 1/4.18\ \text{cal g}^{-1}\ \text{K}^{-1}$

$\therefore$ approximate at. wt. × 1/4.18 = 6.4

$\therefore$ approximate at.wt. = 6.4 × 4.18 = 26.75

Also, $\dfrac{\text{at. weight}}{\text{eq. weight}} = \text{Valence}$

$\therefore$ Valence = 26.75/9 = 2.97 = 3.0

(∵ Valence is integer)

$\therefore$ Exact at. weight = Eq. wt. × valence = 9 × 3 = **27**

Solution 29. Eq. of metal = Eq. of oxygen

wt. of metal = 1 g, wt. of oxygen = 1.08 – 1 = 0.08 g

$$\frac{1}{E_{\text{metal}}} = \frac{0.08}{8}$$

$\therefore$ $E_{\text{metal}} = 100$

Also App. at.wt. × sp. heat = 6.4

$\therefore$ App. at. wt. $= \dfrac{6.4}{0.06} = 106.67$

$\because$ Valence $= \dfrac{\text{at. wt.}}{\text{E. wt.}} = \dfrac{106.67}{100} = 1$ (integer)

exact at. wt. = E × valence = 100 × 1 = **100**

Solution 30. App. at.wt. $= \dfrac{6.4}{0.06} = 106.67$

Also Eq. of metal = Eq. of H_2SO_4

Let Eq. wt. of metal be E.

$$\frac{1.08}{E} = \frac{0.49}{49}$$

$\therefore$ $E_{\text{metal}} = 108$

Also Valence $= \dfrac{\text{at. wt.}}{\text{Eq. wt.}} = \dfrac{106.67}{108} = 1$ (integer)

$\therefore$ Exact at. wt. = Eq.wt. × Valence = 108 × 1 = **108**

Solution 31. Equivalent weight of compound $= \dfrac{\text{Molecular weight}}{\text{Total charge on cation or anion}}$

$$E_{Na_2SO_4} = \frac{x}{2} \qquad \text{(charge on 2Na is +2 or on SO}_4\text{ is –2)}$$

$$E_{Na_3PO_4 \cdot 12H_2O} = \frac{y}{3} \qquad \text{(charge on PO}_4\text{ is –3)}$$

$$E_{Ca_3(PO_4)_2} = \frac{z}{6} \qquad \text{(charge on 2PO}_4\text{ is –6)}$$

Solution 32. **In CuO :** (Cu of bivalent nature) ∴ Eq. wt. of Cu. = 63.6/2
= **31.8**

In Cu_2O : (Cu of monovalent nature) ∴ Eq. wt. of Cu = 63.6/1
= **63.6**

Solution 33. Let metal chloride be MCl_x, then

Mol. wt. of $MCl_x = a + 35.5\,x$,

∴ $2 \times 85 = E.x + 35.5\,(x)$ (∵ a = E.x.)

or $$x = \frac{2 \times 85}{7.01 + 35.5} = 4$$

∴ at. wt. = 7.01 × 4 = **28.04**

Solution 34. Since potassium chromate and K_2SO_4 are isomorphs and thus molecular formula of potassium chromate is K_2CrO_4. Let at. wt. of Cr be a, then formula wt. of K_2CrO_4

$= 39.1 \times 2 + a + 16 \times 4 = 142.2 + a$

∴ % of Cr in $K_2CrO_4 = \frac{a}{142.2 + a} \times 100$;

Also % of Cr given = 26.78

∴ $\frac{100a}{142.2 + a} = 26.78$; a **= 52.0**

Solution 35. ∵ 6.023×10^{23} molecules of CO = 28 g

∴ 10^{21} molecules of CO $= \frac{28 \times 10^{21}}{6.023 \times 10^{23}} = 4.65 \times 10^{-2}$ g

= 46.5 mg

∴ CO left = 280 – 46.5 = 233.5 mg

Also, moles of CO left $= \frac{\text{wt.}}{\text{m. wt.}}$

$= \frac{233.5 \times 10^{-3}}{28} =$ **8.34 × 10^{-3}**

Solution 36. The molecule has C, H and other component.

Wt. of 9 C atoms = 12 × 9 = 108 amu

$$\text{Wt. of 13 H atoms} = 13 \times 1 = 13 \text{ amu}$$

$$\text{Wt. of other component} = \frac{2.33 \times 10^{-23}}{1.66 \times 10^{-24}} = 14.04 \text{ amu}$$

$$\therefore \quad \text{Total weight of one molecule} = 108 + 13 + 14.04$$

$$= 135.04 \text{ amu}$$

$$\therefore \quad \text{Mol. wt. of substance} = \mathbf{135.04}$$

Solution 37. Let the hydrate be $Fe(SCN)_3.mH_2O$

$$\text{molecular weight of hydrate} = 56 + 3 \times (32 + 12 + 14) + 18\,m$$

$$= 230 + 18\,m$$

$$\therefore \quad \% \text{ of } H_2O = \frac{18m \times 100}{230 + 18m} = 19$$

or $\quad m = 3$

$\therefore \quad$ Formula is $\mathbf{Fe(SCN)_3.3H_2O}$

Solution 38. Given, $\quad$ length $= 5000 \times 10^{-8}$ cm, $r = \frac{150}{2} \times 10^{-8}$ cm

$\therefore$ Volume (cylindrical nature of virus) $= \pi r^2 h$

$$= 3.14 \times \left(\frac{150}{2} \times 10^{-8}\right)^2 \times 5000 \times 10^{-8}$$

$$= 8.83 \times 10^{-17} \text{ cm}^3$$

Given that specific volume is $0.75 \text{ cm}^3/\text{g}$

$$\therefore \quad 0.75 \text{ cm}^3 = 1 \text{ g}$$

$$\therefore \quad 8.83 \times 10^{-17} \text{ cm}^3 = \frac{8.83 \times 10^{-17}}{0.75}$$

$$\therefore \quad = 1.18 \times 10^{-16} \text{ g}$$

$$= \text{weight of one virus}$$

$$\therefore \text{ Thus weight of } N \text{ virus molecules} = 1.18 \times 10^{-16} \times 6.023 \times 10^{23}$$

$$= 7.10 \times 10^{7} \text{ g/mol}$$

or $\quad$ Mol. weight $= \mathbf{7.10 \times 10^{7}}$

Solution 39. $\quad Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$

Mole of $Ba(OH)_2$: Mole of CO_2 : : Mole of $BaCO_3$: Mole of H_2O

$$\therefore \quad \frac{\text{Mole of } Ba(OH)_2}{\text{Mole of } BaCO_3} = \frac{1}{1}$$

$$\therefore \quad \text{Mole of } BaCO_3 \text{ formed} = 0.205$$

$$\therefore \quad \text{Weight of } BaCO_3 \text{ formed} = 0.205 \times 197.4 = \mathbf{40.5 \text{ g}}$$

Solution 40. Meq. of AgCl = Meq. of HCl = milli mole of HCl(g) $= \frac{PV}{RT} \times 10^3$

$$\frac{w}{143.5} \times 1000 = \frac{750}{760} \times \frac{10}{1000} \times \frac{10^3}{0.0821 \times 285}$$

$$= 0.422$$

$$\therefore \quad w_{AgCl} = \frac{0.422 \times 143.5}{1000} = \mathbf{0.0605\ g}$$

Solution 41. Standard molar volume of gas is its volume occupied by 1 mole at NTP.

$\because$ 1.429 g of O_2 gas occupies volume = 1 litre

$\therefore$ 32 g of O_2 gas occupies volume $= \frac{32}{1.429}$ litre

$= \mathbf{22.39\ litre\ mol^{-1}}$

Solution 42. Mol. wt. of mixture of NO_2 and $N_2O_4 = 38.3 \times 2 = 76.6$

Let a g of NO_2 be present in 100 g mixture, then

mole of NO_2 + mole of N_2O_4 = mole of mixture

$$\frac{a}{46} + \frac{(100-a)}{92} = \frac{100}{76.6} \qquad \therefore \quad a = 20.10\ g$$

$\therefore$ Mole of NO_2 in mixture = (20.1/46) = **0.437**

Solution 43. Mol. wt. of mixture of NO_2 and $N_2O_4 = 38.3 \times 2 = 76.6$

Let a mole of NO_2 be present in 100 mole mixture

$\therefore$ wt. of NO_2 + wt. of N_2O_4 = wt. of mixture,

$$a \times 46 + (100 - a) \times 92 = 100 \times 76.6$$

$$a = \mathbf{33.48\ mole}$$

Solution 44. For minimum mol. wt., insulin must contain atleast one sulphur atom in its one molecule.

Now 3.4 g sulphur is present then mol. wt. of insulin = 100

$\therefore$ 32 g sulphur is present then mol. wt. of insulin $= \frac{100 \times 32}{3.4}$

$= \mathbf{941.176}$

Solution 45. $\because$ 100 g haemoglobin has iron = 0.25 g

$\therefore$ 89600 g haemoglobin has iron $= \frac{0.25 \times 89600}{100} = 224$ g Fe

1 mole or N molecules of haemoglobin has 224 g Fe

= (224/56) g-atom of Fe

= 4 g-atom of Fe

= 4 N atom of Fe

$\therefore$ 1 molecule of haemoglobin = **4 atom of Fe**

Solution 46. Let at. wt. of P and Q be a and b respectively,

$\therefore$ Mol. wt. of $P_2Q_3 = 2a + 3b$

and Mol. wt. of $PQ_2 = a + 2b$

$\therefore$ $(2a + 3b) \times 0.15 = 15.9$

and $(a + 2b) \times 0.15 = 9.3$ ($\because$ wt. = Mole × Mol. wt.)

Thus, $\boldsymbol{a = 26,\quad b = 18}$

Solution 47. $\because$ 1 mole or 342 g sugar produces 12 mole or 44 × 12 g CO_2

$\therefore$ 1 g sugar produces $\dfrac{44 \times 12}{342} = \mathbf{1.54\ g\ CO_2}$

Also 1 mole or 342 g sugar requires 12 mole O_2

$\therefore$ 1 g sugar requires $\dfrac{12}{342}$ = mole O_2 = $\mathbf{3.5 \times 10^{-2}}$ **mole**

Solution 48. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

$$44\text{ g } CO_2 \equiv 100\text{ g } CaCO_3$$

$$0.88\text{ g } CO_2 \equiv \frac{100 \times 0.88}{44} = 2.0\text{ g } CaCO_3$$

$\therefore$ Percentage purity $= \dfrac{2}{4} \times 100 = \mathbf{50\%}$

Solution 49.

$$C_8H_{18} + \frac{17}{2}O_2 \longrightarrow 8CO + 9H_2O$$

	C_8H_{18}	O_2	$8CO$	$9H_2O$
Moles before reaction	$\dfrac{10^3}{114}$	$\dfrac{10^3}{32}$		
Moles after reaction	$\left[\dfrac{10^3}{114} - \dfrac{10^3 \times 2}{32 \times 17}\right]$	0	$\dfrac{8 \times 10^3 \times 2}{32 \times 17}$	

Mole ratio for reaction is $C_8H_{18} : O_2 :: 1 : \dfrac{17}{2}$

and $O_2 : CO :: \dfrac{17}{2} : 8$

Thus O_2 is limiting reagent and moles of CO formed = 29.41

Mass of CO formed = 29.41 × 28 = **823.48 g**

Solution 50. (i) $\%\,C = \dfrac{12 \times 8.45}{44 \times 4.24} \times 100 = \mathbf{54.35\%}$

$\%\,H = \dfrac{2 \times 3.46}{18 \times 4.24} \times 100 = \mathbf{9.06\%}$

$\%\,O = [100 - 54.35 - 9.06] = \mathbf{36.59\%}$

(ii) %	%/at.wt. = Factor	Factor/Lowest number
C = 54.2	$\frac{54.2}{12} = 4.52$	$\frac{4.52}{2.29} = 2$
H = 9.2	$\frac{9.2}{1} = 9.2$	$\frac{9.2}{2.29} = 4$
O = 36.6	$\frac{36.6}{16} = 2.29$	$\frac{2.29}{2.29} = 1$

∴ Empirical formula of butyric acid is $\mathbf{C_2H_4O}$

(iii) Empirical formula mass = 44

Molecular mass = 88

$$\frac{\text{Molecular mass}}{\text{Empirical mass}} = \frac{88}{44} = 2$$

∴ Mole formula = Empirical formula × n = $\mathbf{C_4H_8O_2}$

Solution 51. Mol.wt. of $Fe_2(SO_4)_3$ = 2 × at.wt. of Fe + 3 × at.wt. of S + 12 × at.wt. of oxygen

$$= 2 \times 56 + 3 \times 32 + 12 \times 16$$
$$= 112 + 96 + 192 = 400$$

∴ $$\% \text{ of Fe} = \frac{112}{400} \times 100 = \mathbf{28\%}$$

∴ $$\% \text{ of S} = \frac{96}{400} \times 100 = \mathbf{24\%}$$

∴ $$\% \text{ of O} = \frac{192}{400} \times 100 = \mathbf{48\%}$$

Solution 52. Molecular mass of welding gas = $\frac{11.6 \times 22.4}{10}$ = **25.98**

CO_2 and H_2O are obtained from welding gas combustion in water.

∴ $$\text{g-atoms of C in gas} = \frac{3.38}{44} = 0.077$$

$$\text{g-atoms of H in gas} = \frac{0.690 \times 2}{18} = 0.077$$

∴ Ratio of C and H atoms in gas is 1 : 1

Thus, empirical formula of welding gas is **CH**

Empirical formula mass of welding gas = 13

Molecular mass = (empirical formula mass) × n

∴ $$n = \frac{25.98}{13} \simeq 2$$

∴ Molecular formula = 2 × empirical formula = 2 × (CH) = $\mathbf{C_2H_2}$

Solution 53.

Element	%	Mole ratio	Simplest mole ratio
C	$\frac{3.758\times100}{5.325}=70.57$	$\frac{70.57}{12}=5.88$	$\frac{5.88}{1.47}=4$
H	$\frac{0.316\times100}{5.325}=5.93$	$\frac{5.93}{1}=5.93$	$\frac{5.93}{1.47}=4$
O	$\frac{1.251\times100}{5.325}=23.50$	$\frac{23.50}{16}=1.47$	$\frac{1.47}{1.47}=1$

∴ Empirical formula is $\mathbf{C_4H_4O}$

Also empirical formula weight = 4 × 12 + 4 × 1 + 16 = 68

$$\because \quad n=\frac{\text{mol. wt.}}{\text{empirical formula wt.}}=\frac{136}{68}=2$$

∴ Molecular formula of methyl benzoate is $(C_4H_4O)_2$ or $\mathbf{C_8H_8O_2}$

Solution 54. $\because 2 \text{ mole } H_2 \simeq 1 \text{ mole } O_2 \simeq 2 \text{ mole } H_2O$

$\because \quad 1 \text{ mole } O_2 \simeq 2 \text{ mole } H_2O;$

$\therefore \quad 1.57 \text{ mole } O_2 \simeq 2 \times 1.57 \text{ mole } H_2O = \mathbf{3.14 \text{ mole } H_2O}$

or, $$\text{Moles of } H_2O = [1.57 \text{ mole of } O_2]\left[\frac{2 \text{ mole } H_2O}{1 \text{ mole } O_2}\right]$$

$$= 1.57 \times \frac{2}{1} = \mathbf{3.14 \text{ mole}}$$

Solution 55. In 100 g KBr, K = 32.9 g, then Br = 67.1 g

(at. wt. of K and Br are 39 and 80 respectively)

$$2K + Br_2 \longrightarrow 2KBr$$

$$\frac{\text{Moles of K}}{\text{Moles of Br}}=\frac{32.9/39}{67.1/80}=\frac{1.0057}{1}$$

$$\therefore \quad \frac{\text{Moles of K}}{\text{Moles of } Br_2}=\frac{1.0057\times2}{1}=\frac{2.0114}{1}$$

	2K	+	Br_2	$\longrightarrow$	2KBr
Given moles	$\frac{3.60}{39}$ = 0.092		$\frac{6.40}{160}$ 0.04		

The reaction ratio for moles of K and Br_2 = 2.0114. Thus, Br_2 will be completely used leaving K.

$\because \quad \text{Moles of } Br_2 \text{ reacting} = 0.04$

$\therefore \quad \text{Moles of K reacting} = 0.04 \times 2.0114$

$= \mathbf{8.01 \times 10^{-2} \text{ mole}}$

Solution 56.

	$Zn(s)$ +	$2HCl(aq.)$ $\longrightarrow$	$ZnCl_2(aq.)$ +	$H_2(g)$
Initial moles	0.30	0.52	0	0
Final moles	0.04	0	0	0.26

∵ Mole ratio of Zn : HCl : H_2 is 1 : 2 : 1

∴ Moles of H_2 formed = **0.26**

Note that HCl is used completely and thus it is limiting reagent.

Solution 57.

	$2Al_{(s)}$ +	$3Cl_2$ $\longrightarrow$	$2AlCl_{3(s)}$
Moles before reaction	1.0	3.0	0
Moles after reaction	0	1.5	1.0

Mole ratio for reactants and products are 2 : 3 : 2

(a) Thus limiting reagent is **Al.**

(b) Moles of $AlCl_3$ formed = **1.0**

(c) Moles of excess reagent Cl_2 left unreacted = **1.5**

Solution 58. The given reaction is, $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

From equation, it is evident :

46 g Na reacts to liberate 1 mole H_2,

∴ 23 g Na reacts to liberate (1 × 23)/46 = **1/2 mole H_2**

∴ Weight of H_2 liberated = (1/2) × 2 = **1 g**

Also, volume of H_2 at STP = 22400 × $\frac{1}{2}$ = **11200 mL**

Alternative method

	$2Na$ +	$2H_2O$ $\longrightarrow$	$2NaOH$ +	H_2
Mole before reaction	23/23 = 1	Excess	0	0
Mole after reaction	0	Excess	1	½

∴ Moles of H_2 formed = **1/2**

Wt. of H_2 formed = (1/2) × 2 = **1 g**

Volume of H_2 formed at STP = 22400 × 1/2 = **11200 mL**

Solution 59.

	$2KClO_3$ $\longrightarrow$	$2KCl$ +	$3O_2$
Mole ratio for reaction	2 mole	2 mole	3 mole

∵ 3 × 22.4 litre O_2 is formed by 2 mole $KClO_3$

∴ 5.6 litre O_2 is formed by $\frac{2 \times 5.6}{3 \times 22.4}$ = **1/6 mole $KClO_3$**

Solution 60.

	$2Na_3PO_4$ +	$3Ba(NO_3)_2$ $\longrightarrow$	$Ba_3(PO_4)_2$ +	$6NaNO_3$
Mole before reaction	(32.8/164) = 0.2	26.1/261 0.1	0 0	0 0
Mole after reaction	[0.2 – (0.1 × 2)/3]	0	0.1/3	(0.1 × 6)/3

Mole ratio for $Na_3PO_4 : Ba(NO_3)_2 : Ba_3(PO_4)_2 : NaNO_3$: : 2 : 3 : 1 : 6

Moles of $Ba_3(PO_4)_2$ formed = 0.1/3

∴ Weight of $Ba_3(PO_4)_2$ formed = $\frac{0.1}{3} \times 602$ = **20.07 g**

Solution 61. 100 kg impure sample has pure $CaCO_3 = 90$ kg

$\therefore$ 300 kg impure sample has pure $CaCO_3 = \frac{90 \times 300}{100} = 270$ kg

$$CaCO_3 \longrightarrow CaO + CO_2$$

$\because$ 100 kg $CaCO_3$ gives $CaO = 56$ kg

$\therefore$ 270 kg $CaCO_3$ gives $CaO = \frac{56 \times 270}{100} = \mathbf{151.20\ kg}$

Solution 62.

Balanced equation is	$2VO$	+	$3Fe_2O_3$	$\longrightarrow$ $6FeO$	+	V_2O_5
Mole before reaction	2/67 = 0.0298		5.75/160 0.0359			
Mole after reaction	[0.0298 – (0.0359 × 2)/3]		0	[0.0359 × 2]		[0.0359 × 1]

$\because$ Mole ratio in reaction is $VO : Fe_2O_3 : FeO : V_2O_5 :: 2 : 3 : 6 : 1$

$\therefore$ Mole of FeO formed = 0.0359 × 2

$\therefore$ Weight of FeO formed = 0.0359 × 2 × 72 = **5.18 g**

The limiting reagent is one which is totally used *i.e.* $\mathbf{Fe_2O_3}$ here.

Solution 63. Let weight of FeO and Fe_3O_4 be a and b g, respectively.

$$2FeO + \tfrac{1}{2}O_2 \longrightarrow Fe_2O_3$$

$$2Fe_3O_4 + \tfrac{1}{2}O_2 \longrightarrow 3Fe_2O_3$$

$\because$ 144 g FeO gives 160 g Fe_2O_3

$\therefore$ a g FeO gives $160 \times a/144$ g Fe_2O_3

Similarly, weight of Fe_2O_3 formed by b g $Fe_3O_4 = \frac{160 \times 3b}{464}$

Now if $a + b = 100$; then $\frac{160 \times a}{144} + \frac{160 \times 3b}{464} = 105$

Solving these two equations : $a = 21.06$ and $b = 78.94$

Percentage of **FeO = 21.06%** and percentage of $\mathbf{Fe_3O_4 = 78.94\%}$

Solution 64. Let a and b g be weight of Al and Zn in mixture $a + b = 1.67$ ...(1)

$Al + 3HCl \longrightarrow AlCl_3 + (3/2)\,H_2$; $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

$\because$ 27 g Al gives (3/2) × 22.4 litre H_2 ($\because$ at.wt. of Al = 27)

$\therefore$ a g Al gives $\frac{3 \times 22.4 \times a}{2 \times 27}$ litre H_2

Similarly 65 g Zn gives 22.4 litre H_2 ($\because$ at.wt. of Zn = 65)

$\therefore$ b g Zn gives $(22.4 \times b)/65$ litre H_2

$\therefore$ $\frac{3 \times 22.4 \times a}{2 \times 27} + \frac{22.4 \times b}{65} = 1.69$ ...(2)

By (1) and (2) $a = \mathbf{1.25\ g}$, $b = \mathbf{0.42\ g}$

Solution 65. $4HCl(aq.) + MnO_2(s) \longrightarrow 2H_2O(l) + MnCl_2(aq.) + Cl_2(g)$

$\because$ 87g MnO_2 reacts will 4 × 36.5 g HCl

$\therefore$ 5 g MnO_2 will react with $\frac{4 \times 36.5 \times 5}{87}$ = **8.39 g HCl**

Solution 66. $\because$ 100 g chlorophyll contains 2.68 g Mg = $\frac{2.68}{24}$ mole Mg

2 g chlorophyll contains $\frac{2.68 \times 2}{24 \times 100}$ mole Mg = 2.2×10^{-3} mole Mg

$\therefore$ No. of Mg atoms = $2.2 \times 10^{-3} \times 6.023 \times 10^{23}$

= **1.345×10^{21} atoms of Mg**

Solution 67. $CaCl_2 \equiv CaCl_2.6H_2O$

$\therefore$ Mole of $CaCl_2.6H_2O$ = Mole of $CaCl_2$

$\therefore$ Mole of $CaCl_2.6H_2O = \frac{5}{111}$ ($\because$ mol.wt. of $CaCl_2$ = 111)

$\therefore$ Mass of $CaCl_2.6H_2O = \frac{5}{111} \times 219$ = **9.9 g $CaCl_2.6H_2O$**

$\therefore$ Mass of water = 100 − 9.9 = **90.1 g**

Solution 68. 25% solution means 25 g solute in 100 g solution

40% solution means 40 g solute in 100 g solution

Mass of solute in 300 g solution = $\frac{25 \times 300}{100}$ = 75 g

Mass of solute in 400 g solution = $\frac{40 \times 400}{100}$ = 160 g

$\therefore$ Total mass of solute = 75 + 160 = 235 g

$\therefore$ Mass % in mixture = $\frac{235}{700} \times 100$ = **33.57%**

Solution 69.

$$\text{mole of } H_{2(n)} = \frac{PV}{RT} = \frac{(780.4 - 17.4) \times 119.7}{760 \times 1000 \times 0.0821 \times 293} = 5 \times 10^{-3}$$

Let eq. wt. of metal be E

Eq. of metal = Eq. of H_2

$$\frac{0.275}{E} = \text{mole of } H_2 \times 2 = 2 \times 5 \times 10^{-3}$$

$$\boldsymbol{E = 27.52}$$

Solution 70. Let the alkane be C_nH_{2n+2}

$$C_nH_{2n+2} + \left[n + \frac{n+1}{2}\right] O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

$$\frac{\text{Mole of } O_2}{\text{Mole of } CO_2} = \frac{n+\frac{n+1}{2}}{n} = \frac{5}{3}$$

$$n = 3$$

Thus alkane is **C_3H_8**

Solution 71. (a) $\text{Meq. of } Ca(OH)_2 = \frac{w}{E} \times 1000 = \frac{111}{74/2} \times 1000 = \mathbf{3000}$

$\left(\because E_{Ca(OH)_2} = \frac{74}{2}\right)$

(b) $\text{Meq. of NaOH} = \frac{30}{40} \times 1000 = \mathbf{750}$ $(\because E_{NaOH} = 40)$

(c) $\text{Meq. of } H_2SO_4 = \frac{4.9}{49} \times 1000 = \mathbf{100}$ $(\because E_{H_2SO_4} = 49)$

Solution 72. $\text{Meq.} = \frac{w}{E} \times 1000$

$\therefore$ $60 = \frac{w}{40} \times 1000$

$\mathbf{w = 2.4\ g}$

Solution 73. $\because$ $N \times V \text{ (in Litre)} = \text{Equivalent}$

$\therefore$ $N \times 3 = \frac{50}{1000}$

or $\mathbf{N = 0.0166}$

Solution 74. $\text{Meq. of } H_2SO_4 = 0.4 \times 1200 = 480$ $(\because \text{Meq.} = N \times V \text{ in mL})$

$\therefore$ $\frac{w}{49} \times 1000 = 480$

$\mathbf{w = 23.52\ g}$

Solution 75. (a) $\text{Meq. of } H_2SO_4 = 100 \times 0.1 = 10$

$\text{Meq. of NaOH} = 50 \times 0.25 = 12.5$

H_2SO_4 and NaOH neutralize each other.

$\text{Meq. of NaOH left} = 12.5 - 10 = 2.5$

Volume of new solution = 100 + 50 = 150 mL

$\therefore$ $N_{NaOH} \text{ left} = 2.5/150 = \mathbf{0.0167}$

(b) $\text{Meq. of } H_2SO_4 = 100 \times 0.2 \times 2 = 40$

$(\because N = M \times \text{Valency})$

$\text{Meq. of HCl} = 200 \times 0.2 \times 1 = 40$

$\therefore$ Total Meq. of acid = 40 + 40 = 80

$\therefore$ Total volume of solution = 300 mL

$\therefore$ $N_{\text{Acid solution}} = 80/300 = \mathbf{0.267}$

(c) Meq. of $H_2SO_4 = 100 \times 0.2 \times 2 = 40$

Meq. of $NaOH = 100 \times 0.2 \times 1 = 20$

Meq. of H_2SO_4 left after reaction = 40 − 20 = 20

Total volume of solution = 100 + 100 = 200 mL

$\therefore$ $N_{H_2SO_4}$ left = 20/200 = **0.1**

(d) Meq. of $NaOH = 1 \times 1000 = 1000$

Meq. of $HCl = 100 \times 0.1 = 10$

Meq. of NaOH left after reaction = 1000 − 10 = 990

Total volume of solution = 100 mL

$\therefore$ N_{NaOH} left = 990/100 = **9.9**

Solution 76. Meq. of conc. solution = 1600 × 0.2050 = 328

Let after dilution of volume becomes V mL

Meq. of dil. solution = $0.20 \times V$

$\therefore$ $328 = 0.20 \times V$

($\because$ Meq. does not change on dilution)

$\therefore$ $V = 1640$ mL

Thus, volume of water used to prepare 1640 mL of 0.20 N solution

= 1640 − 1600 = **40 mL**

Solution 77. Meq. of $Pb(NO_3)_2$ = Meq. of Pb^{2+}

(Meq. = $N \times V$ in mL; $N = M \times$ Valence factor)

$$2 \times 2 \times V = \frac{600 \times 10^{-3}}{208/2} \times 1000$$

$\therefore$ $V = \mathbf{1.44\ mL}$

Solution 78. Let V mL of 2.50 M NaOH be mixed with (3000 − V) mL of 0.40 M NaOH

Meq. of 2.50 M NaOH + Meq. of 0.4 M NaOH = Meq. of 1.0 M NaOH

$2.50 \times V + 0.4\,(3000 - V) = 3 \times 1000 \times 1 \quad (M = N)$

$\therefore$ $V = \mathbf{857.14\ mL}$

$\therefore$ 857.14 mL of 2.50 M NaOH and 2142.96 mL of 0.4 M NaOH are to be mixed.

Solution 79. $\because$ Meq. of Na_2CO_3 = Meq. of H_2SO_4 (for complete neutralization)

Meq. of $Na_2CO_3 = 45.6 \times 0.235$

$$\therefore \quad \frac{w}{106/2} \times 1000 = 45.6 \times 0.235$$

$w = 0.5679$ g

$\because$ 95 g pure Na_2CO_3 is to be taken then weighed sample = 100 g

$\therefore$ 0.5679 g pure Na_2CO_3 is to be taken, weighed sample

$$= \frac{100 \times 0.5679}{95} = \mathbf{0.5978\ g}$$

Solution 80.

$$N = \frac{\text{Equivalent}}{V\,(\text{in litre})}$$

$\because$ Equivalent of $NH_4OH = \frac{2}{35}$, Volume of solution $= \frac{800}{1000}$ litre

$$\therefore \quad N = \frac{2 \times 1000}{35 \times 800} = \mathbf{0.07}$$

Also, $$M = \frac{N}{\text{Valence factor}} = \frac{0.07}{1} = \mathbf{0.07}$$

or $$\text{Molarity} = \frac{\text{moles}}{V\,(\text{in litre})} = \frac{2 \times 1000}{35 \times 800} = \mathbf{0.07}$$

Solution 81. Meq. of H_2SO_4 = Meq. of NaOH ($\because$ Meq. $= N \times V$ in mL)

$$N \times 12 = 15 \times \frac{1}{10},$$

$$N_{H_2SO_4} = \frac{15}{10 \times 12} = 0.125$$

$\therefore$ Strength of $H_2SO_4 = 0.125 \times 49 = \mathbf{6.125\ g\ litre^{-1}}$ ($\because S = N \times E$)

Solution 82. Weight of solution I and II = 300 + 150 = 450 g

$$\text{Weight of } NH_4Cl \text{ in I solution} = \frac{25 \times 300}{100} = 75 \text{ g}$$

$$\text{Weight of } NH_4Cl \text{ in II solution} = \frac{40 \times 150}{100} = 60 \text{ g}$$

$\therefore$ Total weight of NH_4Cl = 75 + 60 = 135 g

$$\therefore \quad \% \text{ by wt. of mixed solution} = \frac{135}{450} \times 100 = \mathbf{30\%}$$

Solution 83. Meq. of NaOH $= N \times V_{\text{in mL}}$ or $\frac{w}{E} \times 1000 = N \times V_{\text{in mL}}$

$$\frac{0.38}{40} \times 1000 = N \times 50$$

$$\therefore \quad N = \mathbf{0.19}$$

Solution 84. Milli-moles of NaOH $= M \times V_{\text{in mL}} = 0.15 \times 27$

$$\therefore \quad \text{Moles of NaOH} = \frac{0.15 \times 27}{1000} = \mathbf{4.05 \times 10^{-3}}$$

Solution 85. Molarity × Volume in mL = Milli-mole = $\frac{w}{M} \times 1000$

$$\therefore \quad \text{Molarity} \times 50 = \frac{0.38}{85} \times 1000$$

[Mol. wt. of $NaNO_3$ = 85]

$$\therefore \quad \text{Molarity} = \mathbf{8.94 \times 10^{-2}}$$

Solution 86.

$$\text{Milli-mole} = M \times V_{\text{in mL}}$$

$$\frac{0.184}{40} \times 1000 = 0.150 \times V$$

$$\therefore \quad V_{\text{NaOH}} = \mathbf{30.67\ mL}$$

Solution 87. (a) Mass of HCl = 38 g; density of solution = 1.19 g/mL,

Mass of solution = 100 g

$$\text{Molarity} = \frac{\text{Moles of HCl}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Mass of HCl}}{\text{Molar mass of HCl} \times \dfrac{\text{weight of solution}}{\text{density of solution} \times 1000}}$$

$$= \frac{38}{36.5 \times \dfrac{100}{1.19 \times 1000}} = \mathbf{12.4}$$

(b) Milli-moles of solute does not change on dilution and thus,

$$\underset{\text{(for conc.)}}{M \times V_{\text{mL}}} = \underset{\text{(for dil.)}}{M \times V_{\text{mL}}}$$

$$12.4 \times V = 0.1 \times 1000$$

$$\therefore \quad V = \mathbf{8.06\ mL}$$

Solution 88. 68% mass of HNO_3 means 100 g solution contains 68 g HNO_3

$\therefore$ Volume of solution = wt. of solution × density = $\frac{100}{1.504}$ = 66.49 mL

$$\text{Molarity } (M) = \frac{\text{mole of } HNO_3}{\text{volume of solution in litre}}$$

$$= \frac{68 \times 1000}{63 \times 66.49} = \mathbf{16.23\ \mathit{M}}$$

Solution 89. 10% (*w/w*) solution of glucose means 100 g solution contains 10 g glucose.

$$\therefore \quad \text{Weight of water} = 100 - 10 = 90 \text{ g}$$

$$\text{Molality } (m) = \frac{10}{180 \times \dfrac{90}{1000}} = \mathbf{0.617\ \mathit{m}}$$

$$\text{Molarity }(M) = \frac{10}{180 \times \dfrac{100}{1.2 \times 1000}} = \mathbf{0.67}\ M$$

$$\text{Mole fraction of glucose} = \frac{10/180}{\dfrac{10}{180} + \dfrac{90}{18}} = \mathbf{0.011}$$

$$\text{Mole fraction of water} = \frac{90/18}{\dfrac{10}{180} + \dfrac{90}{18}} = \mathbf{0.989}$$

Solution 90.

$$\text{Molality of ethylene glycol} = \frac{222.6}{62 \times \dfrac{200}{1000}} = \mathbf{17.95}\ m$$

$$\text{Wt. of solution} = \text{wt. of glycol} + \text{wt. of water}$$
$$= 222.6 + 200 = 422.6\text{ g}$$

$$\text{Volume of solution} = \frac{422.6}{1.072}\text{ mL}$$

$$\text{Molarity of ethylene glycol} = \frac{222.6}{62 \times \dfrac{422.6}{1.072 \times 1000}} = \mathbf{9.11}\ M$$

Solution 91.

$$\text{Molarity of solution} = \frac{1}{10}\ M$$
$$\text{Volume of solution} = 250\text{ mL}$$

$$\text{Milli-mole of oxalic acid} = M \times V_{(\text{mL})} = \frac{1}{10} \times 250$$

$$\frac{w}{126} \times 1000 = \frac{1}{10} \times 250 \quad (\text{mol.wt. of oxalic acid} = 126)$$

$$w = \frac{250 \times 126}{10 \times 1000} = \mathbf{3.15\ g}$$

Solution 92.

$$\text{Volume of solution} = 0.1\text{ dm}^3 = \frac{1}{10}\text{ litre} = 100\text{ mL}$$

$$\text{Weight of solution} = 100 \times 1.038 = 103.8\text{ g}$$

$$\text{Weight of water} = \text{weight of solution} - \text{weight of NaOH}$$
$$= 103.8 - 4 = 99.8\text{ g}$$

(a) $$\text{Mole fraction of NaOH} = \left\{\frac{\dfrac{4}{40}}{\dfrac{4}{40} + \dfrac{99.8}{18}}\right\} = \mathbf{0.018}$$

(b) Molality of solution $= \dfrac{\text{Moles of NaOH}}{\text{Weight of water}} \times 1000$

$$= \frac{4 \times 1000}{40 \times 99.8} = \mathbf{1.002\ m}$$

(c) Molarity of NaOH solution $= \dfrac{\text{Moles of NaOH}}{\text{Volume in litre}}$

$$= \frac{4 \times 1000}{40 \times 100} = \mathbf{1\ M}$$

(d) Normality of NaOH solution $= \dfrac{\text{Equivalent of NaOH}}{\text{Volume in litre}}$

$$= \frac{4 \times 1000}{40 \times 100} = \mathbf{1\ N}$$

Solution 93. Wt. of CH_3COOH dissolved = 5 g

Eq. of CH_3COOH dissolved = 5/60

Volume of ethanol = 1 litre = 1000 mL

$\therefore$ Weight of ethanol = (1000 × 0.789) g = 789 g

$\therefore$ Molality of solution $= \dfrac{\text{Moles of solute}}{\text{wt. of solvent in kg}}$

$$= \left\{\frac{5}{\dfrac{60 \times 789}{1000}}\right\} = \mathbf{0.1056}$$

Solution 94. H_2SO_4 is 90% by volume.

Volume of solution = 100 mL

$\therefore$ Wt. of H_2SO_4 = 90 g $\qquad \therefore$ Moles of H_2SO_4 = 90/98

and Weight of solution = 100 × 1.98 $\qquad \therefore$ Weight of water = 198–90

= 198 g $\qquad$ = 108 g

$$\therefore \quad \text{Molality} = \frac{90}{98 \times 108 / 1000} \qquad \left(m = \frac{\text{moles}}{\text{solvent (in kg)}}\right)$$

$$= \mathbf{8.50}$$

Solution 95. H_2SO_4 is 80% by weight $\therefore$ Wt. of H_2SO_4 = 80 g

Wt. of solution = 100 g

$$\therefore \quad \text{Volume of solution} = \frac{100}{1.787}\ \text{mL} = \frac{100}{1.787 \times 1000}\ \text{litre}$$

$$\therefore \quad M_{H_2SO_4} = \left\{ \frac{\frac{80}{100}}{98 \times \frac{100}{1.787 \times 1000}} \right\}$$

$$= \mathbf{14.59}$$

Let V mL of this H_2SO_4 are used to prepare 1 litre of 0.2 M H_2SO_4, then mM of conc. H_2SO_4 = mM of dil. H_2SO_4

(mM does not change on dilution)

$$V \times 14.59 = 1000 \times 0.2$$

$$V = \mathbf{13.71\ mL}$$

Solution 96.

	$BaCl_2$ +	$Al_2(SO_4)_3 \longrightarrow$	$BaSO_4$ +	$AlCl_3$
Meq. before reaction	30×0.2 $= 6$	40×0.3 $= 12$	0 $= 0$	0 $= 0$
Meq. after reaction	0	6	6	6

6 Meq. of $BaCl_2$ reacts with 6 Meq. of $Al_2(SO_4)_3$ to produce 6 Meq. of $BaSO_4$ and 6 Meq. of $AlCl_3$.

$$\therefore \text{ Meq. of } BaSO_4 \text{ formed } = 6 = \frac{\text{Wt.}}{E} \times 1000; \qquad \left(E = \frac{233}{2}\right)$$

$$\text{wt. of } BaSO_4 \text{ formed } = \frac{6 \times E}{1000} = \frac{6 \times 233}{2 \times 1000} = \mathbf{0.70\ g}$$

Solution 97.

	$Al_2(SO_4)_3$ +	$BaCl_2 \longrightarrow$	$BaSO_4 \downarrow$ +	$AlCl_3$
Meq. before mixing	$20 \times 0.2 \times 6$ $= 24$	$20 \times 0.6 \times 2$ $= 24$	0	0
Meq. after mixing	0	0	24	24

(Meq. = $N \times V$ in mL = $M \times$ valency $\times V$ in mL)

$$\therefore \quad [Al^{3+}] = \frac{24}{40 \times 3} = \mathbf{0.2}\ \boldsymbol{M}$$

$$[Cl^-] = \frac{24}{40} = \mathbf{0.6}\ \boldsymbol{M}$$

No concentration of Ba^{2+} or $SO_4^{\ 2-}$ in solution since $BaSO_4$ gets precipitated.

Solution 98. Milli-mole of $Fe(NO_3)_3 = 50 \times 0.12 = 6$ (mm = $M \times V_{mL}$)

$\therefore$ Milli-mole of $Fe^{3+} = 6$;

Milli-mole of $NO_3^- = 3 \times 6 = 18$

$\therefore$ Milli-mole of $FeCl_3 = 100 \times 0.1 = 10$

Milli-mole of $Fe^{3+} = 10$;

$\therefore$ Milli-mole of $Cl^- = 3 \times 10 = 30$

$\therefore$ Milli-mole of $Mg(NO_3)_2 = 100 \times 0.26 = 26$

Milli-mole of $Mg^{2+} = 26$;
Milli-mole of $NO_3^- = 2 \times 26 = 52$

On mixing these three, total volume he comes 250 mL

Thus $$[Fe^{3+}] = \frac{6+10}{250} = \mathbf{0.064}\boldsymbol{M} \qquad \left[\text{ion} = \frac{\text{milli - mole}}{V_{\text{in mL}}}\right]$$

$$[NO_3^-] = \frac{18+52}{250} = \mathbf{0.28}\boldsymbol{M}$$

$$[Cl^-] = \frac{30}{250} = \mathbf{0.12}\boldsymbol{M}$$

$$[Mg^{2+}] = \frac{26}{250} = \mathbf{0.104}\boldsymbol{M}$$

Solution 99. First balance it $3BaCl_2 + Al_2(SO_4)_3 \longrightarrow 3BaSO_4 + 2AlCl_3$

	$3BaCl_2$	$Al_2(SO_4)_3$	$3BaSO_4$	$2AlCl_3$
mM before reaction	30×0.1 $= 3$	40×0.2 $= 8$	0	0
mM after reaction	0	$(8 - 1)$	3	2

∵ 3 *mM* of $BaCl_2$ reacts with one mole of $Al_2(SO_4)_3$.

∴ mM of $BaSO_4$ formed $= 3 = \dfrac{\text{wt.}}{\text{mol. wt.}} \times 1000,$

∴ wt. of $BaSO_4$ formed $= \dfrac{3 \times 233}{1000} = \mathbf{0.699\ g}$

The above question may also be solved in terms of normality. We have Molarity × Valence factor = Normality. Also balancing of equation is not necessary in this concept.

	$BaCl_2$	$Al_2(SO_4)_3$	$BaSO_4$	$AlCl_3$
Meq. before reaction	$30 \times 0.1 \times 2$ $= 6$	$40 \times 0.2 \times 6$ 48	0	0
Meq. left after reaction	0	42	6	6

Meq. of $BaSO_4$ formed $= 6 = \dfrac{\text{wt.}}{\text{E. wt.}} \times 1000,$

∴ $$w = \frac{6 \times 233}{2 \times 1000} = \mathbf{0.699\ g}$$

Solution 100. $CaCO_3(s) + 2HCl(aq.) \longrightarrow CaCl_2(aq.) + CO_2(g) + H_2O(l).$

Meq. of $CaCO_3$ = Meq. of HCl

$$\frac{w}{100/2} \times 1000 = 25 \times 0.75 \times 1 \quad [\because \text{Meq.} = N \times V_{mL} = (M/1) \times V_{mL}]$$

∴ $w_{CaCO_3} = 0.9375\ g = \mathbf{0.94\ g}$ (For HCl, $M = N$)

Solution 101. Meq. of NaOH = Meq. of HCl = Meq. of NaCl

$$N \times V_{mL} = N \times V_{mL} \; (N_{HCl} = M_{HCl}\,;\; N_{NaOH} = M_{NaOH})$$

$$1 \times V = 2 \times 200$$

$$\therefore \quad V = \mathbf{400\ mL}$$

$$\text{Meq. of NaCl} = 2 \times 200 = 400$$

$$\therefore \quad \frac{w}{58.5} \times 1000 = 400$$

$$\therefore \quad w_{NaCl} = \mathbf{23.4\ g}$$

Solution 102. Let a moles Na_2CO_3 and a moles of $NaHCO_3$ be present in 1 g mixture.

$$\therefore \quad a \times 106 + a \times 84 = 1$$

or $$a = 5.26 \times 10^{-3}$$

Now for reaction :

$$\text{Meq. of HCl} = \text{Meq. of } Na_2CO_3 + \text{Meq. of } NaHCO_3$$

$$0.1 \times 1 \times V = 2 \times 5.26 \times 10^{-3} \times 1000 + 1 \times 5.26 \times 10^{-3} \times 1000$$

$$V = \mathbf{157.8\ mL}$$

Solution 103. $CHCl_3$ present in 15 ppm or 10^6 g (or mL) H_2O contains 15 g $CHCl_3$

(i) $$\%\text{ By mass} = \frac{15}{(15 + 10^6)} \times 100 \approx \mathbf{1.5 \times 10^{-3}}$$

(ii) $$\text{Molality} = \frac{15/119.5}{10^6 \times 10^{-3}} = \mathbf{1.25 \times 10^{-4}\ m}$$

Solution 104. 100 g solution contains 10 g NaCl

$$w = 10\text{ g},\; m_{NaCl} = 58.5,\; \text{Volume of solution} = \frac{100}{1.071 \times 1000}\text{ litre}$$

$$w_{H_2O} = 100 - 10 = 90\text{ g}$$

$$\text{Molarity} = \frac{\text{Wt. of solute}}{\text{mol. wt. of solute} \times V_{\text{in L}}} = \frac{10 \times 1.071 \times 1000}{58.5 \times 100} = \mathbf{1.83}\boldsymbol{M}$$

$$\text{Molality} = \frac{\text{Wt. of solute}}{\text{mol. wt. of solute} \times \text{weight of solvent in Kg}}$$

$$= \frac{10 \times 1000}{58.5 \times 90} = \mathbf{1.90}\boldsymbol{m}$$

$$\text{Mole fraction of NaCl} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}} = \frac{10/58.5}{\frac{10}{58.5} + \frac{90}{18}} = \mathbf{0.03}$$

$$\text{Mole fraction of } H_2O = 1 - 0.03 = \mathbf{0.97}$$

Problems for Self Assessment

1. When a mixture of 10 mole of SO_2, 15 mole of O_2 was passed over catalyst, 8 mole of SO_3 was formed. How many mole of SO_2 and O_2 did not enter into combination?
2. One litre of CO_2 is passed over hot coke. The volume becomes 1.4 litre. Find the composition of products, assuming measurements at NTP.
3. A sample of potato strach was ground in a ball mill to give starch like molecule of low molecular weight. The product analysed 0.086% of phosphorus. If each molecule is assumed to contain one atom of phosphorus, what is the molecular weight of material?
4. A mixture of 1.65×10^{21} molecules of x and 1.85×10^{21} molecules of y weigh 0.688 g. If the molecular weight of y is 187, what is the molecular weight of x?
5. An oxide U_xO_y is obtained on heating $UO_2(NO_3)_2 \cdot zH_2O$ above 800°C. However on heating $UO_2(NO_3)_2\ zH_2O$ gentally only water of hydration is lost. On heating 1.004 g $UO_2(NO_3)_2 \cdot zH_2O$, 0.788 g of $UO_2(NO_3)_2$ is formed. Calculate the water of hydration in sample.
6. A sample of uranium metal (0.169 g) is heated to 800 to 900°C in air to give 0.199 g of a dark green oxide, U_xO_y. How many moles of uranium metal were used? What is the empirical formula of oxide? How many moles of U_xO_y must have been obtained?
7. Three different brands of liquid chlorine are available in the market for the use in purifying water of swimming pools. All are sold at the same rate of Rs. 10 per litre and all are water solutions. Brand *A* contains 10% hypochlorite (ClO^-) (wt./vol.), brand *B* contains 7% available chlorine (Cl) and brand *C* contains 14% sodium hypochlorite (NaClO). Which of the brand you buy?
8. There are available 10 tons of a coal sample containing 2.5% sulphur. Two coal samples containing 0.8% and 1.1% sulphur are also available. How many tons of each of the later two samples should be mixed with the original 10 tons to give 20 tons sample containing 1.7% sulphur?
9. CS_2 and Cl_2 in the weight ratio 1 : 2 are allowed to react according to equation:

   $$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2, \qquad \text{calculate:}$$

   (a) Which reactant is limiting reagent.
   (b) Which reactant and what fraction of it is left over.
10. $K_4[Fe(CN)_6]$ reacts with Zn^{2+} forming $K_2Zn_3[Fe(CN)_6]_2$. What volume of 0.018 *M* $K_4[Fe(CN)_6]$ would be required to react with 150 mg of Zn^{2+} ion in solution.
11. 20 g $KClO_3$ on heating gives enough O_2 to react completely with H_2 produced by the action of Zn on dil. H_2SO_4. Calculate the weight of Zn required for this.
12. Analysis of chlorophyll shows that it contains 2.68 per cent magnesium. How many atoms of magnesium does 1.0 g of chlorophyll contain?
13. A metal oxide XO_3 reacts with H_2 to give metal and water. If 15.99 g of XO_3 yields 6.0 g of water, calculate the atomic weight of *X*.

14. A 25 g charge of the explosive TNT is detonated in an evacuated 5 litre container.

$$2C_7H_5(NO_2)_3 \longrightarrow 12CO(g) + 2C(s) + 5H_2(g) + 3N_2(g)$$

(a) Calculate the mass of carbon deposited.
(b) Calculate the final pressure of the system at 230°C.
(c) Calculate the partial pressure of N_2 under these conditions.

15. Balance the following equation which represents the combustion of pyrites, (FeS_2), a pollution causing impurity in same coals. Calculate:

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

(a) The volume of SO_2 measured at NTP that would have been obtained by complete combustion of 10^3 kg of coal containing 0.05% by mass of pyrite.
(b) The volume of air measured at NTP used in oxidation of pyrite in step (a) assuming that air contains 20% oxygen by volume.
(c) The volume of 6 *M* NaOH required to react with SO_2 produced during step (a).

16. A mixture of oxygen and CO on exposure to UV light gives O_3 and CO_2. If 100 mL of gas mixture were taken in which volume ratio of O_2 and CO were 1.015 : 1, how many mL of each gas will be present in the mixture if it measures 90.34 mL and the ratio of CO_2 and CO in mixture is 0.2419 : 1 volume per cent.

17. 12% solution of urea by weight is diluted by adding 7% urea solution by weight. What weight ratio should the solution be mixed to get a 9% solution by weight.

18. 5.22×10^{-4} mole of a mixture containing H_2, O_2 and N_2 exerted a pressure of 67.4 mm in a certain standard volume. The gas was passed over a hot platinum filament which combined H_2 and O_2 into H_2O which was frozen out. When the gas returned to same volume, the pressure was 14.3 mm. Extra oxygen was added to increase the pressure to 44.3 mm. The combustion was repeated, after which the pressure read 32.9 mm. What was the mole fraction of H_2, O_2 and N_2 in gas sample?

19. A mixture of oxygen and hydrogen is analysed by passing it over hot copper oxide and through a drying tube. Hydrogen reduces the CuO according to the equation: $CuO + H_2 \longrightarrow Cu + H_2O$. Oxygen then oxidises the copper formed: $Cu + \frac{1}{2}O_2 \longrightarrow CuO$. 100 cm^3 of the mixture measured at 25°C and 750 mm yield 84.5 cm^3 of dry oxygen measured at 25°C and 750 mm after passing over CuO and drying agent. What is the mole per cent of H_2 in the mixture?

20. A gas mixture of 3 litre of propane and butane on complete combustion at 25°C produced 10 litre of CO_2. Find out the composition of mixture.

21. A gaseous hydrocarbon was exploded with excess of oxygen. On cooling a contraction of 1.5 times of the volume of hydrocarbon taken was observed. A further contraction equal to double of the volume of hydrocarbon was noted, on treatment with aqueous NaOH. Find out molecular formula of hydrocarbon.

22. A 10 litre box contains 41.4 g of a mixture of gases C_xH_8 and C_xH_{12}. At 44°C the total pressure is 1.56 atm. The analysis of gas mixture shows 87% carbon and 13% H_2. Calculate:

(a) The formula of gases present in the box.
(b) The moles of each gas in the box.

23. A polymeric substance, tetrafluoroethylene, can be represented by the formula $(C_2F_4)x$, where x is a large number. The material was prepared by polymerizing C_2F_4 in the presence of a sulphur-bearing catalyst that served as a nucleus upon which the polymer grew. The final product was found to contain 0.012% S. What is the value of x if each polymeric molecule contains

(a) 1 sulphur atom,

(b) 2 sulphur atoms? In either case, assume that the catalyst contributes a negligible amount to the total mass of the polymer.

24. A gas known to be a mixture of propane (C_3H_8) and methane (CH_4) is confined in a vessel at temperature T and pressure 320 mm of Hg. The gas is burnt in excess O_2 and all the carbon is recovered as CO_2. This CO_2 shows a pressure of 448 mm of Hg if kept in the same vessel at temperature T. Calculate the mole fraction of propane in mixture assuming ideal gas behaviour.

25. 3 g of carbon were heated in a closed vessel with 7 g of oxygen. At the end of the reaction, no solid residue was left behind. Assuming the initial pressure to be 1 atm and the temperature to be 25°C, what would be the weights of CO and CO_2 formed.

26. A known amount of NaCl was heated with conc. H_2SO_4. The gas evolved was completely absorbed in water and then neutralised by NH_4OH. The resulting solution was allowed to react with $NaNO_3$ and a new gas was formed again. This was collected at NTP. The volume collected was 2.464 litre. What weight of NaCl was taken.

27. Calculate the molarity and molality of a given solution of ethanol in water, if the mole fraction of ethanol is 0.04 and its density is 0.97g/mL^{-1}.

28. 135 mL of 0.224 M $MgSO_4$ solution was heated until the solution becomes 105 mL due to evaporation of water. Calculate the molarity of concentrated solution.

29. Two monobasic acids A and B are titrated separately against 1 N Na_2CO_3 solution. 10 mL of A requires 25 mL of Na_2CO_3 solution whereas 40 mL of B requires 25 mL of Na_2CO_3 solution. What volume of A and B should be mixed to produce one litre of 1 N acid solution.

30. You are given one litre each of 0.183 M HCl and 0.381 M HCl. What is the maximum value of 0.243 M HCl which you can make from these solution. (No water is added).

31. A magnesium ribbon, when burnt in air, left an ash containing MgO and Mg_3N_2. The ash was found to consume 0.06 mole of HCl, when it was taken in solution, according to the reactions.

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$
$$Mg_3N_2 + 8HCl \longrightarrow 3MgCl_2 + 2NH_4Cl$$

The solution so obtained was treated with excess of NaOH, when 0.004 mole of NH_3 was evolved. Calculate the weight of magnesium that was burnt.

32. 500 mL of 2M HCl, 100 mL of 2M H_2SO_4 and one g equivalent of a monoacidic alkali are mixed together. 30 mL of this solution required 20 mL of

$Na_2CO_3 \cdot xH_2O$ solution obtained by dissolving 143 g $Na_2CO_3\ xH_2O$ in one litre solution. Calculate water of crystallization of $Na_2CO_3\ xH_2O$.

33. The saponification no. of fat or oil is defined as the no. of mg of KOH required to saponify 1 g oil or fat. A sample of peanut oil weighing 1.5763 g is added to 25 mL of 0.4210 *M* KOH. After saponification is complete, 8.46 mL of 0.2732 *M* H_2SO_4 is needed to neutralize excess of KOH. What is saponification no. of peanut oil?

34. For the standardisation of a $Ba(OH)_2$ solution, 0.2 g of potassium acid phthalate (m. wt. 204.2 g) weighed which was then titrated with $Ba(OH)_2$ solution. The titration requires 27.80 mL $Ba(OH)_2$ solution. What is molarity of base? The equation for reaction is

$$2KHC_8H_4O_4 + Ba(OH)_2 \longrightarrow 2H_2O + 2K^+ + 2C_8H_4O_4^{2-} + Ba^{2+}$$

35. What volume of 6 *M* NaOH would be required to react with SO_2 produced from 10^3 kg of coal containing 0.05% by weight of FeS_2.

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

36. 10 litre of air at NTP were slowly bubbled through 50 mL of $\frac{N}{25}$ $Ba(OH)_2$ solution and the final solution rendered red with phenolphthalein. After filtering the solution and rejecting the precipitate of $BaCO_3$, the filtrate required 22.5 mL of $\frac{N}{12.5}$ HCl to become just colourless. Calculate the % of CO_2 (by volume) in the air.

37. You are given an acid and told only that it could be citric acid (molar mass = 192.1 g/mol) or tartaric acid (molar mass = 150.1 g/mol). To determine which acid you have, you react it with NaOH. The appropriate reactions are,

Citric acid : $C_6H_8O_7 + 3NaOH \longrightarrow Na_3C_6H_5O_7 + 3H_2O$

Tartaric acid: $C_4H_6O_6 + 2NaOH \longrightarrow Na_2C_4H_5O_6 + 2H_2O$

You find that a 0.956 g sample requires 29.1 mL of 0.513 *M* NaOH for a stoichiometric amount. What is the unknown acid?

Answers

1. $SO_2 = 2$ mole, $O_2 = 11$ mole ;
2. $CO_2 = 0.6$ litre, $CO = 0.8$ litre ;
3. 3.6×10^4 ;
4. 230 ;
5. 6 mole H_2O ;
6. 3.56×10^{-3} mole U_3O_8, 7.10×10^{-4} of uranium ;
7. Brand '*B*' contains maximum conc. of Cl_2, *i.e.*, 1.97×10^{-1} *M* ;
8. 3.3 tons of 1.1% and 6.7 tons of 0.8% ;
9. (a) Cl_2, (b) 0.286 of CS_2 in excess ;
10. 84.98 mL ;
11. 31.83 g ;
12. 6.72×10^{20} atoms ;
13. 95.91 ;
14. (a) 1.32 g C, (b) 9.1 atm, (c) 1.365 atm ;
15. (a) 186.67 litre SO_2, (b) 1.283×10^3 litre air, (c) 2.78 litre NaOH ;
16. $O_2 = 31.04$ mL , $CO = 39.97$ mL, $CO_2 = 9.67$ mL, $O_3 = 9.67$ mL ;
17. 2 : 3 ;
18. $H_2 = 0.623$, $O_2 = 0.262$, $N_2 = 0.114$;
19. 10.33% ;
20. $C_3H_8 = 2$ litre, $C_4H_{10} = 1$ litre ;
21. C_2H_2 ;
22. (a) C_5H_8 and C_5H_{12}, (b) $C_5H_8 = 0.45$ mole and $C_5H_{12} = 0.15$ mole ;
23. (a) 2.7×10^3 formula unit/mol, (b) 5.3×10^3 formula unit/mol ;
24. 0.2 ;
25. $CO = 1.75$ g, $CO_2 = 8.25$ g ;
26. 6.435 g ;
27. Molality = 2.315, Molarity = 2.029 ;
28. 0.288 *M* ;
29. *A* = 200 mL, *B* = 800 mL ;
30. 1434.78 mL, **Note:** 0.183 *M* HCl is to be fully used ;
31. 0.672 g ;
32. 10 H_2O ;
33. 209.8 ;
34. 0.0176 *M* ;
35. 2.80 mL
36. 0.0224% ;
37. Citric acid = 14.93 Meq. of citric acid requires 14.93 Meq. of NaOH.

3

Atomic Structure

Chapter at a Glance

1. **Mass of electron at high speed,** $m' = \frac{m}{\sqrt{[1-(u/c)^2]}}$

   (m is mass in rest, u is velocity of electron and c is velocity of light)

2. **Frequency,** $\nu = \frac{c}{\lambda}$

3. **Energy/photon,** $E = h\nu = \frac{hc}{\lambda}$ Also, $E = \frac{12375}{\lambda}$ eV. if λ is in Å

4. **Electronic energy change during transition,** $\Delta E = E_{n_2} - E_{n_1}$

   $n_2 > n_1$, emission spectra if electron jumps from n_2 to n_1 shell and absorption spectra if electron excites from n_1 to n_2 shell

5. **Radius of nth Bohr orbit of H atom,** $r_n = \frac{n^2h^2}{4\pi^2 me^2}$, (in C.G.S.)

   r_1 for H = 0.529 Å ; r_1 for H like atom = $\frac{r_1 \text{ for H}}{Z}$

6. **Velocity of electron in nth Bohr orbit of H atom,** $u_n = \frac{2\pi e^2}{nh}$ (in C.G.S.)

   u_1 for H = 2.1847×10^8 cm sec^{-1}, u_1 for H like atom = u_1 for H × Z

7. **Energy of electron in nth Bohr orbit of H atom,** $E_n = \frac{2\pi^2 me^4}{n^2h^2}$ (in C.G.S.)

   E_1 for H = -21.72×10^{-12} erg = $-$ 13.6 eV, E_1 for H like atom = E_1 for H × Z^2

8. **Wavelength emitted during transition in H atom,**

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \frac{2\pi^2 me^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{(in C.G.S.)}$$

9. **Mosley's law,** $\sqrt{\nu} = a(Z-b)$, where ν is frequency of X-rays given out by metal of at. no. Z

10. **Average atomic weight** $= \frac{\Sigma A_1 X_1}{\Sigma X_{Total}}$

11. **Photo electric effect** $h\nu = w + \frac{1}{2}mu^2$ or $h\nu$ = I.E. + K.E.

12. **Possible transitions for a jump from n_2 to n_1** $= \Sigma(n_2 - n_1)$

13. **Angular momentum of electron in an orbit** = $n.\,(h/2\pi)$

14. **Angular momentum of electron in an orbital** = $(h/2\pi)\sqrt{[l(l+1)]}$

15. **Total spin** = $\pm\left(\frac{1}{2}\times n\right)$; where n is no. of unpaired electrons

16. **Magnetic moment of an atom** = $\sqrt{[n\,(n+2)]}$ B.M.; where n is no. of unpaired electrons.

17. **Nodal planes** : Radial nodes = $n - l - 1$
Angular nodes = l
Total nodes = $(n-1)$

18. **de Broglie equation :**

$$\lambda = \frac{h}{mu} = \sqrt{\frac{h^2}{2\times KE\times m}}$$

where λ is wavelength, m is mass and u is velocity of particle.

19. **Heisenberg uncertainty principle :**

$$\Delta p\,.\,\Delta x > \frac{h}{4\pi}$$

$$\Delta u\,.\,\Delta x > \frac{h}{4\pi m}$$

where Δp, Δu and Δx are uncertainties in momentum, velocity and position respectively h is Planck's constant and m is mass of subatomic particle.

The Basic Problems with Solutions

➤ **Problem 1.** Nucleus of an atom has 6 protons and 8 neutrons. Calculate at. no., mass no. and no. of electrons in neutral atom. What is the symbol of atom?

➤ **Problem 2.** Uranium has at. no. 92 and atomic weight 238.029. Calculate the number of protons, neutrons and electrons in uranium atom.

➤ **Problem 3.** (i) Calculate the number of electrons which will together weigh one gram.

(ii) Calculate the mass and charge on one mole of electrons.

➤ **Problem 4.** (i) Calculate the total number of electrons present in 1 mole of methane.

(ii) Find (a) the total number and

(b) the total mass of neutrons in 7 mg of ^{14}C.

(Assume that mass of a neutron = 1.675×10^{-27} kg).

(iii) Find (a) the total number of protons and (b) the total mass of protons in 34 mg of NH_3 at STP.

Will the answer change if the temperature and pressure are changed?

➤ **Problem 5.** Nitrogen atom has at. no. 7 and oxygen has at. no. 8. Calculate the total no. of electrons in a nitrate ion.

➤ **Problem 6.** Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν), wave number and energy of yellow light photon.

➤ **Problem 7.** Find energy of each of the photons which :

(a) correspond to light of frequency 3×10^{15} Hz,

(b) have wavelength of 0.50 Å.

➤ **Problem 8.** The Vividh Bharati Station of All India Radio, Delhi broadcasts on a frequency of 1368 kHz (kilo hertz). Calculate the wavelength and wave number of the electromagnetic radiation emitted by the transmitter. Which part of the electromagnetic spectrum does it belong to?

➤ **Problem 9.** Calculate the mass of a photon with wavelength 3.6 Å.

➤ **Problem 10.** Calculate the wavelength, frequency and wave number of a light wave whose period is 2.0×10^{-10} s.

➤ **Problem 11.** What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy?

➤ **Problem 12.** Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

➤ **Problem 13.** A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57 μm. Calculate the rate of emission of quanta per second.

➤ **Problem 14.** Calculate the mass of a photon of sodium light having wavelength 5894 Å and velocity, 3×10^8 ms^{-1}, $h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}.

➤ **Problem 15.** Show that radius of II shell of H-atom is almost four times of I shell.

➤ **Problem 16.** The ionisation energy of He^+ is 19.6×10^{-18} J atom^{-1}. Calculate the energy of first stationary state of Li^{2+}

➤ **Problem 17.** What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

➤ **Problem 18.** How much energy is required to ionise a H-atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization energy of H-atom (energy required to remove the electron from $n = 1$ orbit).

➤ **Problem 19.** The energy associated with the first orbit in the hydrogen atom is -2.17×10^{-18} J atom^{-1}. What is the energy associated with the fifth orbit?

➤ **Problem 20.** Calculate the radius of Bohr's fifth orbit for hydrogen atom.

➤ **Problem 21.** Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. ($R_H = 109677$ cm^{-1})

➤ **Problem 22.** What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

➤ **Problem 23.** The electron energy in hydrogen atom is given by $En = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

➤ **Problem 24.** According to Bohr's theory, the electronic energy of H-atom in n^{th} Bohr orbit is given by $E_n = -\dfrac{21.76 \times 10^{-19}}{n^2}$ joule. Calculate the longest λ of light that will be needed to remove an electron from III Bohr's orbit of He^+ ion.

➤ **Problem 25.** Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity to stationary state for one H-atom. Given $E_1 = -13.6$ eV.

➤ **Problem 26.** What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum?

➤ **Problem 27.** How much energy is needed to obtain to H-atom in first excited state from ground state.

➤ **Problem 28.** Calculate the energy required for the process;

$$He^+(g) \longrightarrow He^{2+}(g) + e$$

The ionization energy for the H-atom in the grounds state is 2.18×10^{-18} J atom^{-1}.

➤ **Problem 29.** Calculate the wavelength of 1000 kg rocket moving with a velocity of 3000 km per hour. ($h = 6.626 \times 10^{-34}$ Js).

➤ **Problem 30.** A 1.0 g particle is shot from a gun with velocity of 100 m/sec. Calculate its de Broglie wavelength.

➤ **Problem 31.** Calculate the wavelength of a moving electron having 4.55×10^{-25} J of kinetic energy.

➤ **Problem 32.** Calculate the wavelength of an electron moving with a velocity of 2.05×10^{7} ms^{-1}.

➤ **Problem 33.** The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

➤ **Problem 34.** Two particles A and B are in motion. If the wavelength associated with particle A is 5×10^{-8} m, calculate the wavelength associated with particle B if its momentum is half of A.

➤ **Problem 35.** Calculate the uncertainty in the velocity of a wagon of mass 2000 kg whose position is known to an accuracy of ±10 m.

➤ **Problem 36.** Calculate the uncertainty in position of a dust particle with mass equal to 1 mg if the uncertainty in its velocity is 5.5×10^{-20} ms^{-1}.

➤ **Problem 37** A dust particle having mass equal to 10^{-11} g, diameter 10^{-4} cm and velocity 10^{-4} cm sec^{-1}. The error in measurement of velocity is 0.1%. Calculate uncertainty in its position. Comment on the result.

➤ **Problem 38.** A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate :

(i) the energy of the photon (eV),

(ii) the kinetic energy of the emission, and

(iii) the velocity of the photoelectron (1 eV = 1.6020×10^{-19} J).

➤ **Problem 39.** Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (υ_0) and work function (W_0) of the metal.

➤ **Problem 40.** The minimum energy required for the emission of photoelectron from the surface of a metal is 4.95×10^{-19} J. Calculate the critical frequency and the corresponding wavelength of the photon required to eject the electron. $h = 6.6 \times 10^{-34}$ J sec^{-1}.

➤ **Problem 41.** The energy required to remove an electron from the surface of sodium metal is 2.3 eV. What is the longest wavelength of radiation with which it can show photoelectric effect?

➤ **Problem 42.** Light of wavelength 300×10^{-9} m strikes a metal surface with photoelectric work function of 2.13 eV. Find out the kinetic energy of the most energetic photoelectron.

➤ **Problem 43.** The critical frequency for emitting photoelectrons from a metal surface is 5×10^{14} sec^{-1}. What should be the frequency of radiation to produce photoelectrons having twice the kinetic energy of those produced by the radiation of frequency 10^{15} sec^{-1}.

➤ Problem 44. A metal surface of threshold frequency 5.3×10^{14} sec^{-1} is exposed to a photon of radiation having energy 3.5×10^{-19} J. Will it exhibit photoelectric effect?

➤ Problem 45. Point out the followings :

(a) How many energy subshells are possible in $n = 3$ level.

(b) How many orbitals of all kinds are possible in $n = 3$ level.

➤ Problem 46. How many electrons may enter the orbital denoted by

(a) $2p$, (b) $1s$, (c) $3p$, (d) $3d$

➤ Problem 47. What values are assigned to quantum numbers n, l, m for :

(a) $3s$, (b) $4p_z$, (c) $4d_{x^2-y^2}$, (d) $5d_{z^2}$.

➤ Problem 48. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

(a) $n = 3$ (b) $n = 5$ (c) $n = 4$ (d) $n = 2$ (e) $n = 4$
$l = 1$ $l = 2$ $l = 1$ $l = 0$ $l = 2$
$m = -1$ $m = 0$ $m = \pm 1$ $m = 0$ $m = \pm 2$

➤ Problem 49. Calculate the angular momentum of the following :

(a) 3rd orbit, (b) $4p$ orbital, (c) $3d$ orbital.

➤ Problem 50. What are the numbers of nodes present in :

(a) $1s$, (b) $2s$, (c) $2p$, (d) $3p$ orbitals ?

➤ Problem 51. An atom of an element has 13 electrons. Its nucleus has 14 neutrons. Find out atomic no. and approximate atomic weight. Indicate the arrangement of electrons and the electrovalency of the element.

➤ Problem 52. A neutral atom of an element has $2K$, $8L$, $9M$ and $2N$ electrons. Find out the following:

(a) Atomic no., (b) Total no. of s-electrons,
(c) Total no. of p-electrons, (d) Total no. of d-electrons,
(e) Valency of element, (f) No. of unpaired electrons.

➤ Problem 53. If there were three possible values (–½, 0, +½) for the spin magnetic quantum number, m_s how many elements would there be in the 4th period of periodic table in $4s$, $4p$, $4d$ respectively.

➤ Problem 54. Calculate total spin, magnetic moment for the atoms having at. no. 7, 24, 34 and 36.

➤ Problem 55. The sodium flame test has a characteristic yellow colour due to emissions of wavelength 589 nm. What is the mass equivalence of one photon of this wavelength?

➤ Problem 56. Write electronic configuration of Fe^{2+}, Mn^{4+}, N^{3-} and O^{2-} ions.

➤ Problem 57. What is the maximum number of emission lines when the excited electron of a H-atom in $n = 6$ drops to the ground state?

➤ Problem 58. Calculate the magnitude of spin angular momentum of an electron.

➤ Problem 59. What is the significance of ψ_{210}. Find out angular momentum, spherical nodes and angular node for ψ_{210}.

Answers

1. $6,\ 14,\ {}_6C^{14}$; **2.** 92, 92, 146;

3. (i) 1.097×10^{27} electron, (ii) 5.48×10^{-4} g, 9.99×10^{4} Coulomb;

4. (i) 6.023×10^{24} electron, (ii) (a) 24.09×10^{20}, (b) 40.35×10^{-7} kg,
(iii) (a) 1.2046×10^{22}, (b) 2.014×10^{-5} kg;

5. 32;

6. 5.17×10^{14} Hz, $1.724 \times 10^{6}\ m^{-1}$, 34.25×10^{-20} J/photon;

7. 1.988×10^{-18} J, 3.98×10^{-15} J;

8. 219.3 m, $4.56 \times 10^{-3}\ m^{-1}$ (radiowave);

9. 6.135×10^{-33} kg

10. $5.0 \times 10^{9}\ s^{-1}$, 6.0×10^{-2} m, $16.66\ m^{-1}$;

11. 4.97×10^{-17} J, 2.01×10^{16} photons; **12.** 494.48 kJ mol^{-1};

13. $7.17 \times 10^{19}\ s^{-1}$; **14.** 3.73×10^{-36} kg;

15. See solution; **16.** 44.1×10^{-18} J $atom^{-1}$;

17. 485.2 nm; **18.** -8.71×10^{-20} J, 0.04;

19. -8.68×10^{-20} J; **20.** 1.3225 nm;

21. $1.523 \times 10^{6}\ m^{-1}$; **22.** 2.09×10^{-11} erg, 951 Å;

23. 3646 Å; **24.** 2061 Å;

25. 21.79×10^{-21} J, 912 Å; **26.** 1, 2;

27. 10.275 eV/atom; **28.** 8.72×10^{-18} J;

29. 7.95×10^{-40} m; **30.** 6.63×10^{-33} m;

31. 7.27×10^{-7} meter; **32.** 3.52×10^{-11} m;

33. 8966 Å; **34.** 1×10^{-7} m;

35. $2.64 \times 10^{-39}\ ms^{-1}$; **36.** 9.6×10^{-10} m;

37. 0.527×10^{-9}, 0.527×10^{-5};

38. 4.97×10^{-19} J, 0.97 eV, $5.85 \times 10^{5}\ ms^{-1}$;

39. 2.92×10^{-19} J, $4.41 \times 10^{12}\ sec^{-1}$; **40.** $7.5 \times 10^{14}\ s^{-1}$, 4×10^{-7} m;

41. 5.4×10^{-7} m; **42.** 3.216×10^{-19} J;

43. $15 \times 10^{14}\ sec^{-1}$; **44.** $5.28 \times 10^{14}\ sec^{-1}$;

45. (a) 3, (b) 9; **46.** 2, 2, 6, 10;

47. See solution; **48.** See solution;

49. $3\hbar,\ \frac{h}{\sqrt{2\pi}},\ \frac{\sqrt{3}}{\sqrt{2}} \cdot \frac{h}{\pi}$

50. (a) zero, (b) one spherical node, (c) one angular node, (d) two angular node;

51. 13, 27, +3;

52. (a) 21, (b) 8, (c) 12, (d) 1, (e) +2 & +3, (f) 1 (of 3*d*);

53. See solution;

54. ±3/2, ±3, ±1, 0, magnetic momentum = $\sqrt{(15)}$, $\sqrt{(48)}$, $\sqrt{(8)}$, $\sqrt{(0)}$;

55. 3.74×10^{-36} kg **56.** See solution;

57. 15; **58.** $\dfrac{\sqrt{3}}{4}\dfrac{h}{\pi}$

59. $n = 2, l = 1, m = 0$; $\dfrac{h}{\sqrt{2}\pi}$; 0, 1

Solution

Solution 1. At. no. of element (Z) = number of protons

$\therefore$ $Z = \mathbf{6}$

Mass no. of element (A) = no. of protons + no. of neutrons

$= 6 + 8$

$\therefore$ $A = \mathbf{14}$

no. of electrons in neutral atom = 6

$\therefore$ Symbol of element = ${}_6C^{14}$

Solution 2. At. no. of uranium = 92

$\therefore$ no. of protons = **92**

no. of electrons = **92**

Also, **mass no. ≈ At. wt; (Mass no. is integer value)**

$\therefore$ mass no. = 238

$\because$ $A = Z + n$

$\therefore$ $n = 238 - 92 = \mathbf{146}$

Solution 3. (i) 9.108×10^{-28} g = 1 electron

$\therefore$ $$1\ \text{g} = \frac{1}{9.108\times10^{-28}} = \mathbf{1.097\times10^{27}\ electron}$$

(ii) Mass of 1 mole electron = $9.108 \times 10^{-28} \times 6.023 \times 10^{23}$

$= \mathbf{5.48 \times 10^{-4}\ g}$

Charge of 1 mole electron = $1.66 \times 10^{-19} \times 6.023 \times 10^{23}$

$= \mathbf{9.99 \times 10^{4}\ Coulomb}$

Solution 4. (i) 1 mole CH_4 = N molecule CH_4

$= N \times 10$ electron = $\mathbf{6.023 \times 10^{24}}$ **electron**

(ii) (a) An atom of ${}_6C^{14}$ has 8 neutrons

7 mg ${}_6C^{14} = 7 \times 10^{-3}$ g

$$= \frac{7\times10^{-3}}{14}\ \text{mole} = \frac{7\times10^{-3}\times6.023\times10^{23}}{14}\ \text{atom}$$

$\therefore$ $$\text{No. of neutron} = \frac{7\times10^{-3}\times6.023\times10^{23}\times8}{14} = \mathbf{24.09\times10^{20}}$$

(b) Mass of neutrons = $24.09 \times 10^{20} \times 1.675 \times 10^{-27}$

$= \mathbf{40.35 \times 10^{-7}\ kg}$

(iii) $$34\ \text{mg}\ NH_3 = 34\times10^{-3}\ \text{g}\ NH_3 = \frac{34\times10^{-3}}{17}\ \text{mole}\ NH_3$$

$= 2 \times 10^{-3}$ mole NH_3

$= 2 \times 10^{-3} \times 6.023 \times 10^{23}$ molecule NH_3

$= 12.046 \times 10^{20}$ molecule NH_3

(a) ∴ Number of proton in 1 molecule $NH_3 = 10$

∴ Total no. of proton $= 12.046 \times 10^{20} \times 10$

$= \mathbf{1.2046 \times 10^{22}}$

(b) Mass of total proton $= 1.2046 \times 10^{22} \times 1.672 \times 10^{-27}$

$= \mathbf{2.014 \times 10^{-5}\ kg}$

No, the answer will not change since mass of NH_3 does not depend on *P* and *T*.

Solution 5. Formula of nitrate ion $= NO_3^-$

∴ No. of electron in NO_3^- = Electrons in N + 3 × electrons in O + 1

$= 7 + 3 \times 8 + 1 = \mathbf{32.}$

Solution 6. $$\text{Frequency } (\upsilon) = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}}{580 \times 10^{-9}} = \mathbf{5.17 \times 10^{14}\ Hz\ or\ s^{-1}}$$

$$\text{Wave no. } (\bar{\upsilon}) = \frac{1}{\lambda} = \frac{1}{580 \times 10^{-9}} = \mathbf{1.724 \times 10^{6}\ m^{-1}}$$

$$E = h.\upsilon = 6.625 \times 10^{-34} \times 5.17 \times 10^{14}$$

$$= \mathbf{34.25 \times 10^{-20}\ J/photon}$$

Solution 7. (a) $E = h\upsilon = 6.625 \times 10^{-34} \times 3.0 \times 10^{15} = \mathbf{1.988 \times 10^{-18}\ J}$

(b) $$E = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{0.50 \times 10^{-10}} = \mathbf{3.98 \times 10^{-15}\ J}$$

Solution 8. Given $\upsilon = 1368 \times 10^{3}$ Hz (sec^{-1}), Also $c = 3.0 \times 10^{8}\ ms^{-1}$

$$\because \quad \lambda = \frac{c}{\upsilon} \quad \text{and} \quad \frac{1}{\lambda} = \bar{\upsilon} \text{ (wave no.)}$$

$$\therefore \quad \lambda = \frac{3.0 \times 10^{8}}{1368 \times 10^{3}} = \mathbf{219.3\ m}$$

$$\text{Also} \quad \bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{219.3} = \mathbf{4.56 \times 10^{-3}\ m^{-1}}$$

The wavelength lies in the range of radio wavelengths ($\lambda = 10^{3}$ to 10^{4} m)

Solution 9. For dual nature of light : $\lambda = \dfrac{h}{mc}$

$$\text{or} \quad m = \frac{h}{\lambda c} = \frac{6.626 \times 10^{-34}}{3.6 \times 10^{-10} \times 3.0 \times 10^{8}} = \mathbf{6.135 \times 10^{-33}\ kg}$$

Solution 10. $$\text{Frequency} = \frac{1}{\text{Period}} = \frac{1}{2 \times 10^{-10}} = \mathbf{5.0 \times 10^{9}\ s^{-1}}$$

$$\text{Wavelength} = \frac{c}{\upsilon} = \frac{3.0 \times 10^{8}}{5 \times 10^{9}} = \mathbf{6.0 \times 10^{-2}\ m}$$

$$\text{Wave no.} = \frac{1}{\lambda} = \frac{1}{6.0 \times 10^{-2}} = \mathbf{16.66\ m^{-1}}$$

Solution 11. $$E/\text{photon} = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{4000 \times 10^{-12}} = \mathbf{4.97 \times 10^{-17}\ J}$$

$$\therefore \quad \text{No. of photon 1 J energy} = \frac{1}{4.97 \times 10^{-17}} = \mathbf{2.01 \times 10^{16}\ photons}$$

Solution 12. $$E/\text{photon} = \text{Ionisation energy of Na} = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{242 \times 10^{-9}}$$

$$\begin{aligned} \therefore \quad & = 8.21 \times 10^{-19}\ \text{J/atom} \\ & = 8.21 \times 10^{-19} \times 10^{-3}\ \text{kJ/atom} \\ & = 8.21 \times 10^{-19} \times 10^{-3} \times 6.023 \times 10^{23}\ \text{kJ/mol} \\ \therefore \quad & = \mathbf{494.48\ kJ/mol} \end{aligned}$$

Solution 13. $$E/\text{photon} = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{0.57 \times 10^{-6}} = 34.86 \times 10^{-20}\ \text{J}$$

$$\text{Watt} = \text{No. of photons emitted/sec.} \times E/\text{photon} \quad (\text{Watt} = 25\ \text{Js}^{-1})$$

$$25 = \text{No. of photon} \times 34.86 \times 10^{-20}$$

$$\therefore \quad \text{No. of photons emitted} = \frac{25}{34.86 \times 10^{-20}} = \mathbf{7.17 \times 10^{19}\ s^{-1}}$$

Solution 14. Wavelength of photon, $\lambda = 5894\ \text{Å} = 5894 \times 10^{-10}$ m

Velocity of light, $c = 3 \times 10^{8}\ \text{m s}^{-1}$

$$\text{Mass of photon} = \frac{h}{c\lambda} = \frac{6.6 \times 10^{-34}}{3 \times 10^{8} \times 5894 \times 10^{-10}} = \mathbf{3.73 \times 10^{-36}\ kg}$$

Solution 15. $\because \quad r_n \propto n^2$

Thus, $r_1 \propto 1^2$

and $r_2 \propto 2^2$

$\therefore \quad r_2 = 4 \times r_1$

Solution 16. $$E_1 \text{ for He}^+ = E_1 \text{ for H} \times z^2 = E_1 \times 4$$

$$E_1 \text{ for Li}^{2+} = E_1 \text{ for H} \times z^2 = E_1 \times 9$$

$$\begin{aligned} \therefore \quad E_1 \text{ for Li}^{2+} & = E_1 \text{ for He}^+ \times 9/4 = 19.6 \times 10^{-18} \times 9/4 \\ & = \mathbf{44.1 \times 10^{-18}\ J\ atom^{-1}} \end{aligned}$$

Solution 17. $$\Delta E = E_4 - E_2 = \frac{-13.6}{4^2} - \left(-\frac{13.6}{2^2}\right) \quad \left(\because E_n = \frac{E_1}{n^2}\right)$$

$$\Delta E = \frac{+13.6 \times 3}{16}\ \text{eV}$$

$$\therefore \quad \frac{12375}{\lambda} = \frac{13.6\times 3}{16} \qquad (\lambda \text{ in Å})$$

$$\therefore \quad \lambda = 4852 \text{ Å} = \mathbf{485.2\ nm}$$

Solution 18. $E_1 = -13.6$ eV;

$$E_5 = \frac{-13.6}{5^2} = -0.544 \text{ eV}$$

$$= -0.544 \times 1.6022 \times 10^{-19} \text{ J} = \mathbf{-8.71 \times 10^{-20}\ J}$$

Thus, **0.544 eV** energy is required to ionise H atom if electron is in 5th orbit.

Also, $$\frac{E_5}{E_1} = \frac{0.544}{13.6} = \mathbf{0.04}$$

Solution 19. $$E_1 = -2.17 \times 10^{-18} \text{ J}$$

$$E_5 = \frac{E_1}{5^2} = \frac{-2.17\times 10^{-18}}{25} = \mathbf{-8.68 \times 10^{-20}\ J}$$

Solution 20. $$r_n = r_1 \times n^2 = 0.529 \times 5^2 = \mathbf{13.225\ Å = 1.3225\ nm}$$

Solution 21. For Balmer series $n_1 = 2$

If this line possesses longest wavelength (*i.e*, lowest energy) then $n_2 = 3$

$$\bar{\upsilon} = \frac{1}{\lambda} = 109677\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 1.523 \times 10^4 \text{ cm}^{-1} = \mathbf{1.523 \times 10^6\ m^{-1}}$$

Solution 22. $$E_1 = -2.18 \times 10^{-11} \text{ erg}$$

$$E_5 = \frac{-2.18\times 10^{-11}}{25} \text{ erg}$$

$$\therefore \quad \Delta E = E_5 - E_1 = \frac{-2.18\times 10^{-11}}{25} + 2.18 \times 10^{-11}$$

$$= \mathbf{2.09 \times 10^{-11}\ erg}$$

Thus, energy released during transition will also be 2.09×10^{-11} erg

Also, $$\Delta E = \frac{hc}{\lambda}$$

$$\therefore \quad \lambda = \frac{6.625\times 10^{-27} \times 3.0\times 10^{10}}{2.09\times 10^{-11}}$$

$$\therefore \quad = \mathbf{9.51 \times 10^{-6}\ cm = 951\ Å}$$

Solution 23. $$E_2 = -\frac{2.18\times 10^{-18}}{2^2} = \mathbf{5.45 \times 10^{-19}\ J}$$

Also $$E_2 = \frac{hc}{\lambda} = \frac{2.18\times 10^{-18}}{2^2}$$

$$\therefore \quad \lambda = \frac{6.625\times10^{-34}\times3.0\times10^{8}\times2^{2}}{2.18\times10^{-18}}$$

$$= 36.46\times10^{-8}\text{ m}$$

$$\therefore \quad = \mathbf{36.46\times10^{-6}\ cm = 3646\ \text{Å}}$$

This will be longest wavelength causing the transition.

Solution 24.

$$E_{3\text{H}} = -\frac{21.76\times10^{-19}}{3^{2}} = -2.41\times10^{-19}\text{ joule}$$

$$E_{3\text{He}^{+}} = z^{2}\times E_{3\text{H}} = -2.41\times10^{-19}\times4 = -9.64\times10^{-19}\text{ joule}$$

Now if electron is to be removed from III orbit energy equivalent to 9.64×10^{-19} must be provided. Therefore

$$E_{3} = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{E_{3}} = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{9.64\times10^{-19}} = 2.061\times10^{-7}\text{ m}$$

$$= 2061\times10^{-10}\text{ m} = \mathbf{2061\ \text{Å}}$$

Solution 25. Given : $n_1 = 1,\ n_2 = \infty$

$$\therefore \quad \Delta E = E_{\infty} - E_{1} = 0 - (-13.6) = 13.6\text{ eV}$$

$$= 13.6\times1.602\times10^{-19}\text{ J} = \mathbf{217.9\times10^{-20}\ J}$$

Also

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{6.625\times10^{-34}\times3.0\times10^{8}}{217.9\times10^{-20}} = 9.12\times10^{-8}\text{ m}$$

$$= 912\times10^{-10}\text{ m} = \mathbf{912\ \text{Å}}$$

Solution 26. For He^{+} :

$$\frac{1}{\lambda} = R_{\text{H}}\times Z^{2}\left[\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}}\right];$$

$$\frac{1}{\lambda} = R_{\text{H}}\times4\left[\frac{1}{2^{2}} - \frac{1}{4^{2}}\right] \qquad \text{...(1)}$$

For H atom :

$$\frac{1}{\lambda} = R_{\text{H}}\left[\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}}\right] \qquad \text{...(2)}$$

For same λ, By eq. (1) and (2);

$$\therefore \quad 2^{2}\left[\frac{1}{2^{2}} - \frac{1}{4^{2}}\right] = \left[\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}}\right]; \qquad \left[\frac{1}{1^{2}} - \frac{1}{2^{2}}\right] = \left[\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}}\right]$$

$$\therefore \quad \mathbf{n_1 = 1} \text{ and } \mathbf{n_2 = 2}$$

Solution 27. The excitation to first excited state from ground state means that electron in H-atom is boosted upto 2nd shell from 1st shell. Thus,

$$\Delta E = E_2 - E_1 \qquad \left(\because \; E_n = -\frac{13.7}{n^2}\,\text{eV / atom}\right)$$

$$= \left[\frac{-13.7}{4} + 13.7\right] = \mathbf{10.275\ eV/atom}$$

Solution 28.

$$He^{+}(g) \longrightarrow He^{2+}(g) + e$$

$\therefore$ E_1 for $He^{+} = -2.18 \times 10^{-18} \times Z^2$

$$= -2.18 \times 10^{-18} \times 4 = -8.72 \times 10^{-18}\ J$$

$\therefore$ Energy required for the ionisation of $He^{+} = \mathbf{8.72 \times 10^{-18}\ J.}$

Solution 29.

$$\lambda = \frac{h}{mu} \qquad \left(\text{Given } m = 10^3\ \text{kg},\ u = \frac{3000 \times 10^3}{60 \times 60}\ \text{m/sec}\right)$$

$$\lambda = \frac{6.626 \times 10^{-34} \times 60 \times 60}{10^3 \times 3000 \times 10^3} = \mathbf{7.95 \times 10^{-40}\ m}$$

Solution 30.

$$\lambda = \frac{h}{mu} \quad (\text{Given } m = 1.0\ g = 10^{-3}\ kg;\ u = 100\ m/s)$$

$$\lambda = \frac{6.626 \times 10^{-34}}{1 \times 10^{-3} \times 100} = \mathbf{6.626 \times 10^{-33}\ m}$$

Solution 31.

$$\text{Kinetic energy} = \frac{1}{2}mu^2 = 4.55 \times 10^{-25}\ J$$

$$\therefore \quad u^2 = \frac{2 \times 4.55 \times 10^{-25}}{9.108 \times 10^{-31}} \qquad \therefore \qquad u = 10^3\ \text{m sec}^{-1}$$

$$\therefore \quad \lambda = \frac{h}{mu} = \frac{6.626 \times 10^{-34}}{9.108 \times 10^{-31} \times 10^3} = \mathbf{7.27 \times 10^{-7}\ meter}$$

Solution 32.

$$\lambda = \frac{h}{mu}$$

$$\text{Mass of electron in motion } (m') = \frac{m}{\sqrt{1 - \left(\frac{u}{c}\right)^2}}$$

$$\text{Mass of electron } m' = \frac{9.11 \times 10^{-31}}{\sqrt{1 - \left(\frac{2.05 \times 10^7}{3.0 \times 10^8}\right)^2}} = 9.16 \times 10^{-31}$$

$$\therefore \qquad \lambda = \frac{6.626 \times 10^{-34}}{9.16 \times 10^{-31} \times 2.05 \times 10^{7}} = \mathbf{3.52 \times 10^{-11}\ m}$$

Solution 33.

$$\text{K.E.} = \frac{1}{2} mu^2 \qquad \text{...(1)}$$

$$\therefore \qquad u = \frac{h}{m\lambda} \qquad \text{...(2)}$$

By eq. (1) and (2),

$$\text{K.E.} = \frac{1}{2} m \frac{h^2}{m^2\lambda^2} \qquad \text{or} \qquad \therefore \lambda = \sqrt{\frac{h^2}{2m \times \text{K.E.}}}$$

$$\therefore \qquad \lambda = \sqrt{\frac{6.626 \times 10^{-34} \times 6.626 \times 10^{-34}}{2 \times 9.1 \times 10^{-31} \times 3.0 \times 10^{-25}}}$$

$$= \mathbf{8966 \times 10^{-10}\ m = 8966\ \text{Å}}$$

Solution 34.

$$\lambda_A = \frac{h}{p_A} \quad \text{and} \quad \lambda_B = \frac{h}{p_B}$$

$$\frac{\lambda_A}{\lambda_B} = \frac{p_B}{p_A} \qquad \left(\text{Given } P_B = \frac{1}{2} P_A\right)$$

$$\frac{5 \times 10^{-8}}{\lambda_B} = \frac{1}{2}$$

$$\mathbf{\lambda_B = 1 \times 10^{-7}\ m}$$

Solution 35.

$$\Delta u \,.\, \Delta x = \frac{h}{4\pi m} \qquad (\text{Given } \Delta x = 10\ \text{m},\ m = 2000\ \text{kg})$$

$$\therefore \qquad \Delta u \times 10 = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 2000}$$

$$\therefore \qquad \mathbf{\Delta u = 2.64 \times 10^{-39}\ ms^{-1}}$$

Solution 36.

$$\Delta u \,.\, \Delta x = \frac{h}{4\pi m}$$

$$(\text{Given } \Delta u = 5.5 \times 10^{-20}\ \text{ms}^{-1};\ m = 1 \times 10^{-3} \times 10^{-3}\ \text{kg})$$

$$5.5 \times 10^{-20} \times \Delta x = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-3} \times 10^{-3}}$$

$$\mathbf{\Delta x = 9.6 \times 10^{-10}\ m}$$

Solution 37.

$$u = 10^{-4}\ \text{cm sec}^{-1}$$

$$\therefore \qquad \Delta u = \frac{0.1 \times 10^{-4}}{100} = 1 \times 10^{-7}\ \text{cm sec}^{-1}$$

Now, $$\Delta u.\Delta x = \frac{h}{4\pi m}$$

$$\therefore \quad \Delta x = \frac{6.626\times10^{-27}}{4\times3.14\times10^{-11}\times10^{-7}} = 0.527 \times 10^{-9}\ \text{cm}$$

The uncertainty in position as compared to particle $= \dfrac{\Delta x}{\text{diameter}}$

$$= \frac{0.527\times10^{-9}}{10^{-4}} = \mathbf{0.527 \times 10^{-5}}$$

The factor is very small and almost negligible for microscopic particles.

Solution 38. (a) $$E/\text{photon} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3.0\times10^{8}}{4\times10^{-7}} = \mathbf{4.97\times10^{-19}\ J}$$

(b) $$E = \frac{1}{2}mu^2 + w$$

$$4.97\times10^{-19} = \frac{1}{2}mu^2 + 2.13\times1.6022\times10^{-19}$$

$$\therefore \quad \text{K.E.} = \frac{1}{2}mu^2 = 4.97\times10^{-19} - 3.41\times10^{-19}$$

$$\therefore \quad = \mathbf{1.56\times10^{-19}\ J = 0.97\ eV}$$

(c) $$\frac{1}{2}mu^2 = \text{K.E.}$$

$$\frac{1}{2}\times9.108\times10^{-31}\times u^2 = 1.56\times10^{-19}$$

$$\therefore \quad \mathbf{u = 5.85\times10^{5}\ ms^{-1}}$$

Solution 39. $$E/\text{photon} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3.0\times10^{8}}{6800\times10^{-10}} = 2.92\times10^{-19}\ \text{J}$$

E/photon = **2.92 × 10^{-19}** J = work function.

(The ejection has zero velocity)

Threshold frequency $= \dfrac{c}{\lambda} = \dfrac{3\times10^{8}}{6800\times10^{-10}} = \mathbf{4.41\times10^{14}\ sec^{-1}}$

Solution 40. Minimum energy required for the emission of photoelectrons $= 4.95\times10^{-19}$ J

Let the critical frequency or threshold frequency of the photon to eject the electron be ν sec^{-1}.

We know, $E = h\nu$ or $\nu = \dfrac{E}{h} = \dfrac{4.95\times10^{-19}}{6.6\times10^{-34}} = \mathbf{7.5\times10^{14}\ s^{-1}}$

Also $$\lambda = \frac{c}{\upsilon} = \frac{3 \times 10^8}{7.5 \times 10^{14}} = \mathbf{4 \times 10^{-7}\ m}$$

Solution 41. Energy required to show photo emission = 2.3 eV

$$= 2.3 \times 1.6 \times 10^{-19}\ \text{J}$$

Thus $$E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2.3 \times 1.6 \times 10^{-19}}$$

$$= \mathbf{5.4 \times 10^{-7}\ m}$$

Thus longest wavelength to show photoelectric effect = $\mathbf{5.4 \times 10^{-7}\ m}$

Solution 42. Energy of photon = Work function + Kinetic energy

Kinetic energy = Energy of photon − Work function

$$= \frac{hc}{\lambda} - \text{work function}$$

($\because$ work function = 2.13 eV = $2.13 \times 1.6 \times 10^{-19}$ J)

$$= \left[\frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{300 \times 10^{-9}}\right] - 2.13 \times 1.6 \times 10^{-19}$$

$$= 6.626 \times 10^{-19} - 3.41 \times 10^{-19}$$

$$\text{K.E.} = \mathbf{3.216 \times 10^{-19}\ J}$$

This is the kinetic energy of most energetic photoelectron.

Solution 43. Given critical frequency = 5×10^{14} sec^{-1}

When surface is exposed to frequency of 10^{15} sec^{-1}

Energy of photon = $h\upsilon_0$ + K.E.

$$h \times 10^{15} = h \times 5 \times 10^{14} + \text{K.E.}$$

$$\therefore \quad \text{K.E.} = 10 \times h \times 10^{14} - 5 \times h \times 10^{-14}$$

$$= 5 \times h \times 10^{14}$$

Now for II case, if K.E. becomes twice of this, then

$$\text{New K.E.} = 2 \times 5 \times h \times 10^{14}$$

The energy of photon = $h\nu_0$ + K.E.

$$h\nu = 5 \times 10^{14} \times h + 2 \times 5 \times h \times 10^{14}$$

$$\therefore \quad \nu = \mathbf{15 \times 10^{14}\ sec^{-1}}.$$

Solution 44. E/photon = $h\nu$ or $$\nu = \frac{3.5 \times 10^{-19}}{6.626 \times 10^{-34}} = \mathbf{5.28 \times 10^{14}\ sec^{-1}}$$

Since the frequency of the radiation used $\nu < \nu_0$, *i.e.*, threshold frequency or minimum frequency to show photoelectric effect, it will not show photoelectric effect.

Solution 45. **(a)** No. of subshells in a shell = no. of shells = **3**

(b) No. of orbitals = (no. of shell)^2 = 3^2 = **9**

Solution 46. (a) 6, (b) 2, (c) 6, (d) 10

Solution 47. (a) $3s$: $n = 3$, $l = 0$, $m - 0$

(b) $4p_z$: $n = 4$, $l = 1$, $m = 0$

(c) $4d_{x^2-y^2}$: $n = 4$, $l = 2$, $m = -2$ or $+2$

(d) $5d_{z^2}$: $n = 5$, $l = 2$, $m = 0$

Solution 48. (a) $\because$ $n = 3$ and $l = 1$ $\therefore$ $3p$

Also $m = -1$ $\therefore$ $3p_x$ or $3p_y$

(b) $5d_{z^2}$ (c) $4p_x$ or $4p_y$

(d) $2s$ (e) $4d_{x^2-y^2}$ or $4d_{xy}$

Solution 49. (a) Angular momentum of 3rd orbit $= n.\dfrac{h}{2\pi} = \dfrac{3h}{2\pi} = 3\hbar$

$$\text{(where } \hbar = \frac{h}{2} \text{ and } \hbar = \frac{h}{2\pi}\text{)}$$

(b) Augular momentum of $4p$ orbital $= \dfrac{h}{2\pi}\sqrt{l(l+1)} = \dfrac{h}{2\pi}\sqrt{2} - \dfrac{h}{\sqrt{2}\pi}$

(c) Angular momentum of $3d$ orbital $= \dfrac{h}{2\pi}\sqrt{6} = \dfrac{\sqrt{3}}{\sqrt{2}}.\dfrac{h}{\pi}$

Number of spherical nodes $= n - l - 1$

Number of angular nodes $= l$

Total nodes $= (n - 1)$

Solution 50. (a) Zero, (b) One spherical node,

(c) One angular node, (d) Two angular node.

Solution 51. No. of 'e' = 13

$\therefore$ No. of protons = 13

$\therefore$ No. of neutrons = 14

Atomic no. = No. of proton = **13**

App. at. wt. = No. of proton + No. of neutron

= 13 + 14 = **27**

Electronic configuration : $\mathbf{1s^2, 2s^2\,2p^6, 3s^2\,3p^1}$

Electrovalency = **+ 3** *i.e.*, no. of electrons in outermost shell.

Solution 52. Electronic configuration of neutral atom :

$$\underset{K}{\underline{1s^2}},\ \underset{L}{\underline{2s^2 2p^6}},\ \underset{M}{\underline{3s^2 3p^6 3d^1}},\ \underset{N}{\underline{4s^2}}$$

(a) At. no. = Total no. of electron in neutral atom = **21**

(b) Total no. of s-electrons = **8**

(c) Total no. of p-electrons = **12**

(d) Total no. of d-electrons = **1**

(e) Valency of element = **+2** and **+3**

(due to no. of electrons in outer shell and penultimate *d*-subshell)

(f) No. of unpaired electrons = **1** (of 3*d*)

Solution 53. $n = 4 \quad l = 0 \quad m_l = 0 \quad m_s = -\frac{1}{2}, 0, +\frac{1}{2}$ for each m_l *i.e.*, 3 in 4*s*

$l = 1 \quad m_l = -1, 0, +1$ *i.e.*, 9 in 4*p*

$l = 2 \quad m_l = \pm 2, 1, 0$ *i.e.*, 15 in 3*d*

Thus $4s^3$, $4p^9$ and $3d^{15}$ *i.e.*, in all 27 elements would have been in 4th period.

Solution 54. The electronic configuration are :

${}_{7}N$: $1s^2, 2s^2\,2p^3$ unpaired electron = 3
${}_{24}Cr$: $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^5, 4s^1$ unpaired electron = 6
${}_{34}Se$: $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^4$ unpaired electron = 2
${}_{36}Kr$: $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6$ unpaired electron = 0

∴ Total spin for an atom = ±1/2 × no. of unpaired electron

For ${}_{7}N$, it is = **±3/2**
For ${}_{24}Cr$, it is = **±3**
For ${}_{34}Se$, it is = **±1**
For ${}_{36}Kr$, it is = **0**

Also magnetic moment = $\sqrt{[n(n+2)]}$ Bohr magneton

For ${}_{7}N$, it is = $\sqrt{(15)}$
For ${}_{24}Cr$, it is = $\sqrt{(48)}$
For ${}_{34}Se$, it is = $\sqrt{(8)}$
For ${}_{36}Kr$, it is = $\sqrt{(0)}$

Solution 55. $\lambda = \frac{h}{mu}$ or $m = \frac{h}{\lambda . u} = \frac{6.626 \times 10^{-34}}{589 \times 10^{-9} \times 3.0 \times 10^{8}} = \mathbf{3.74 \times 10^{-36}\ kg}$

Solution 56. ${}_{26}Fe$: $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^6, 4s^2$

∴ Fe^{2+} : $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^6$;

(Note the removal of electron from outermost shell)

${}_{25}Mn^{4+}$: $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^3$
${}_{7}N^{3-}$: $1s^2, 2s^2\,2p^6$
${}_{8}O^{2-}$: $1s^2, 2s^2\,2p^6$

Solution 57. $n_2 = 6;\ n_1 = 1$

No. of lines emitted during transition from 6th orbit to 1st orbit = $\Sigma \Delta n$

$= \Sigma(6 - 1) = \Sigma 5$

$= \mathbf{15}$

Solution 58. The spin angular momentum of electron $= \dfrac{h}{2\pi}\sqrt{s(s+1)}$

$s = ½$, The spin angular momentum of electron $= \dfrac{h}{2\pi}\sqrt{\dfrac{3}{2}\times\dfrac{1}{2}}$

$$= \frac{\sqrt{3}h}{4\pi}$$

$$= \frac{\sqrt{3}}{2}\hbar\left(\hbar = \frac{h}{2\pi}\right)$$

Solution 59. ψ represents an orbital and ψ_{210} has $n = 2$, $l = 1$, $m = 0$ *i.e.*, $2s$ subshell.

The angular momentum $= \dfrac{h}{2\pi}\sqrt{l(l+1)}$

$$= \frac{h}{2\pi}\times\sqrt{2}$$

$$= \frac{h}{\sqrt{2}\pi}$$

Also spherical node in $2s = n - l - 1 = 2 - 1 - 1 = 0$

Angular node $= l = 1$

Selected Problems with Solutions

➤ **Problem 1.** A monoatomic (X) ion has a charge of +3. The nucleus of the ion has a mass number of 45. The number of neutrons in the nucleus is 1.14 times that of number of protons. Find out:

(a) Number of electrons in atom X.

(b) Number of electrons in X^{3+} ion.

(c) Configuration of X, X^{3+} and X^{1+} ion.

(d) Suggest which of these (X, X^{3+} and X^{+}) are paramagnetic.

(e) The total magnetic moment of X^{+} ion.

➤ **Problem 2.** The eyes of a certain member of the raptile family pass a visual signal to the brain when the visual receptors are struck by photons of wavelength 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photon that must strike the receptor. ($h = 6.6 \times 10^{-34}$)

➤ **Problem 3.** The dissociation energy of H_2 is 430.53 kJ mol^{-1}. If H_2 is exposed to radiation energy of wavelength 253.7 nm, what % of radiant energy will be converted into kinetic energy?

➤ **Problem 4.** O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom, 1.967 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen requires 498 kJ m o^{-1}l. What is the maximum wavelength effective for photochemical dissociation of O_2?

➤ **Problem 5.** A certain dye absorbs light of $\lambda = 4530$ Å and then fluorescence light of 5080 Å. Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorescence, calculate the ratio of quanta emitted out to the no. of quanta absorbed.

➤ **Problem 6.** A photon of 300 nm is absorbed by a gas and then re-emits two photons. One re-emitted photon has wavelength 496 nm. Calculate energy of other photon re-emitted out.

➤ **Problem 7.** Two carbon discs of 1.0 g each are 1.0 cm apart have equal and opposite charges. If forces of attractions between them is 1.00×10^{-5} N, calculate the ratio of excess electrons to total atoms on the negatively charged disc. (Permitivity constant is 9.0×10^{9} N m^{2} C^{-2}).

➤ **Problem 8.** Calculate the wavelength of first line of Lyman series of ten times ionised sodium atom ($Z = 11$) and compare with the wavelength of first line of Balmer series of H atom.

➤ **Problem 9.** What is the difference in energy between 1s and 2p-orbitals in the hydrogen atom? In the X-ray spectrum of Cu, radiation of 1.54 Å wavelength is emitted when an electron changes from 2p to 1s-orbital. What is the energy difference between these orbitals in copper?

➤ Problem 10. The ionisation energy of a H like Bohr's atom is 4 Rydberg.

(i) Calculate the wavelength radiated when electron jumps from the first excited state to ground state.

(ii) What is the radius of I orbit of this atom?

Given $1R_h = 2.18 \times 10^{-18}$ J.

➤ Problem 11. Calculate the frequency, energy and wavelength of radiations corresponding to spectral line of lowest frequency in Lyman series in the spectra of H atom. Also calculate the energy of corresponding line in the spectra of Li^{2+}.

($R_H = 1.09678 \times 10^7$ m^{-1}, $c = 3 \times 10^8$ m sec^{-1}, $h = 6.625 \times 10^{-34}$ J sec)

➤ Problem 12. The IP_1 of H is 13.6 eV. It is exposed to electromagnetic waves of 1028 Å and gives out induced radiations. Find the wavelength of these induced radiations.

➤ Problem 13. 1.8 g hydrogen atoms are excited to radiations. The study of spectra indicates that 27% of the atoms are in 3rd energy level and 15% of atoms in 2nd energy level and the rest in ground state. IP of H is 13.6 eV. Calculate:

(a) No. of atoms present in III and II energy level.

(b) Total energy evolved when all the atoms return to ground state.

➤ Problem 14. Consider three electron jumps described below for the hydrogen atom

X : $n = 3$ to $n = 1$
Y : $n = 4$ to $n = 2$
Z : $n = 5$ to $n = 3$

(a) The photon emitted in which transition X, Y or Z will have shortest wavelength?

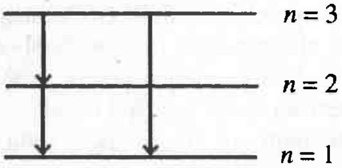
(b) For which transition will the electron experience the longest change in orbit radius?

➤ Problem 15. A series of lines in the spectrum of atomic H lies at wavelengths 656.46, 486.27, 434.17, 410.29 nm. What is the wavelength of next line in this series?

➤ Problem 16. A hydrogen-like atom (atomic number Z) is in a higher excited state of quantum number *n*. This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV respectively. Determine the values of *n* and Z.

➤ Problem 17. Calculate the Rydberg constant R_H if He^+ ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.

➤ **Problem 18.** Consider the following two electronic transition possibilities in a hydrogen atom as pictured below:



(1) The electron drops from third Bohr's orbit to second Bohr's orbit followed with the next transition from second to first Bohr's orbit.

(2) The electron drops from third Bohr's orbit to first Bohr's orbit directly.

Show that:

(a) The sum of the energies for the transitions $n = 3$ to $n = 2$ and $n = 2$ to $n = 1$ is equal to the energy of transition for $n = 3$ to $n = 1$.

(b) Are wavelengths and frequencies of the emitted spectrum are also additive in the same way as their energies are?

➤ **Problem 19.** The angular momentum of an electron in a Bohr's orbit of H-atom is 4.2178×10^{-34} kg-m^2/sec. Calculate the spectral line emitted when electron falls from this level to next lower level.

➤ **Problem 20.** Find the quantum no. '*n*' corresponding to the excited state of He^+ ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm.

➤ **Problem 21.** Calculate the angular frequency of an electron occupying the second Bohr's orbit of He^+ ion.

➤ **Problem 22.** Two hydrogen atoms collide head on and end up with zero kinetic energy. Each atom then emits a photon of wavelength 121.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before collision?

$R_H = 1.097 \times 10^7$ m^{-1} and $m_H = 1.67 \times 10^{-27}$ kg.

➤ **Problem 23.** The kinetic energy of an electron in H like atom is 6.04 eV. Find the area of the third Bohr orbit to which this electron belong. Also report the atom.

➤ **Problem 24.** How many spectral lines are emitted by atomic hydrogen excited to the *n*th energy level?

➤ **Problem 25.** The hydrogen atom in the ground state is excited by mass of monochromatic radiations of wavelength λ Å. The resulting spectrum consists of maximum 15 different lines What is the value of λ.

$R_H = 109737$ cm^{-1}

➤ **Problem 26.** A single electron orbit around a stationary nucleus of charge $+Ze$, where Z is constant and e is the magnitude of the electronic charge. It requires 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Calculate:

(a) The value of Z.

(b) The energy required to excite the electron from the third orbit to the fourth Bohr orbit.

(c) The wavelength of the electromagnetic radiation required to remove the electron from the first Bohr orbit to infinity.

(d) The kinetic energy, potential energy and angular momentum of electron in the first Bohr orbit.

(e) The radius of the first Bohr orbit.

(Given $E_{1\,H} = -13.6$ eV, $c = 3 \times 10^{10}$ cm/sec; $h = 6.6 \times 10^{-27}$ erg-sec, $r_{1\,H} = 0.539$ Å.)

➤ **Problem 27.** Determine de-Broglie wavelength of an electron having kinetic energy of 1.6×10^{-6} erg. ($m_e = 9.11 \times 10^{-28}$ g, $h = 6.62 \times 10^{-27}$ erg-sec).

➤ **Problem 28.** Show that de-Broglie wavelength of electron accelerated through V volt is nearly given by:

$$\underset{(\text{in Å})}{\lambda} = \left[\frac{150}{V}\right]^{1/2}$$

➤ **Problem 29.** Calculate the momentum of electron moving with 1/3rd velocity of light.

➤ **Problem 30.** Calculate the accelerating potential that must be imparted to a proton beam to give it an effective wavelength of 0.005 nm.

➤ **Problem 31.** An electron in a hydrogen like atom, is in an excited state. It has a total energy of –3.4 eV. Calculate:

(a) The kinetic energy of electron.

(b) The de Broglie wavelength of electron.

($h = 6.6 \times 10^{-34}$, $m_e = 9.108 \times 10^{-31}$ kg)

➤ **Problem 32.** A green ball weighs 75 g and comes travelling towards you at 400 cm/sec. A photon of light emitted from green ball has a wavelength of 5×10^{-5} cm. Assuming that the error in the position of ball is the same as the wavelength of itself, calculate the error in momentum of the green ball.

➤ **Problem 33.** A stationary He^+ ion emitted a photon corresponding to the first line (H_α) of the Lyman series. That photon liberated a photo-electron from a stationary H atom in ground state. What is the velocity of photo-electron? $R_H = 109678\ \text{cm}^{-1}$.

➤ **Problem 34.** 2.4 mole of H_2 sample was taken. In one experiment 60% of the sample was exposed to continuous radiations of frequency 4.47×10^{15} Hz, of which all the electrons are removed from the atom. In another experiment, remaining sample was irradiated with light of wavelength 600 Å, when all the electrons are removed from the surface. Calculate the ratio of maximum velocity of the ejected electrons in the two cases. Also report the velocity of ejected electron in each case. Assume that ejected electrons do not interact with any photon. (Ionization Potential of H = 13.6 eV).

➤ **Problem 35.** What is the maximum precision with which the momentum of an electron can be known if the uncertainty in the position of electron is ±0.001 Å? Will there be any problem in describing the momentum if it has a value of $\frac{h}{2\pi a_0}$, where a_0 is Bohr's radius of first orbit, *i.e.*, 0.529 Å?

➤ **Problem 36.** The photo-electric emission requires a threshold frequency ν_0. For a certain metal $\lambda_1 = 2200$ Å and $\lambda_2 = 1900$ Å produce electrons with a maximum kinetic energy KE_1 and KE_2, if $KE_2 = 2KE_1$, calculate ν_0 and corresponding λ_0.

➤ **Problem 37.** Point out the angular momentum of an electron in,

(a) 4*s* orbital (b) 3*p* orbital (c) 4th orbit.

Answers

1. (a) 21, (b) 18, (c) —do— , (d) X, X^1, (e) $\sqrt{8}$ B.M. ;

2. 1.37×10^5 photons ;

3. 8.68% ;

4. 1740.2 Å ;

5. 0.527 ;

6. 2.625×10^{-19} joule ;

7. 4.17×10^{-14} electron/atom ;

8. 6565 Å , 1.523×10^{-3} times of λ_H ;

9. 1.635×10^{-11} erg, 1.29×10^{-15} J ;

10. (i) 303.89 Å, (ii) 2.645×10^{-9} cm ;

11. $\lambda = 1215$ Å, $\nu = 2.469 \times 10^{15}$ Hz, $E = 16.36 \times 10^{-19}$ J, $E_{Li^{2+}} = 14.7 \times 10^{-18}$ J

12. I induced = 1028 Å, II induced = 1216 Å, III induced = 6568 Å ;

13. (a) 292.68×10^{21} atoms, 162.62×10^{21} atoms, (b) 832.50 kJ ;

14. (a) 'X' (b) 'Z' ;

15. 397.2 nm ;

16. $n - 6$, $Z = 3$;

17. 1.095×10^7 m^{-1} ;

18. See solution ;

19. 1.8×10^{-4} cm ;

20. 5th orbit ;

21. 2.067×10^{16} sec^{-1} ;

22. 4.43×10^4 m sec^{-1} ;

23. 17.80×10^{-16} cm^2, He$^+$;

24. $\frac{1}{2} n \ (n - 1)$;

25. 937.3 Å ;

26. (a) 5, (b) 16.53 eV, (c) 36.4×10^{-8} cm,
(d) P.E. = – 668.75 eV, K.E. = + 334.37 eV, $h/2\pi$
(e) 1.078×10^{-9} cm ;

27. 0.0087 Å ;

28. See solution ;

29. 9.69×10^{-18} g cm sec^{-1} ;

30. 32.85 Volt ;

31. (a) 3.4 eV, (b) 6.618×10^{-10} m ;

32. 1.055×10^{-23} ;

33. 3.09×10^8 cm sec^{-1} ;

34. 0.83 or 1.22 ;

35. 5.27×10^{-22} Ns, 2×10^{-24} Ns ;

36. $\nu_0 = 1.1483 \times 10^{15}$ sec^{-1}, $\lambda_0 = 2612.6$ Å ;

37. (a) 0 , (b) $\frac{h}{\sqrt{2}\pi}$, (c) $\frac{2h}{\pi}$.

Problems for Self Assessment

1. A monoatomic ion has a charge of +2. The nucleus of the ion has a mass number of 62. The number of neutrons in the nucleus is 1.21 times that of the number of protons. How many electrons are in the ion? What is the name of the element?

2. Infrared lamps are used in restaurants and cafeterias to keep food warm. The infrared radiation is strongly absorbed by water raising its temperature and that of the food in which it is incorporated. How many photons per second of infrared radiation are produced by an infrared lamp that consumes energy at the rate of 100 watt (100 J s^{-1}) and is 12% efficient in converting this energy to infrared radiation? Assume that infrared radiation has a wavelength of 1500 nm.

3. Which has a shorter wavelength : 10 eV photon or 10 eV electron. Also report their values.

4. If n_1 and n_2 are the quantum numbers for levels which are involved in spectral transition and $n_1 + n_2 = 7$ and $n_2 - n_1 = 1$, find the wavelength of the first line of this series in hydrogen atom.

5. To which quantum level does the electron jump in H atom from the lowest level if it is given an energy corresponding to 99% of the ionisation potential?

6. An electron in a hydrogen like species is in the excited state n_2. The wavelength for the transition n_2 to $n_1 = 2$ is 48.24 nm. The corresponding wavelength for the transition from n_2 to $n_1 = 3$ is 142.46 nm. Find the value of n_2 and Z and report the H like atom.

7. Calculate the frequency, energy and wavelength of radiations corresponding to spectral line of lowest frequency in Lyman series in the spectra of H atom. Also calculate the energy of corresponding line in the spectra of Li^{2+}.
$R_H = 1.09678 \times 10^7$ m^{-1}, $c = 3 \times 10^8$ m sec^{-1}, $h = 6.625 \times 10^{-34}$ J sec.

8. A hydrogen like atom (described by the Bohr's model) is observed to emit six wavelength, originating from all possible transitions between a group of levels. These levels have energies between –0.85 eV and –0.544 eV (including both these values).
   (a) Find the atomic number of the atom.
   (b) Calculate the smallest wavelength emitted in these transitions.
   (use hc = 1240 eV–nm, $E_{1\,H} = -13.6$ eV)

9. A hydrogen like atom of atomic number Z is in an excited state of quantum number $2n$. It can emit a maximum energy photon of 204 eV. If it makes a transition to quantum state n, a photon of energy 40.8 eV is emitted. Find out n and Z and the ground state energy in eV for this atom. Also calculate the minimum energy in eV that can be emitted by this atom during deexcitation. Ground state energy of H atom is –13.6 eV.

10. Hydrogen atom in its ground state is excited by means of monochromatic radiations of wavelength 975 Å. How many different lines are possible in the resulting spectrum. Calculate the longest wavelength among them. $E_1 = -13.6$ eV

11. A doubly ionised lithium atom is hydrogen like with atomic number 3.

(a) Find the wavelength of the radiation required to excite the electron in Li^{2+} from the first to the third Bohr orbit.

(b) How many spectral lines are observed in the emission spectrum of above excited system. ($E_{1\,H} = -13.6$ eV)

12. Electrons in hydrogen like atom ($Z = 3$) make transition from the fifth to the fourth orbit and from the fourth to the third orbit. The resulting radiations are incident normally on a metal plate and ejects photo-electrons. The stopping potential for the photo-electrons ejected by the shorter wavelength is 3.95 V.Calculate the work function of the metal and stopping potential for the photo-electrons ejected by the longer wavelength. ($R_H = 1.094 \times 10^7$ m^{-1})

13. A particle of charge equal to that of an electron and mass 208 times the mass of electron (*i.e.*, mu-meson) moves in a circular orbit around a nucleus of charge $+3e$. (Take the mass of the nucleus to be infinite). Assuming that the Bohr model of the atom is applicable to this system. ($R_H = 1.097 \times 10^7$ m^{-1}).

(i) Derive an expression for the radius of Bohr orbit.

(ii) Find the value of n for which the radius of the orbit is approximately the same as that of the first Bohr orbit for H-atom.

(iii) Find the wavelength of the radiation emitted when the mu-meson jumps from the third orbit to the first orbit.

14. Compare the energy of $n = 5$ to $n = 4$ transition of an electron plus nucleus $Z = 3$ with the energy of $n = 2$ to $n = 1$ transition for an electron plus nucleus with $Z = 2$.

15. Calculate the wavelength of CO_2 molecule moving with velocity of 440 m sec^{-1}.

16. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 1 Å. What is the uncertainty involved in the measurement of its velocity.

17. When would the wavelength associated with an electron be equal to wavelength of proton? (mass of electron = 9.10×10^{-28} g; mass of proton = 1.6725×10^{-24} g).

18. When a beam of 10.6 eV photons of intensity 2.00 W/m^2 falls on a platinum surface of area 1.0×10^{-4} m^2 and work function 5.6 eV, 0.53% of the incident photons eject photo-electron. Find the number of photo-electrons emitted per second and their minimum energies (in eV). 1 eV = 1.6×10^{-19}J.

19. When light frequency, v is shone on a metal surface with threshold frequency v_0, photoelectrons are emitted with maximum kinetic energy = 1.3×10^{-18} J. If the ratio, $v : v_0 = 3 : 1$, calculate the threshold frequency v_0.

20. Write down the electronic configuration of following species and calculate total spin, magnetic moment and unpaired electrons in each (a) 44 Ru (b) $_{25}Mn^+$.

Answers

1. ${}_{28}Ni^{62}$, Ni^{2+} , 26 ; **2.** 9.05×10^{17} photon s^{-1} ;

3. $\lambda_e = 3.88$ Å , $\lambda_{photon} = 1240$ Å ; **4.** 1875.6×10^{-9} m ;

5. 10 ; **6.** $n_2 = 5$, $Z = 3$, Li^{2+} ;

7. $\nu = 2.467 \times 10^{15}$ Hz, $E_H = 16.36 \times 10^{-19}$, $\lambda = 1215.6$ Å , $E_{Li^{3+}} = 14.7 \times 10^{-18}$ J ;

8. Li^{2+}, 4060 nm ; **9.** $n = 2$, $Z = 4$, $E_1 = -217.6$ eV ;

10. 6 lines (from 4th to 1), 18800 Å ; **11.** (a) 113.7 Å, (b) 3 ;

12. $W = 3.193 \times 10^{-19}$ J , $V_s = 0.756$ V ;

13. (i) $r = n^2 \left[\dfrac{h^2 \times 4\pi\,\varepsilon_0}{4\pi^2\, m'\, Ze^2}\right] = n^2 \times 8.44 \times 10^{-14}$ m

(ii) $n = 25$, (iii) 5.48×10^{-11} m

14. $E_1/E_2 = 0.0675$; **15.** 2.06×10^{-11} metre ;

16. 6.626×10^{-22} m s^{-1} ; **17.** $\dfrac{u_e}{u_p} = 1.8 \times 10^3$, *i.e.*, velocity ratio ;

18. $n = 1.179 \times 10^{14}$, minimum energy = 0, maximum energy = 5.0 eV ;

19. 9.81×10^{4} Hz ; **20.** (a) ±2, $\sqrt{24}$, 4, (b) ±3, $\sqrt{48}$, 6.

4

Radioactivity

Chapter at a Glance

1. **Binding energy (B.E.)** $\Delta E = 931.478 \times \Delta m'$ MeV ($\Delta m'$ is mass decay)
2. **Binding energy/nucleon** $= \dfrac{\text{Total B.E.}}{\text{No. of nucleons}}$
3. **Rate of decay** $= K \times$ No. of atoms at that time $= K \times N$
4. **Decay constant** $(K) = \dfrac{2.303}{t} \log_{10} \dfrac{N_0}{N}$ or $K = \dfrac{1}{t} \log_e \dfrac{N_0}{N}$

   or $\dfrac{N_0}{N} = e^{Kt}$ or $\dfrac{N}{N_0} = e^{-Kt}$

   (N_0 is no. of atoms at $t = 0$, N is no. of atoms at $t = t$)
5. **Half life** $(t_{1/2}) = \dfrac{0.693}{K}$
6. **Average life** $(\tau) = \dfrac{1}{K} = t_{1/2} \times 1.44$
7. **Amount left after** n **halves** $= \dfrac{N_0}{2^n}$
8. **Amount decayed after** n **halves** $= \dfrac{N_0\,[2^n - 1]}{2^n}$
9. **Different units of rate of decay:**

   1 Curie $= 3.7 \times 10^{10}$ dps $= 3.7 \times 10^{10}$ Bq. $= 3.7 \times 10^4$ rd (SI unit is Bq. or dps)
10. **Radioactive equilibrium:**

    $$\therefore \frac{K_A}{K_B} = \frac{N_B}{N_A} = \frac{(t_{1/2})_B}{(t_{1/2})_A} = \frac{\tau_B}{\tau_A}$$
11. **Parallel path decay :** $K_{\text{av.}} = K_{\text{I path}} + K_{\text{II path}}$
12. **Maximum yield of daughter element :** $t_{\max} = \dfrac{2.303}{K_B - K_A} \log_{10} \left[\dfrac{K_B}{K_A}\right]$

The Basic Problems with Solutions

➤ **Problem 1.** What is meant by nuclear binding energy? Calculate the binding energy per nucleon of Li isotope, which has the isotopic mass of 7.016 amu. The individual masses of neutron and proton are 1.008665 amu and 1.007277 amu, respectively and the mass of electron = 0.000548 amu.

➤ **Problem 2.** The atomic mass of ^{16}O is 15.995 amu while the individual masses of proton and neutron are 1.0073 amu and 1.0087 amu respectively. The mass of electron is 0.000548 amu. Calculate the binding energy of the oxygen nucleus.

➤ **Problem 3.** The isotopic masses of $^{2}_{1}H$ and $^{4}_{2}He$ are 2.0141 and 4.0026 amu respectively and the velocity of light in vacuum is 2.998×10^8 m/s. Calculate the quantity of energy (in J) liberated when two mole of $^{2}_{1}H$ undergo fusion to form one mole of $^{4}_{2}He$.

➤ **Problem 4.** How many α- and β-particles will be emitted when $_{90}Th^{232}$ changes into $_{82}Pb^{208}$?

➤ **Problem 5.** $_{90}Th^{234}$ disintegrates to give $_{82}Pb^{206}$ as the final product. How many α and β-particles are emitted out during this process?

➤ **Problem 6.** Write the nuclear reactions for the following radioactive decay :

(a) $_{92}U^{238}$ undergoes α-decay. (b) $_{91}Pa^{234}$ undergoes β^--decay.

(c) $_{11}Na^{22}$ undergoes β^+-decay.

➤ **Problem 7.** Give one example each of (a) α-emission, (b) β^+-emission, and (c) K-capture. Write the equation for these nuclear changes.

➤ **Problem 8.** Complete the following nuclear reactions :

(a) $^{96}_{42}Mo\ (\ldots,\ n)\ ^{97}_{43}Tc$ (b) $\ldots\ (\alpha,\ 2n)\ ^{211}_{85}At$

(c) $^{55}_{25}Mn\ (n,\ \gamma)\ \ldots$ (d) $^{246}_{96}Cm + ^{12}_{6}C \longrightarrow \ldots + 4\,^{1}_{0}n$

(e) $^{27}_{13}Al\ (\alpha,\ n)\ \ldots$ (f) $^{235}_{92}U\ (\alpha,\ \beta^-)\ \ldots$

➤ **Problem 9.** Complete the equations for the following nuclear processes :

(a) $^{35}_{17}Cl + ^{1}_{0}n \longrightarrow \ldots + ^{4}_{2}He$

(b) $^{235}_{92}U + ^{1}_{0}n \longrightarrow \ldots + ^{137}_{54}Xe + 2\,^{1}_{0}n$

(c) $^{27}_{13}Al + ^{4}_{2}He \longrightarrow \ldots + ^{1}_{0}n$

(d) $\ldots\ (n,\ p)\ ^{35}_{16}S$

(e) $^{239}_{94}Pu\ (\alpha,\ \beta^-)\ \ldots$

➤ **Problem 10.** Calculate the no. of α- and β-particles given out during the change :

$$_{93}Np^{237} \longrightarrow {}_{83}Bi^{209}$$

Also report the nature and name of this radioactive series.

➤ **Problem 11.** Calculate the mass of ^{140}La in a sample whose activity is 3.7×10^{10} Bq (1 Becquerel, Bq = 1 disintegration per second) given that its $t_{1/2}$ is 40 hour.

➤ **Problem 12.** The half life of $_{38}Sr^{90}$ is 20 year. If the sample of this nucleide has an activity of 8,000 disintegrations min^{-1} today, what will be its activity after 80 year?

➤ **Problem 13.** A sample of wooden air craft is found to undergo 9 dpm g^{-1} of C^{14}. What is approximate age of air craft? The half life of $_6C^{14}$ is 5730 year and rate of disintegration of wood recently cut down is 15 dpm g^{-1} of $_6C^{14}$?

➤ **Problem 14.** A piece of wood from an archeological source shows a ^{14}C activity which is 60% of the activity found in fresh wood today. Calculate the age of the archeological sample. ($t_{1/2}$ ^{14}C = 5770 year)

➤ **Problem 15.** The β^--activity of a sample of CO_2 prepared from a contemporary wood gave a count rate of 25.5 counts per minute (c.p.m.). The same mass of CO_2 from an ancient wooden statue gave a count rate of 20.5 cpm., in the same counter condition. Calculate its age to the nearest 50 year taking $t_{1/2}$ for ^{14}C as 5770 year. What would be the expected count rate of an identical mass of CO_2 from a sample which is 4000 year old?

➤ **Problem 16.** The radioactive isotope $^{60}_{27}Co$ which has now replaced radium in the treatment of cancer can be made by a (n, p) or (n, γ) reaction. For each reaction, indicate the appropriate target nucleus. If the half-life of $^{60}_{27}Co$ is 7 year, evaluate the decay constant in s^{-1}.

➤ **Problem 17.** A piece of charcoal from the ruins of a settlement in Japan was found to have C^{14}/C^{12} ratio that was 0.617 times that found in living organisms. How old is this piece of charcoal? $t_{1/2}$ for C^{14} is 5770 year?

➤ **Problem 18.** The half of U^{238} decomposed to Pb^{206} in 4.5×10^8 year. What will be the age of rock that contains equal weight of both?

➤ **Problem 19.** $_{92}U^{238}$ by successive radioactive decays changes to $_{82}Pb^{206}$. A sample of uranium ore was analysed and found to contain 1.0 g U^{238} and 0.1 g Pb^{206}. Assuming that Pb^{206} has accumulated due to decay of uranium, find out the age of ore. $t_{1/2}$ for $U^{238} = 4.5 \times 10^9$ year.

➤ **Problem 20.** The isotopic composition of rubidium is ^{85}Rb –72 per cent and ^{87}Rb –28 per cent. ^{87}Rb is weakly radioactive and decay by β^--emission with a decay constant of 1.1×10^{-11} per year. A sample of the mineral pollucite was found to contain 450 mg Rb and 0.72 mg of ^{87}Sr. Estimate the age of mineral pollution, stating any assumption made.

➤ **Problem 21.** A 0.2 mL sample of a solution containing 1.0×10^{-7} curie of $_1H^3$ is injected to the blood stream of an animal. After sufficient time for circulatory equilibrium to be established, 0.10 mL of blood is found to have an activity of 20 dpm. Calculate the volume of blood in animal, assuming no change in activity of sample during criculatory equilibrium.

➤ **Problem 22.** Calculate the density of the nucleus of $_{47}Ag^{107}$ assuming r_{nucleus} is $1.4 A^{1/3} \times 10^{-13}$ cm. Where A is mass number of nucleus. Compare its density with density of metallic silver 10.5 g cm^{-3}.

➤ **Problem 23.** A sample of $_{53}I^{131}$ as iodide ion was adminstered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4 days 67.7% of initial radioactivity was detected in the thyroid gland of the patient. What mass of stable iodide ion had migrated to thyroid gland. $t_{1/2}$ for iodide ion = 8 day.

➤ **Problem 24.** A solution of 1 litre has 0.6 g of non-radioactive Fe^{3+} with mass no. 56. To this solution 0.209 g of radioactive Fe^{2+} is added with mass no. 57 and the following reaction occured.

$$^{57}Fe^{2+} + {}^{56}Fe^{3+} \longrightarrow {}^{57}Fe^{3+} + {}^{56}Fe^{2+}$$

At the end of one hour, it was found that 10^{-5} moles of non-radioactive $^{56}Fe^{2+}$ was obtained and the rate of reaction was 3.38×10^{-7} mol l^{-1} hr^{-1}. Neglecting any change in volume, calculate the activity of the sample at the end of 1 hr. $t_{1/2}$ for $^{57}Fe^{2+} = 4.62$ hr.

➤ **Problem 25.** A radioactive element decays by β-emission. If mass of parent and daughter nucleide are m_1 and m_2 respectively calculate energy liberated during the emission.

Answers

1. 40.0 MeV, 5.71 MeV;
2. 0.137 amu, 12.32×10^{12} J mol^{-1};
3. 2.3×10^{12} J;
4. $\alpha = 6$, $\beta = 4$;
5. 7α, 6β ;
6. See solution;
7. See solution;
8. (a) ${}^{2}_{1}H$, (b) ${}^{209}_{83}Bi$, (c) ${}^{56}_{25}Mn$, (d) ${}^{254}_{102}No$, (e) ${}^{30}_{15}P$, (f) ${}^{242}_{95}Am$.
9. (a) ${}^{32}_{15}P$, (b) ${}^{97}_{38}Sr$, (c) ${}^{30}_{15}P$, (d) ${}^{35}_{17}Cl$, (e) ${}^{243}_{97}Bk$.
10. $\alpha = 7$, $\beta = 4$;
11. 1.79×10^{-6} g;
12. 500 dpm ;
13. 4224.47 yr ;
14. 4253 yr ;
15. 1817 yr., 15.77 cpm ;
16. 3.14×10^{-9} sec^{-1};
17. 4021.29 yr;
18. 4.99×10^{8} yr;
19. 7.1×10^{8} yr;
20. 5.202×10^{8} yr.;
21. 1109.8 mL;
22. 1.38×10^{13};
23. 95.8 %;
24. 2.85×10^{20} dph;
25. $[m_1 - m_2 - 2m_e]c^2$;

Solution

Solution 1. The total energy given out as mass decay during binding up of nucleons in nucleus is known as binding energy.

Mass of ${}_3Li^7$ isotope = 7.016 amu

Mass of 3 protons in it = 3 × 1.007277 = 3.022 amu

Mass of 4 neutrons in it = 4 × 1.008665 = 4.035 amu

Mass of 3 electrons in it = 3 × 0.000548 = 0.002 amu

$\therefore$ Mass defect = [3.022 + 4.035 + 0.002] – 7.016

= 0.043 amu

$\Delta E = 931.478 \times \Delta m'$ MeV = 0.043 × 931.478

= **40.0 MeV**

$\therefore$ Binding energy per nucleon = (40/7) = **5.71 MeV**

Solution 2. Mass of ${}_8O^{16}$ = 15.995 amu

Mass of 8 protons = 8 × 1.0073 = 8.0584

Mass of 8 neutrons = 8 × 1.0087 = 8.0696

Mass of 8 electrons = 8 × 0.000548 = 0.0044

$\therefore$ Mass defect = [8.0584 + 8.0696 + 0.0044] – 15.995

= **0.137 amu**

$\because$ $\Delta E = mc^2$

$\therefore$ $\Delta E = 0.137 \times 1.66057 \times 10^{-27} \times 6.02 \times 10^{23} \times (2.998 \times 10^8)^2$ J

$= \mathbf{12.32 \times 10^{12}\ J\ mol^{-1}}$

Solution 3.

$$2\,{}_1^2H \longrightarrow {}_2^4He + \text{Energy}$$

Mass defect = 2 × 2.0141 – 4.0026 = 0.0256 amu

$\therefore$ $\Delta E = \Delta m \times c^2$

$= 0.0256 \times 1.66057 \times 10^{-27} \times 6.02 \times 10^{23} \times (2.998 \times 10^8)^2$

$= \mathbf{2.3 \times 10^{12}\ J}$

Solution 4. Suppose $\;{}_{90}Th^{232} \longrightarrow {}_{82}Pb^{208} + m\,{}_2^4He + n\,{}_{-1}^{\;0}e$

Equating mass numbers, 232 = 208 + 4 m or $m = 6$

Equating atomic numbers : 90 = 82 + 12 + (– n) or $n = 4$

Thus, 6α and 4β^- particles will be emitted.

Solution 5. Given : $\;{}_{90}Th^{234} \longrightarrow {}_{82}Pb^{206} + m\,{}_2^4He + n\,{}_{-1}^{\;0}e$

Where m 'α' particles and n 'β' particles are given out

Equating mass number : 234 = 206 + 4m + 0

$\therefore$ $m = 7$

Equating atomic number : 90 = 82 + 2m + n × (–1)

$\therefore$ $n = 6$ ($\because m = 7$)

Solution 6. (a) $${}_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}^{4}_{2}He$$

(b) $${}_{91}Pa^{234} \longrightarrow {}_{92}U^{234} + {}^{0}_{-1}e$$

(c) $${}_{11}Na^{22} \longrightarrow {}_{10}Ne^{22} + {}^{0}_{+1}e$$

Solution 7. (a) $${}^{235}_{92}U \longrightarrow {}^{231}_{90}Th + {}^{4}_{2}He \quad (\alpha\text{-emission})$$

(b) $${}^{22}_{11}Na \longrightarrow {}^{22}_{10}Ne + {}^{0}_{+1}e \quad (\beta^{+}\text{-emission})$$

(c) $${}^{133}_{56}Ba + e^{-} \longrightarrow {}^{133}_{55}Cs + \text{X-ray} \quad (\text{K-capture})$$

Solution 8. (a) ${}^{2}_{1}H$, (b) ${}^{205}_{83}Bi$, (c) ${}^{56}_{25}Mn$,

(d) ${}^{254}_{102}No$, (e) ${}^{30}_{15}P$, (f) ${}^{242}_{95}Am$.

Solution 9. (a) ${}^{32}_{15}P$, (b) ${}^{77}_{38}Sr$, (c) ${}^{30}_{15}P$,

(d) ${}^{35}_{17}Cl$, (e) ${}^{242}_{97}Bk$.

Solution 10. (a) $${}_{93}Np^{237} \longrightarrow {}_{83}Bi^{209} + a\,{}_{2}He^{4} + b\,{}_{-1}e^{0}$$

Where *a* and *b* are α- and β-particles given out during change.
Equating mass number

$$237 = 209 + 4a + 0 \times b$$
$$a = 7$$

Equating atomic numbers, keeping $a = 7$

$$93 = 83 + 2 \times 7 + b \times (-1)$$
$$b = 4$$

Thus 7α- and 4β- are given out during the change also 237/4 = 59 with remainder 1 and thus it is $(n + 1)$ series, the artificial radioactive series also called as naptunium series with $n = 59$.

Solution 11. $$\text{Rate of decay} = K.\,N_0 = \frac{\lambda \times w \times \text{Av.No.}}{140}$$

$$\left[\text{Let } w \text{ is weight of La}^{140}\text{, then } N_0 = \frac{w \times \text{Av.No.}}{140}\right]$$

$$3.7 \times 10^{10} = \frac{0.693}{40 \times 60 \times 60} \times \frac{w \times 6.02 \times 10^{23}}{140}$$
$$w = \mathbf{1.79 \times 10^{-6}\ g}$$

Solution 12. Given, $r_0 = 8000$ dpm, $t_{1/2} = 20$ year or $K = \frac{0.693}{20}\ \text{yr}^{-1}$

$$r_0 \propto N_0$$
$$r \propto N$$

$$\therefore \quad \frac{r_0}{r} = \frac{N_0}{N}$$

Now $$t = \frac{2.303}{K} \log \frac{r_0}{r}$$

$$\therefore \quad 80 = \frac{2.303 \times 20}{0.693} \log \frac{8000}{r}$$

$$\therefore \quad r = \mathbf{500\ dpm}$$

Solution 13. Given, $r_0 = 15$ dpm, $r = 9$ dpm, $t_{1/2} = 5730$ yr

$$t = \frac{2.303}{K} \log \frac{r_0}{r}$$

$$= \frac{2.303 \times 5730}{0.693} \log \frac{15}{9}$$

$$= \mathbf{4224.47\ yr}$$

Solution 14. $$t = \frac{2.303}{K} \log \frac{N_0}{N} \qquad r_0 \propto N_0 \quad \text{and} \quad r \propto N$$

$$= \frac{2.303 \times 5770}{0.693} \log \frac{100}{60} \qquad \left[\because \frac{r_0}{r} = \frac{N_0}{N} = \frac{100}{60}\right]$$

$$= \mathbf{4253\ yr.}$$

Solution 15. $r = 20.5$ cpm., $r_0 = 25.5$ cpm.

$$\because \quad r_0 \propto N_0 \quad \text{and} \quad r \propto N \quad \therefore \quad \frac{r_0}{r} = \frac{N_0}{N}$$

Also $$t = \frac{2.303}{K} \log \frac{N_0}{N} = \frac{2.303}{\lambda} \log \frac{r_0}{r}$$

$$t = \frac{2.303 \times 5770}{0.693} \log \frac{25.5}{20.5} = \mathbf{1817\ year}$$

Also, if $t = 4000$ yr then

$$4000 = \frac{2.303 \times 5770}{0.693} \log \frac{25.5}{r}$$

$$r = \mathbf{15.77\ cpm}$$

Solution 16. $$^{60}_{28}\text{Ni} + {}^{1}_{0}n \longrightarrow {}^{60}_{27}\text{Co} + {}^{1}_{+1}\text{P}$$

$$^{59}_{27}\text{Co} + {}^{1}_{0}n \longrightarrow {}^{60}_{27}\text{Co} + \gamma$$

Thus, target nucleus is $^{60}_{27}$Ni for (n, p) and $^{59}_{27}$Co for (n, γ) reaction.

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{7 \times 365 \times 24 \times 60 \times 60}$$

$$= \mathbf{3.14 \times 10^{-9}\ sec^{-1}}$$

Solution 17. Given, $t_{1/2} = 5770$ yr.

$$\frac{N_{C^{14}}}{N_{C^{12}}} = 0.617 \times \frac{N_{0C^{14}}}{N_{0C^{12}}}$$

$\because$ C^{14} undergoes decay and C^{12} does not $\therefore$ $N_{0C^{12}} = N_{0C^{12}}$

$$\therefore \quad \frac{N_{0C^{14}}}{N_{C^{14}}} = \frac{1}{0.617}$$

$$t = \frac{2.303}{K} \log \frac{N_0}{N}$$

$$= \frac{2.303 \times 5770}{0.693} \log \frac{1}{0.617}$$

$$= \mathbf{4021.29\ yr.}$$

Solution 18.

		U^{238}	$\longrightarrow$	Pb^{206}	
No. of atom	$t = 0$	N_0			
No. of atom	$t = t$	$N_0 - N$		N	
Wt. of metal	$t = t$	w		w	$(\because w_{Pb} = w_U)$

$$\because \quad N_U \text{ left} = \frac{w}{238} \qquad N_{Pb} \text{ formed} = \frac{w}{206}$$

$$N_{0U} = \frac{w}{238} + \frac{w}{206}$$

Now $$t = \frac{2.303}{K} \log \frac{N_{0U}}{N_U}$$

$$= \frac{2.303 \times 4.5 \times 10^8}{0.693} \cdot \log \frac{\frac{w}{238} + \frac{w}{206}}{\frac{w}{238}}$$

$$= \mathbf{4.99 \times 10^8\ yr}$$

Solution 19.

	U^{238}	$\longrightarrow$	Pb^{206}
Weight at $t = t$	1 g		0.1 g
Mole at $t = t$	$\frac{1}{238}$		$\frac{0.1}{206}$

$$\therefore \quad N_{0U^{238}} = \frac{1}{238} + \frac{0.1}{206} \quad \text{and} \quad N_{U^{238}} = \frac{1}{238}$$

$$t = \frac{2.303}{K} \log \frac{N_0}{N}$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693} \log \frac{\frac{1}{238} + \frac{0.1}{206}}{\frac{1}{238}}$$

$$= \mathbf{7.1 \times 10^8\ yr}$$

Solution 20. $^{85}Rb = 72\%$

$$^{87}Rb = 28\% \xrightarrow{K = 1.1 \times 10^{-11}\ yr^{-1}} {}^{87}Sr$$

Sample contains 450 mg ^{87}Rb and 0.72 mg ^{87}Sr

$$\text{The average isotopic mass of Rb} = \frac{72 \times 85 + 28 \times 87}{100}$$

$$= 85.56$$

Now 0.72 mg of Sr is formed from Rb, following β-emission

thus, mass of ^{87}Rb lost = 0.72 mg

Thus, initially the pollucite mineral contains Rb = 450 mg + 0.72 mg

= 450.72 mg

$$^{87}Rb \text{ present of originally in it} = \frac{28}{100} \times 450.72$$

$$= 126.20 \text{ mg}$$

$$^{87}Rb \text{ present at time } t = 126.20 - 0.72 = 125.48 \text{ mg}$$

Thus, $$t = \frac{2.303}{1.1 \times 10^{-11}} \log \frac{126.20}{125.48} = \mathbf{5.202 \times 10^8\ yr.}$$

Solution 21. Let volume of blood be V mL.

Thus total volume = $V + 0.2$ mL after injection of sample

$$0.1 \text{ mL sample has rate} = \frac{20}{60} \text{ dps}$$

$$\therefore (V + 0.2) \text{ mL sample has rate} = \frac{20 \times (V + 0.2)}{60 \times 0.1} \text{ dps}$$

Since rate is constant, thus

$$\frac{20 \times (V + 0.2)}{60 \times 0.1} = 1.0 \times 10^{-7} \times 3.7 \times 10^{10} \text{ dps}$$

$$\mathbf{V = 1109.8\ mL}$$

Solution 22. Volume of $_{47}Ag^{107}$ nucleus $= \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times [1.4 \times (107)^{1/3} \times 10^{-13}]^3$

$$= 1.23 \times 10^{-36} \text{ cm}^3$$

$$\therefore \quad \text{density of nucleus} = \frac{m}{V}$$

$$= \frac{107}{6.023 \times 10^{23} \times 1.23 \times 10^{-36}}$$

$$= 1.445 \times 10^{14} \text{ g/cm}^3$$

$$\text{Thus } \frac{\text{density of nucleus}}{\text{density of atom}} = \frac{1.445 \times 10^{14}}{10.5} = \mathbf{1.38 \times 10^{13}}$$

Solution 23. If $t = 4$ days, $K = \frac{0.693}{8}$, then

$$t = \frac{2.303}{K} \log \frac{r_0}{r}$$

$$4 = \frac{2.303 \times 8}{0.693} \log \frac{r_0}{r}$$

$$\therefore \quad r = 0.707\, r_0$$

Thus iodide ion left is 0.707 part of initially injected sample, however the rate decreases only 67.7% or 0.677 in 4 days, thus

If 0.707 is left then iodide ion migrated to thyroid = 1

Thus 0.677 is left then iodide ion migrated to thyroid $= \frac{1 \times 0.677}{0.707} = \mathbf{0.958}$

or **95.8%** of the iodide ion is migrated to gland.

Solution 24.

	$^{57}\text{Fe}^{2+}$ +	$^{56}\text{Fe}^{3+}$ $\longrightarrow$	$^{57}\text{Fe}^{3+}$ +	$^{56}\text{Fe}^{2+}$
Before reaction	$\frac{0.209}{57}$	$\frac{0.6}{56}$	0	0
After reaction	$\left[\frac{0.209}{57} - 10^{-5}\right]$	$\left[\frac{0.6}{56} - 10^{-5}\right]$	10^{-5}	10^{-5}

$^{57}\text{Fe}^{2+}$ left after reaction $= 3.667 \times 10^{-3} - 10^{-5} = 366.6 \times 10^{-5}$ mole

or $\quad N_0 = 366.6 \times 10^{-5} \times 6.023 \times 10^{23} = 2.208 \times 10^{21}$

Also $\quad t = \frac{2.303}{K} \log \frac{N_0}{N}$

$$1 = \frac{2.303 \times 4.62}{0.693} \log \frac{2.208 \times 10^{21}}{N}$$

$$\therefore \quad N = 1.9 \times 10^{21}$$

$$\therefore \quad \text{Rate of decay} = K \times N = \frac{0.693}{4.62} \times 1.9 \times 10^{21}$$

$$= \mathbf{2.85 \times 10^{20}\ dph}$$

Solution 25. The masses of parent and daughter elements nuclide are m_1 and m_2 respectively

Mass of parent element = $m_1 + Zm_e$

(where Z is at. no. of parent element)

Mass of daughter element = $m_2 + (Z+1)m_e$

(As at. no. of element increases by one due to β-emission)

∴ Mass decay = mass of parent atom – one β loss – [mass of daughter atom along with one electron]

$$= m_1 + Zm_e - m_e - [m_2 + (Z+1)\,m_e]$$

$$= [m_1 - m_2 - 2m_e]$$

Energy liberated = $[m_1 - m_2 - 2m_e]\,c^2$

Selected Problems with Solutions

▶ Problem 1. How much energy must a γ-ray photon have to produce a proton and anti-proton each having kinetic energy 10 MeV. $m_p = 1.007825$ amu. Assume 1 amu = 931 MeV.

▶ Problem 2. The sun radiates energy at the rate of 4×10^{26} Joule sec^{-1}. If the energy of fusion process

$$4\,{}^1_1H \longrightarrow {}^4_2He + 2\,{}^0_1e$$

is 27 MeV, calculate amount of hydrogen atoms that would be consumed per day for the given process.

▶ Problem 3. Calculate the energy released in joules and MeV in the following nuclear reaction:

$${}^2_1H + {}^2_1H \longrightarrow {}^3_2He + {}^1_0n$$

Assume that the masses of ${}^2_1H$, ${}^3_2He$ and neutron (n) respectively are 2.0141, 3.0160 and 1.0087 in amu.

▶ Problem 4. Consider an α-particle just in contact with a $_{92}U^{238}$ nucleus. Calculate the coulombic repulsion energy (*i.e.*, the height of coulombic barrier between U^{238} and α-particle) assuming that the distance between them is equal to the sum of their radii.

▶ Problem 5. Natural nitrogen atoms has found to exist in two isotopic forms, $_7N^{14}$ with mass 14.0031 and $_7N^{15}$ with mass 15.0001 amu. Which isotope is more stable. Assume mass of n and p to be 1.00893 and 1.00757 amu.

▶ Problem 6. $_{92}U^{238}$ is a natural an α-emitter. After α-emission the residual nucleus called UX_1 in turns emits a β^--particle to produce another nucleus UX_2. Find out the atomic and mass numbers of UX_1 and UX_2. Also if uranium belongs to III gp. to which group UX_1 and UX_2 belong.

▶ Problem 7. How much heat would be developed per hour from 1 curie of C^{14} source if all the energy of beta decay were imprisoned? Atomic masses of C^{14} and N^{14} are 14.00324 and 14.00307 amu respectively.

▶ Problem 8. In a nuclear reactor U^{235} undergoes fission liberating 200 MeV of energy. The reactor has a 10% efficiency and produces 1000 MW power. If the reactor is to function for 10 years, find the total mass of uranium needed.

▶ Problem 9. α-particles of 6 MeV energy is scattered back from a silver foil. Calculate the maximum volume in which the entire positive charge of the atom is supposed to be concentrated? (Z for silver = 47).

▶ Problem 10. The activity of a radioactive isotope falls to 12.5% in 90 days. Compute the half life and decay constant of isotope.

▶ Problem 11. A mixture is to be analysed for penicillin. You add 10.0 mg of penicillin labeled with ^{14}C that has a specific activity of 0.785 μ Ci mg^{-1}. From this mixture you are able to isolate only 0.42 mg of pure penicillin. The specific activity of the isolated penicillin is 0.102 μ Ci mg^{-1}. How much penicillin was in the original mixture?

➤ **Problem 12.** An archaeological specimen containing ^{14}C gives 40 counts in 5 minutes per gram of carbon. A specimen of freshly cut wood gives 20.3 counts per gram of carbon per minute. The counter used recorded a back ground count of 5 counts per minute in absence of any ^{14}C-containing sample. What is the age of the specimen? [T_{50} of $^{14}C = 5668$ year].

➤ **Problem 13.** Upon irradiating californium with neutrons, a scientist discovered a new nuclide having mass number of 250 and a half-life of 0.50 hr. Three hours after the irradiation, the observed radioactivity due to the nuclide was 10 dis/min. How many atoms of the nuclide were prepared initially?

➤ **Problem 14.** Equal masses of two samples of charcoal *A* and *B* are burnt separately and the resulting carbon dioxide is collected in two vessels. The radioactivity of ^{14}C is measured for both the gas samples. The gas from the charcoal *A* gives 2100 counts per week and the gas from the charcoal *B* gives 1400 counts per week. Find the age difference between the two samples? Half-life $^{14}C = 5730$ yr.

➤ **Problem 15.** One g of $_{79}Au^{198}$ ($t_{1/2} = 65$ hr) decays by β-emission to produce stable Hg.

(a) Write nuclear reaction for process.

(b) How much Hg will be present after 260 hr.

➤ **Problem 16.** 1 g Ra^{226} is placed in an evacuated tube whose volume is 5 cc. Assuming that each Ra nucleus yields for He atoms which are retained in the tube, what will be the pressure of He produced at 27°C after the end of 1590 year? $t_{1/2}$ for Ra is 1590 year.

➤ **Problem 17.** The activity of the hair of an egyptian mummy is 7 disintegration minute^{-1} of C^{14}. Find the age of mummy. Given $t_{0.5}$ of C^{14} is 5770 year and disintegration rate of fresh sample of C^{14} is 14 disintegration minute^{-1}.

➤ **Problem 18.** The decay constant for an α-decay of Th^{232} is 1.58×10^{-10} sec^{-1}. Find out the no. of α-decays that occur from 1 g sample in 365 days.

➤ **Problem 19.** 1 g atom of Ra^{226} is placed in an evacuated tube of volume 5 litre. Assuming that each $_{88}Ra^{226}$ nucleus is an α-emitter and all the contents are present in tube, calculate the total pressure of gases and partial pressure of He collected in tube at 27°C after the end of 800 year. $t_{1/2}$ of Ra is 1600 year. Neglect volume occupied by undecayed Ra.

➤ **Problem 20.** A sample of $^{14}CO_2$ was mixed with ordinary $^{12}CO_2$ for studying a biological tracer experiment. The 10 mL of this mixture at STP possess the rate of 10^4 disintegration per minute. How many milli-curie of radioactive carbon is needed to prepare 60 litre of such a mixture?

➤ **Problem 21.** A solution contains 1 milli-curie of L-phenyl alanine C^{14} (uniformly labelled) in 2.0 mL solution. The activity of labelled sample is given as 150 milli curie/milli-mole. Calculate:

(a) The concentration of sample in the solution in mole/litre.
(b) The activity of the solution in terms of counting per minute/mL at a counting efficiency of 80%.

► **Problem 22.** A sample of pitch blende is found to contain 50% uranium and 2.425% lead. Of this lead only 93% was Pb^{206} isotope. If the disintegration constant is 1.52×10^{-10} yr^{-1}, how old could be the pitch blende deposits?

► **Problem 23.** The half life of ^{32}P is 14.3 day. Calculate the specific activity of a phosphorus containing specimen having 1.0 part per million ^{32}P (Atomic weight of P = 31).

► **Problem 24.** A mixture of Pu^{239} and Pu^{240} has a specific activity of 6×10^9 dps per g sample. The half lives of the isotopes are 2.44×10^4 year and 6.58×10^3 years respectively. Calculate the composition of mixture.

► **Problem 25.** 54.5 mg of Na_3PO_4 contains P^{32} (15.6% of sample) and P^{31} atoms. Assuming only P^{32} atoms radioactive, calculate the rate of decay for the given sample of Na_3PO_4. The half life period for P^{32} = 14.3 days; mol. wt. of Na_3PO_4 = 161.2.

► **Problem 26.** The isotopic composition of rubidium is ^{85}Rb, 72% and ^{87}Rb, 28%. ^{87}Rb is weakly radioactive and decays by β-emission with a decay constant of 1.1×10^{-11} per year. A sample of the mineral pollucite was found to contain 450 mg Rb and 0.72 mg of ^{87}Sr. Estimate the age of pollucite?

► **Problem 27.** A sample contains two radioactive nuclei x and y with half-lives 2 hour and 1 hour respectively. The nucleus x-decays to y and y-decays into a stable nucleus z. At $t = 0$ the activities of the components in the same were equal. Find the ratio of the number of the active nuclei of y at $t = 4$ hours to the number at $t = 0$.

► **Problem 28.** Tritium, ${}_1T^1$ (an isotope of H) combine with fluorine to form a weak acid TF which ionises to give T^+. Tritium is radioactive and is a β-emitter. A freshly prepared dilute aqueous solution of TF has a pT (equivalent of pH) of 1.7 and freezes at – 0.372°C. If 600 mL of freshly prepared solution were allowed to stand for 24.8 years, calculate:
(i) Ionisation constant of TF.
(ii) Charge carried by β-particles emitted by tritium in Faraday.
Given : K_f for H_2O = 1.86, $t_{1/2}$ (T) = 12.4 yrs.

► **Problem 29.** A solution contains a mixture of isotopes of X^{A_1} ($t_{1/2}$ = 14 days) and X^{A_2} ($t_{1/2}$ = 25 days). Total activity is 1 curie at $t = 0$. The activity reduces by 50% in 20 days. Find:
(a) The initial activities of X^{A_1} and X^{A_2}.
(b) The ratio of their initial no. of nuclei.

► **Problem 30.** The mean lives of a radioactive substance are 1620 year and 405 year for α-emission and β-emission respectively. Find out the time during which three fourth of a sample will decay if it is decaying both by α-emission and β-emission simultaneously.

➤ Problem 31. For the following sequential reaction, $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, find out the concentration of C at time $t = 1$ day, given the $K_1 = 1.8 \times 10^{-5}\ s^{-1}$ and $K_2 = 1.1 \times 10^{-2}\ s^{-1}$ and initial molar concentration of A is 1.8.

➤ Problem 32. A radioactive isotope decays as ${}_{Z}A^{m} \longrightarrow {}_{Z-2}B^{m-4} \longrightarrow {}_{Z-1}C^{m-4}$. The half lives of A and B are 6 months and 10 months respectively. Assuming that initially only A was present, will it be possible to achieve radioactive equilibrium for B. If so what would be the ratios of A and B at equilibrium. What would happen if the half lives A and B were 10 months and 6 months respectively.

➤ Problem 33. A radioactive isotope decays as ${}_{Z}A^{n} \longrightarrow {}_{Z-2}B^{m-4} \longrightarrow {}_{Z-1}C^{m-4}$. The half lives of A and B are 6 months and 10 months respectively. Assuming that initially only A was present, will it be possible to achieve radioactive equilibrium for B. If so, what would be the ratio of nuclei of A and B at equilibrium. What would happen if the half lives of A and B were 10 month and 6 month.

➤ Problem 34. The half life of Pb^{212} is 10.6 hour. It undergoes decay to its daughter (unstable) element Bi^{212} of half life 60.5 minute. Calculate the time at which daughter element will have maximum activity?

➤ Problem 35. A very small amount of radioactive isotope of Pb^{213} was mixed with a non-radioactive lead salt containing 0.01 g of Pb (atomic mass 207). The whole lead was brought into solution and lead chromate was precipitated by addition of a soluble chromate. Evaporation of 10 cm^3 of the supernatent liquid gave a residue having a radioactivity $\frac{1}{24000}$ of that of the original quantity of Pb^{213}. Calculate the solubility of lead chromate in mol dm^{-3}.

➤ Problem 36. The nuclei of two radiotactive isotopes of same substance A^{236} and B^{234} are present in the ratio of 4 : 1 in an ore obtained from some other planet. Their half lives are 30 and 60 minutes respactively. Both isotopes are alpha emitters and activity of isotope A^{236} is 1 rutherford (10^6 dps). Calculate :

(a) after how much time their activities will become identical

(b) the time required to bring the ratio of their atoms to 1 : 1.

Answers

1. 1886.57 MeV ; **2.** 53.16×10^{18} g ;
3. 5.223×10^{-13} J, 3.260 MeV ; **4.** 26.14 MeV ;
5. 7.7149 MeV, N^{15} ; **6.** 90, 234, 91, 234, III gp. ;
7. 3.37 J ; **8.** 3.8451×10^4 kg ;
9. 48×10^{-42} m^3 ; **10.** 30 day ;
11. 66.96 mg ; **12.** 13327.8 year ;
13. 2.766×10^4 atoms ; **14.** 3353.16 year ;
15. (a) See solution, (b) 15/16 g Hg ; **16.** 43.54 atm ;
17. 5770 year ; **18.** 1.298×10^{19} α-atom ;
19. 2.887 atm, 1.443 atm ; **20.** 0.027 mCi ;
21. (a) 3.33×10^{-2} M, (b) 88.8×10^7 cpm/mL ;
22. 6.3×10^8 year ; **23.** 0.295 Ci per g ;
24. 38.95%, 61.05% ; **25.** 1.78×10^{13} dps ;
26. 5.18×10^8 year ; **27.** 0.25 ;
28. (i) $2.5 \times 10^{-}$[illegible], (ii) 0.054 Faraday ;
29. (a) 0.3669 Ci, 0.6331 Ci, (b) 0.3245 ;
30. 119.24 year ; **31.** 1.42 M ;
32. 0.6, 1.66 ; **33.** 0.6, No ;
34. 227.1 minute ; **35.** 2.0×10^{-7} mol dm^{-3} ;
36. (a) 180 min., (b) 120 min.

Problems for Self Assessment

1. Calculate the threshold wavelength for proton anti-proton production. The rest mass of a proton or anti-proton is 1.007825 amu. 1 amu = 931 MeV.
2. In a nuclear transition,

$$\underset{\text{(Excited state)}}{{}_{8}O^{19}} \longrightarrow \underset{\text{(Ground state)}}{{}_{8}O^{19}} + \Delta E$$

with what mass per mol the two nuclei differ? Given that $\Delta E = 1.06 \times 10^8$ kcal mol^{-1}.

3. Calculate the amount of ${}_{92}U^{235}$ which must go nuclear fission to produce the same amount of energy as produced by 1 ton of coal. The heat of combustion of coal is 8×10^3 cal/g. The fission of ${}_{92}U^{235}$ produces 200 MeV energy per fission. (use 1 cal = 4.2 J; 1 ton = 10^6 g; Av. no. = 6.023×10^{23} and 1.602×10^{-19} J = 1 eV)
4. A reactor is developing energy at the rate of 32×10^6 watts. How many atoms of U^{235} undergo fussion per second? Assume that on an average energy of 200 MeV is released per fusion.
5. Calculate the density of nucleus of ${}_{47}Ag^{107}$ and compare it with the density of metallic silver (10.5 g/cm^3). use $r_{\text{nucleus}} = 1.33\, A^{1/3} \times 10^{-13}$.
6. It is proposed to use the nuclear fusion reaction in a nuclear reactor of 200 MW rating. If the energy from the above reaction is used with 25% efficiency in the reactor, how many gram of deuterium fuel will be needed per day. (The masses of ${}_{1}^{2}H$ and ${}_{2}^{4}He$ are 2.0141 amu and 4.0026 amu respectively.

$${}_{1}^{2}H + {}_{1}^{2}H \longrightarrow {}_{2}^{4}He$$

7. Calculate the number of alpha-particles emitted per second by 1 g of pure thorium dioxide ($t_{1/2}$ $Th^{232} = 1.39 \times 10^{10}$ year). Assume 1 Th^{232} atom decays to give one alpha particle.
8. The absolute abundance ratio of N^{14}/N^{15} in atmospheric nitrogen was found to be 272. Calculate at. wt. of atmospheric nitrogen.
9. One microgram of Na^{24} is injected into the blood of a patient. How long will it take the radioactivity to fall to 10% of its initial value. ($t_{1/2}$ for Na^{24} is 14.8 hour).
10. Prior to the use of nuclear weapons, the specific activity of C^{14} in soluble ocean carbonates was found to be 16 dis/min/g carbon. The amount of carbon in these carbonates has been estimated as 4.5×10^{16} kg. How many MCi of C^{14} did the ocean carbonates contain (1 Ci = 3.7×10^{10} dps).
11. Benis and Collegnes at OaK Ridge national laboratory confirmed the identification of an element no. 104, a man made atom with half life of only 4.5 sec. Only 3000 atoms of element were created in a test. How many atoms were left in 4.5 sec, 9.0 sec and 13.5 sec?

12. A certain radioactive isotope ${}_{Z}X^{A}$ ($t_{1/2} = 10$ day) decays to give ${}_{Z-4}X^{A-8}$. If 1 g atom of ${}_{Z}X^{A}$ is kept in a sealed vessel, how much of He will accumulate in 20 day at STP?

13. At a given instant these are 25% undecayed radioactive nuclei in a sample. After 10 second, the number of undecayed nuclei reduces to 12.5% calculate:
    (a) Mean life of nuclei.
    (b) The time in which the number of undecayed nuclei will further reduce to 6.25% of the reduced number.

14. ${}_{92}U^{238}$ by successive radioactive decays changes to ${}_{82}Pb^{206}$. A sample of uranium ore was analysed and found to contain 1.0 g U^{238} and 0.1 g Pb^{206}. Assuming that Pb^{206} has accumulated due to decay of uranium, find out the age of ore. $t_{1/2}$ for $U^{238} = 4.5 \times 10^{9}$ year.

15. In an ore containing uranium the ratio of U^{238} to Pb^{206} nuclei in 3. Calculate the age of ore, assuming that all the lead present in the ore is the final stable product of U^{238}. $t_{1/2}$ for $U^{238} = 4.5 \times 10^{9}$ year.

16. In a sample of pitch blende, the atomic ratio of $Pb^{206} : U^{238}$ is 0.23 : 1. Calculate the age of mineral if half life of uranium is 4.5×10^{9} year. All lead originated from uranium.

17. A sample of radioactive substance shows an intensity of 2.3 milli-curie at a time t and an intensity of 1.62 milli-curie after 600 second. What is the half life period of radioactive material.

18. What is the closest distance of approach of an α-particle of energy 6 MeV to a gold nucleus ($Z = 79$).

19. An ancient wooden statue weighing 40 kg is found to have C^{14} activity of 40800 dpm. If 15.3 dpm per g is the activity of contemporary ${}^{14}C$, calculate the time elapsed since the wood was cut. The half life of C^{14} is 5600 years.

20. A drug is known to be ineffective after it has decomposed 30%. The original concentration of one sample was 500 units/mL. When analysed 20 months later, the concentration was found to be 420 units/mL. Assuming that decomposition is of I order, what will be the expiration time of the drug. What is the half life of drug.

21. The ratio of two nuclei of radioactive isotopes of A^{236} and A^{234} was found to be 4 : 1 in an ore obtained from a planet. Their half lives are 30 and 60 minutes respectively. Both isotopes are α-emitter and activity of A^{236} is 1 rutherford. Calculate :
    (a) the time in which their activity becomes identical.
    (b) the time required to bring the ratio of their atoms 1 : 1.

Answers

1. 6.62×10^{-6} Å ;
2. 5×10^{-3} g ;
3. 0.4145 g ;
4. 10^{18} atoms ;
5. 1.68×10^{4} g/cm^{3} , 1.6×10^{13} times of metallic Ag ;
6. 121.28 g/day ;
7. 3.6024×10^{3} s^{-1} ;
8. 14.003 ;
9. 2.05 days ;
10. 324 MCi ;
11. 1500, 750, 375 atom ;
12. 33.6 litre ;
13. (a) 14.43 s, (b) 40 s ;
14. 7.1×10^{8} year ;
15. 1.8684×10^{9} year ;
16. 1.35×10^{9} year ;
17. 1186 sec ;
18. 37.9 Fermi ;
19. 3.27×10^{3} year ;
20. 40.91 min., $t_{1/2} = 79.48$ min.
21. (a) 180 minute, (b) 120 minute.

5

Oxidation-reduction

Chapter at a Glance

Oxidation-reducation

1. Oxidation is process which liberates electrons, *i.e.*, de-electronation.

$$M \longrightarrow M^{n+} + ne$$

$$A^{n-} \longrightarrow A + ne$$

$$n_2 > n_1 \qquad M^{n_1+} \longrightarrow M^{n_2-} + (n_2 - n_1)e$$

$$n_1 > n_2 \qquad A^{n_1-} \longrightarrow A^{n_2-} + (n_1 - n_2)e$$

2. Reduction is a process which gains electrons, *i.e.*, electronation.

$$M^{n+} + ne \longrightarrow M$$

$$A + ne \longrightarrow A^{n-}$$

$$M^{n_2+} + (n_2 - n_1)e \longrightarrow M^{n_1+}$$

$$A^{n_2-} + (n_1 - n_2)e \longrightarrow A^{n_1-}$$

3. Oxidants are substances which:
   (a) oxidize other.
   (b) are reduced themselves.
   (c) show electronation.
   (d) show a decrease in oxidation no. during a redox change.
   (e) has higher oxidation no. in a conjugate pair of redox.
4. Reductants are substances which:
   (a) reduce other.
   (b) are oxidized themselves.
   (c) show de-electronation.
   (d) show an increase in oxidation no. during a redox change.
   (e) has lower oxidation no. in a conjugate pair of redox.
5. A redox change is one in which a reductant is oxidized to liberate electrons, which are then used up by an oxidant to get itself reduced.

$$\begin{array}{ll} M_1 \longrightarrow M_1^{n+} + ne & \text{Oxidation} \\ \underline{M_2^{n+} + ne \longrightarrow M_2} & \text{Reduction} \\ M_1 + M_2^{n+} \longrightarrow M_1^{n+} + M_2 & \text{Redox reaction} \end{array}$$

6. A redox change occurs simultaneously.

The Basic Problems with Solutions

➤ Problem 1. Determine the ox. no. of underlined atom in each of the following :

(a) $K\underline{C}rO_3Cl$,	(b) $K_2\underline{Fe}O_4$,	(c) $Ba(H_2\underline{P}O_2)_2$
(d) $Rb_4Na[H\underline{V}_{10}O_{28}]$;	(e) $Ba_2\underline{Xe}O_6$	(f) $Na_2\underline{S}_2$
(g) $K_2\underline{Mn}O_4$	(h) $K_2\underline{Cr}_2O_7$	(i) $\underline{Mn}O_4^-$
(j) $\underline{S}O_4^{2-}$	(k) $\underline{P}O_4^{3-}$	(l) $\underline{C}O_3^{2-}$
(m) $\underline{Cu}(NH_3)_4^{2+}$	(n) $\underline{Ni}(CO)_4$	(o) $\underline{C}S_2$
(p) $(NH_4)_6\underline{Mo}_7O_{24}$	(q) $[\underline{Co}F_4]^-$	(r) $\underline{Os}O_4$
(s) $Na_4\underline{Xe}O_6$	(t) $K\underline{Cr}O_3Cl$	(u) $\underline{F}_2H_2$

➤ Problem 2. Find the oxidation number of carbon in the following compounds :
CH_3OH, CH_2O, $HCOOH$, C_2H_2 .

➤ Problem 3. Point out the oxidation number of C in the following :
CH_4, C_3H_8, C_2H_6, C_4H_{10}, CO, CO_2 and HCO_3^-, CO_3^{2-}

➤ Problem 4. Arrange the following in order of :
(a) Increasing oxidation no. of Mn: $MnCl_2$, MnO_2, $Mn(OH)_3$, $KMnO_4$
(b) Decreasing oxidation no. *X*: HXO_4, HXO_3, HXO_2, HXO
(c) Increasing oxidation no. I: I_2, HI, HIO_4, ICl, IF_3, IF_5
(d) Increasing oxidation no. of N: N_2, NH_3, N_3H, NH_2NH_2, NH_2OH, KNO_2, KNO_3, N_2O

➤ Problem 5. Select the nature or type of redox change in the following reactions :

(a) $2Cu^+ \longrightarrow Cu^{2+} + Cu^0$

(b) $Cl_2 \longrightarrow ClO^- + Cl^-$

(c) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(d) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

(e) $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$

(f) $5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

● ➤ Problem 6. Identify the oxidised and reduced species in the following reactions :
(a) $CH_{4(g)} + 4Cl_{2(g)} \longrightarrow CCl_{4(g)} + 4HCl_{(g)}$
(b) $MnO_{2(s)} + C_2H_2O_{4(aq.)} \xrightarrow{2H^+} Mn^{2+}_{(aq.)} + 2CO_{2(g)} + 2H_2O_{(l)}$
(c) $I_{2(aq.)} + 2S_2O_{3\,(aq.)}^{2-} \longrightarrow 2I^-_{(aq.)} + S_4O_6^{2-}$
(d) $Cl_{2(g)} + 2Br^-_{(aq.)} \longrightarrow 2Cl^-_{(aq.)} + Br_{2(aq.)}$

➤ Problem 7. Identify the substance acting as oxidant or reductant if any in the following :

(i) $AlCl_3 + 3K \longrightarrow Al + 3KCl$

(ii) $SO_2 + 2H_2S \longrightarrow 3S + H_2O$

(iii) $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$

(iv) $3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$

➤ Problem 8. Write the half reactions for the following redox reactions :

(a) $2Fe^{3+}_{(aq.)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq.)} + I_{2(aq.)}$

(b) $Zn_{(s)} + 2H^+_{(aq.)} \longrightarrow Zn^{2+}_{(aq.)} + H_{2(g)}$

(c) $Al_{(s)} + 3Ag^+_{(aq.)} \longrightarrow Al^{3+}_{(aq.)} + 3Ag_{(s)}$

➤ Problem 9. How many mole of electrons are involved in balancing the following equations :

(a) $H_2S + NO_3^- \longrightarrow S + NO$

(b) $Mn(OH)_2 + H_2O_2 \longrightarrow MnO_2 + 2H_2O$

(c) $Cr_2O_7^{2-} + Fe^{2+} + C_2O_4^{2-} \longrightarrow Cr^{3+} + Fe^{3+} + CO_2$ (acid medium)

(d) $Br_2 + OH^- \longrightarrow BrO_3^- + Br^-$

➤ Problem 10. How many mole of $FeSO_4$, $H_2C_2O_4$ and FeC_2O_4 are oxidised separately by one mole of $KMnO_4$ in acid medium.

Answers

1. (a) + 6, (b) + 6, (c) + 1, (d) + 5, (e) + 8, (f) – 1, (g) + 6, (h) + 6, (i) + 7, (j) + 6, (k) +5, (l) + 4, (m) +2, (n) 0, (o) +4, (p) +6, (q) +3, (r) +8, (s) +8, (t) +6, (u) –1

2. CH_3OH : –2, CH_2O : 0, HCOOH : +2, C_2H_2 : –1 ;

3. CH_4 : –4; $C_3H_8 : -\frac{8}{3}$; C_2H_6 : – 3; C_4H_{10} : – (10/4); CO : + 2 ; CO_2 : + 4 ; HCO_3^- : + 4.;

4. See solution;

5. See solution;

6.

	Reduced	Oxidised
(a)	Cl_2	CH_4
(b)	MnO_2	$C_2H_2O_{4(aq)}$
(c)	I_2	$S_2O_3^{2-}$
(d)	Cl_2	Br^-

7. See solution;

8. See solution.

9. (a) 6*N*, (b) 2*N*, (c) 3*N*, (d) 10*N* ;

10. 5, $\frac{5}{2}$, $\frac{5}{3}$

Solution

Solution 1. (a) Let ox. no. of Cr be '*a*', then

$$1 + a + 3 \times (-2) + 1 \times (-1) = 0$$
$$\therefore \quad a = +6$$

(b)
$$2 \times 1 + a + 4 \times (-2) = 0$$
$$\therefore \quad a = +6$$

(c)
$$2 + [2 \times 1 + a + 2 \times (-2)] = 0$$
$$\therefore \quad a = +1$$

(d)
$$4 \times 1 + 1 + [1 + 10 \times a + 28 \times (-2)] = 0$$
$$\therefore \quad a = +5$$

(e)
$$2 \times 2 + a + 6 \times (-2) = 0$$
$$\therefore \quad a = +8$$

(f)
$$1 \times 2 + 2 \times a = 0$$
$$\therefore \quad a = -1$$

(g)
$$2 \times 1 + a + 4 \times (-2) = 0$$
$$\therefore \quad a = +6$$

(h)
$$2 \times 1 + 2 \times a + 7 \times (-2) = 0$$
$$\therefore \quad a = +6$$

(i)
$$a + 4 \times (-2) = -1$$
$$\therefore \quad a = +7$$

(j)
$$a + 4 \times (-2) = -2$$
$$\therefore \quad a = +6$$

(k)
$$a + 4 \times (-2) = -3$$
$$\therefore \quad a = +5$$

(l)
$$a + 3 \times (-2) = -2$$
$$\therefore \quad a = +4$$

(m)
$$a + 4 \times 0 = +2$$
$$a = +2$$

(n)
$$a + 4 \times 0 = 0$$
$$a = 0$$

(o)
$$a + 2 \times (-2) = 0$$
$$\therefore \quad a = +4$$

(p)
$$1 \times 6 + 7 \times a + 24 \times (-2) = 0$$
$$\therefore \quad a = +6$$

(q)
$$a + 4 \times (-1) = -1$$
$$\therefore \quad a = +3$$

(r)
$$a + 4 \times (-2) = 0$$
$$\therefore \quad a = +8$$

(s) $4 \times 1 + a + 6 \times (-2) = 0$

$\therefore \quad a = +8$

(t) $1 + a + 3 \times (-2) + 1 \times (-1) = 0$

$\therefore \quad a = +6$

(u) $2 \times a + 2 \times (1) = 0$

$\therefore \quad a = -1$

Solution 2. Let the oxidation number of carbon be a

CH_3OH : $a + 3 \times 1 + 1 \times (-2) + 1 \times 1 = 0$

$\therefore \quad a = -2$

CH_2O : $a + 2 \times 1 + 1 \times (-2) = 0$

$\therefore \quad a = 0$

$HCOOH$: $1 + a + 2 \times (-2) + 1 = 0$

$\therefore \quad a = +2$

C_2H_2 : $2 \times a + 2 \times 1 = 0$

$\therefore \quad a = -1$

Solution 3. $CH_4 : -4$; $\quad C_3H_8 : -\frac{8}{3}$ $\quad C_2H_6 : -3$; $\quad C_4H_{10} : -\frac{10}{4}$;

$CO : +2$; $\quad CO_2 : +4$; $\quad HCO_3^- : +4 \quad CO_3^{2-} : +4$

Solution 4.

(a)	$MnCl_2$	<	$Mn(OH)_3$	<	MnO_2	<	$KMnO_4$
ox. no. of Mn	+ 2		+ 3		+ 4		+ 7

(b)	HXO_4	>	HXO_3	>	HXO_2	>	HXO
ox. no. of X	+ 7		+ 5		+ 3		+ 1

(c)	HI	<	I_2	<	ICl	<	IF_3	<	IF_5	<	HIO_4
ox. no. of I	− 1		0		+ 1		+3		+5		+7

(d) $NH_3 < N_2H_4 < NH_2OH < N_3H < N_2 < N_2O < KNO_2 < KNO_3$

ox. no. of N −3 $\quad$ −2 $\quad$ −1 $\quad$ −1/3 $\quad$ 0 $\quad$ +1 $\quad$ +3 $\quad$ +5

Solution 5. (i) (a) and (b) represents auto-redox or disproportionation in which same substance is oxidised and reduced as well.

(ii) (c) and (d) represents intramolecular redox change in which one element of a compound is oxidised and the other element is reduced.

(iii) (e) and (f) represents intermolecular redox in which one of the two reactant is oxidised and other is reduced.

Solution 6.

	Reduced	**Oxidised**
(a)	Cl_2	CH_4
(b)	MnO_2	$C_2H_2O_{4(aq)}$
(c)	I_2	$S_2O_3^{2-}$
(d)	Cl_2	Br^-

Solution 7. In a conjugate pair, oxidant has higher ox. no.

(i) **For $AlCl_3$:** $Al^{3+} + 3e \longrightarrow Al^0$; **For K :** $K^0 \longrightarrow K^{1+} + e$

$\therefore$ **oxidant $AlCl_3$** and **reductant K.**

(ii) **For SO_2 :** $S^{4+} + 4e \longrightarrow S^0$; **For H_2S:** $S^{2-} \longrightarrow S^0 + 2e$

$\therefore$ **oxidant SO_2** and **reductant H_2S.**

(iii) No change in ox. no. of either of the conjugate pair.

$\therefore$ **None is oxidant or reductant.**

(iv) **For I_2 .** $I_2{}^0 \longrightarrow 2I^{5+} + 10e$ and $I_2{}^0 + 2e \longrightarrow 2I^{1-}$

$\therefore$ **I_2 acts as oxidant and reductant both.**

Solution 8. (a) $Fe^{3+} + e \longrightarrow Fe^{2+}$;

$I^- \longrightarrow \frac{1}{2}I_2 + e$

(b) $Zn \longrightarrow Zn^{2+} + 2e$;

$H^+ + e \longrightarrow \frac{1}{2}H_2$

(c) $Al \longrightarrow Al^{3+} + 3e$

$Ag^+ + e \longrightarrow Ag$

Solution 9.

$$\text{(a)}\ \left.\begin{array}{r}S^{2-} \longrightarrow S^0 + 2e\\ N^{5+} + 3e \longrightarrow N^{2+}\end{array}\right]\text{6N electron}$$

$$\text{(b)}\ \left.\begin{array}{r}Mn^{2+} \longrightarrow Mn^{4+} + 2e\\ O_2{}^{1-} + 2e \longrightarrow O_2{}^{2-}\end{array}\right]\text{2N electron}$$

$$\text{(c)}\ \left.\begin{array}{r}Cr_2{}^{6-} + 3e \longrightarrow 2Cr^{3+}\\ Fe^{2+} + C_2{}^{3+} \longrightarrow Fe^{3+} + 2C^{4+} + 3e\end{array}\right]\text{3N electron}$$

$$\text{(d)}\ \left.\begin{array}{r}Br_2{}^0 + 2e \longrightarrow 2Br^-\\ Br_2{}^0 \longrightarrow 2Br^{5+} + 10e\end{array}\right]\text{10N electron}$$

Solution 10. **$FeSO_4$:**

$$\begin{array}{r}Fe^{2+} \longrightarrow Fe^{3+} + e\\ Mn^{7+} + 5e \longrightarrow Mn^{2+}\\ \hline\end{array}$$

Thus $5Fe^{2+} + Mn^{7+} \longrightarrow Fe^{3+} + Mn^{2+}$

or 5 mole of $FeSO_4$ are oxidised by 1 mole $KMnO_4$

$H_2C_2O_4$:

$$\begin{array}{r}C_2{}^{3+} \longrightarrow 2C^{4+} + 2e\\ Mn^{7+} + 5e \longrightarrow Mn^{2+}\\ \hline 5C_2{}^{3+} + 2Mn^{7+} \longrightarrow 10C^{4+} + 2Mn^{2+}\end{array}$$

or 5/2 mole of $H_2C_2O_4$ are oxidised by 1 mole $KMnO_4$

FeC_2O_4 :

$$\begin{array}{r}Fe^{2+} + C_2{}^{3+} \longrightarrow Fe^{3+} + 2C^{4+} + 3e\\ Mn^{7+} + 5e \longrightarrow Mn^{2+}\\ \hline 5FeC_2O_4 + 3Mn^{5+} \longrightarrow 5Fe^{3+} + 10C^{4+} + 3Mn^{2+}\end{array}$$

or 5/3 mole of FeC_2O_4 are oxidised by 1 mole $KMnO_4$

Selected Problems with solutions

➤ Problem 1. Determine the oxidation no. of following elements given in bold letters:

(a) $K\mathbf{Mn}O_4$; (b) $H_2\mathbf{S}O_5$; (c) $H_2\mathbf{S}_2O_8$;
(d) $\mathbf{N}H_4\mathbf{N}O_3$; (e) $K_4\mathbf{Fe}(CN)_6$; (f) $\mathbf{Os}O_4$;
(g) HCN ; (h) HNC ; (i) $H\mathbf{N}O_3$;
(j) $K\mathbf{O}_2$; (k) $\mathbf{Fe}_3O_4$; (l) $K\mathbf{I}_3$;
(m) $\mathbf{N}_3H$; (n) $\mathbf{Fe}(CO)_5$; (o) $\mathbf{Fe}_{0.94}O$;
(p) $\mathbf{N}H_2{\cdot}\mathbf{N}H_2$; (q) $\mathbf{Fe}SO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$;
(r) $\mathbf{N}OCl$; (s) $NOClO_4$; (t) $Na_2[\mathbf{Fe}(CN)_5NO]$;
(u) $[\mathbf{Fe}(NO)(H_2O)_5]SO_4$; (v) $Na_2\mathbf{S}_4O_6$;
(w) Dimethyl sulphoxide or $(CH_3)_2SO$; (x) $Na_2\mathbf{S}_2O_3$;
(y) $\mathbf{Cr}O_5$ or $\mathbf{Cr}O(O_2)_2$; (z) $CaO\mathbf{Cl}_2$.

➤ Problem 2. Determine the oxidation number of following elements given in bold letters.

(i) $\mathbf{Cu}H$; (ii) $Na_2\mathbf{S}_3O_6$; (iii) $\mathbf{N}_2O$;
(iv) $Ba_2\mathbf{Xe}O_6$; (v) $\mathbf{C}_3O_2$; (vi) $\mathbf{V}(BrO_2)_2$;
(vii) $Ca(\mathbf{Cl}O_2)_2$; (viii) $Cs_4Na(H\mathbf{V}_{10}O_{28})$;
(ix) $Li\mathbf{Al}H_4$; (x) $K[\mathbf{Co}(C_2O_4)_2{\cdot}(NH_3)_2]$;
(xi) $[\mathbf{Ni}(CN)_4]^{2-}$; (xii) $Na_2\mathbf{S}_2$; (xiii) $\mathbf{Fe}(CO)_5$;
(xiv) $[\mathbf{OCN}]^-$; (xv) $\mathbf{S}_2O_4^{2-}$; (xvi) $\mathbf{S}_2O_8^{2-}$

➤ Problem 3. Predict the highest and lowest possible oxidation state of each of the following elements:

(a) Ta ; (b) Te ; (c) Tc ; (d) Ti ; (e) Tl ; (f) N ; (g) P ; (h) F ; (i) Cl ; (j) Zn ; (k) C.

➤ Problem 4. Select the type of redox reaction from the following on the basis of type of redox changes (a) intermolecular redox ; (b) intramolecular redox ; (c) auto redox. If none, write none.

(i) $C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$

(ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

(iii) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

(iv) $NO_3^- + H_2S + H_2O + H^+ \longrightarrow NH_4^+ + HSO_4^-$

(v) $Fe + N_2H_4 \longrightarrow NH_3 + Fe(OH)_2$

(vi) $2KOH + Br_2 \longrightarrow KBr + KBrO$

(vii) $2Cu^+ \longrightarrow Cu + Cu^{2+}$

(viii) $Ag(NH_3)_2^+ \xrightarrow{2H^+} Ag^+ + 2NH_4^+$

(ix) $5KI + KIO_3 + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$

➤ Problem 5. Select the oxidant/reductant atoms in the following change. Also report the number of electrons involved in redox change.

$$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$$

➤ Problem 6. In the reaction $Al + Fe_3O_4 \longrightarrow Al_2O_3 + Fe$

(a) Which element is oxidized and which is reduced?

(b) Total no. of electrons transferred during the change.

➤ Problem 7. Identify the substance acting as oxidant or reductant if any in the following:

(i) $AlCl_3 + 3K \longrightarrow Al + 3KCl$

(ii) $SO_2 + 2H_2S \longrightarrow 3S + H_2O$

(iii) $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$

(iv) $3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$

➤ Problem 8. Find out the value of *n* in

$$MnO_4^- + 8H^+ + ne \longrightarrow Mn^{2+} + 4H_2O$$

➤ Problem 9. Both VO_2^+ and VO^{2+} are known as vanadyl ion.

(a) Determine the oxidation number of vanadium in each.

(b) Which one of them is oxovanadium(iv) ion and which are is dioxovanadium(v) ion.

➤ Problem 10. One mole of N_2H_4 loses 10 mole electrons to form a new compound *Y*. Assuming that all the N_2 appears in new compound, what is oxidation state of N in *Y*? There is no change in oxidation state of H.

➤ Problem 11. HNO_3 acts only as oxidant whereas, HNO_2 acts as reductant and oxidant both.

➤ Problem 12. Balance the following equations:

(a) $BaCrO_4 + KI + HCl \longrightarrow BaCl_2 + I_2 + KCl + CrCl_3 + H_2O$

(b) $SO_2 + Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(c) $C_2H_5OH + I_2 + OH^- \longrightarrow CHI_3 + HCO_2^- + H_2O + I^-$ (Basic)

(d) $As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

(e) $\ldots\ldots + HC_2O_4^- \longrightarrow CO_3^{2-} + Cl^-$ (Acid)

(f) $HgS + HCl + HNO_3 \longrightarrow H_2HgCl_4 + NO + S + H_2O$

(g) $Mn_2O_7 \longrightarrow MnO_2 + O_2$

➤ Problem 13. $KMnO_4$ oxidises NO_2^- to NO_3^- in basic medium. How many moles of NO_2^- are oxidised by 1 mole of $KMnO_4$.

Answers

1. (a) +7, (b) +6, (c) +6, (d) −3, +5, (e) +2, (f) +8, (g) +2, −3, (h) +2
(i) +5, (j) $-\frac{1}{2}$, (k) $+\frac{8}{3}$, (l) $-\frac{1}{3}$, (m) $-\frac{1}{3}$, (n) 0, (o) $\frac{200}{94}$, (p) −2,
(q) +2, (r) +3, (s) +7, (t) +2, (u) +1, (v) $+\frac{5}{2}$, (w) 0, (x) +2,
(y) +6, (z) −1, +1 ;

2. (i) −1, (ii) +10/3, (iii) +1, (iv) +8, (v) + 4/3, (vi) +2, (vii) +3, (viii) +5,
(ix) +3, (x) +3, (xi) +2, (xii) −1, (xiii) 0, (xiv) −2, +4, −3 (xv) +3, (xvi) +6

3. (a) +5, 0, (b) +6, −2, (c) +7, 0, (d) +4, 0, (e) +3, 0,
(f) +5, −3, (g) +5, −3, (h) 0, −1, (i) +7, −1, (j) +2, 0, (k) +4, −4 ;

4. (a) (iv), (v), (ix), (b) (iii), (c) (i), (vi), (vii) ;

5. 84 ;

6. Al is oxidized and $Fe^{8/3+}$ is reduced , (b) 24 ;

7. (i) Oxidant—$AlCl_3$, Reductant K
(ii) Oxidant—SO_2, Reductant H_2S
(iii) None
(iv) Oxidant—I_2, Reductant I_2 ;

8. 5 ;

9. (a) +5, +4, (b) VO^{2+} is oxovanadium(iv) ion ; VO_2^+ is dioxovanadium (v) ion ;

10. +3 ; **11.** See solution ;

12. (a) $2BaCrO_4 + 6HI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6KCl + 2BaCl_2 + 8H_2$
(b) $3SO_2 + 2Na_2CrO_4 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + Cr_2(SO_4)_3 + 2H_2O$
(c) $C_2H_5OH + 4I_2 + 6OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + 5H_2O$
(d) $4H_2O + 3As_2S_3 + 28HNO_3 \longrightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$
(e) $Cl_2 + HC_2O_4^- + 2H_2O \longrightarrow 2Cl^- + 2CO_3^{2-} + 5H^+$
(f) $3HgS + 2HNO_3 + 12HCl \longrightarrow 3H_2HgCl_4 + 3S + 2NO + 4H_2O$
(g) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

13. 1.5 mole NO_2.

Problems for Self Assessment

1. Find out the oxidation number of underlined atoms:

(a) $\underline{Xe}O_6^{4-}$; (b) $K\underline{O}_2$; (c) $\underline{S}O_2F_2$; (d) $CuFe\underline{S}_2$; (e) $Fe\underline{S}_2$

(f) $\underline{Na}FeO_2$; (g) $\underline{Fe}_3Br_8$; (h) $Rb_3Cs_2[H\underline{V}_{10}O_{28}]$; (i) $H\underline{V}_6O_{11}^{3-}$;

(j) $Y\underline{Ba}_2Cu_3O_7$.

2. Identify the type of redox changes in the examples given below:

(a) $$2CH_3CHO \xrightarrow{Al(OEt)_3} CH_3COOC_2H_5$$

(b) $$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

(c) $$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

(d) $$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

(e) $$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(f) $$2MnO_2 + 4KOH \longrightarrow 2K_2MnO_4 + 2H_2O$$

3. FeC_2O_4 is oxidised by $KMnO_4$ in acid medium. What is the ratio of mole of $KMnO_4$ used per mole of FeC_2O_4.

4. Arrange the following ions in increasing order of oxidation number of sulphur atom. SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, HS^-, $S_4O_6^{2-}$, S_8, HSO_4^-.

5. Calculate the number of moles of $KMnO_4$ that will be needed to react with 1 mole of SO_3^{2-} in acidic solution.

6. Explain, why?

(a) H_2S acts as reductant whereas, SO_2 acts as reductant and oxidant both.

(b) H_2O_2 acts as reductant and oxidant both.

7. What may be the values of x in the reaction:

$$2ICl_x + 2xK \longrightarrow 2xKCl + I_2?$$

8. Calculate the number of electrons lost or gained during the changes:

(a) $$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

(b) $$AlCl_3 + 3K \longrightarrow Al + 3KCl$$

9. Six mole of Cl_2 undergo a loss and gain of 10 mole of electrons to form two oxidation states of Cl. Write down the two half reactions and find out the oxidation number of each Cl atom involved.

10. Complete and balance the following equations:

(a) $$KMnO_4 + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + MnSO_4 + H_2O + \ldots$$

(b) $$Cu^{2+} + I^- \longrightarrow Cu^+ + I_2$$

11. Balance the following in basic medium:

(i) $CrI_3 + H_2O_2 + OH^- \longrightarrow CrO_4^{2-} + IO_4^- + H_2O$

(ii) $KOH + K_4Fe(CN)_6 + Ce(NO_3)_4 \longrightarrow Fe(OH)_3 + Ce(OH)_3 + K_2CO_3 + KNO_3 + H_2O$

12. Balance the following equations using desired medium:

(a) $Cr_2O_7^{2-} + C_2H_4O + H^+ \longrightarrow C_2H_4O_2 + Cr^{3+}$

(b) $SbCl_3 + KIO_3 + HCl \longrightarrow SbCl_5 + ICl + H_2O + KCl$

(c) $FeC_2O_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CO_2 + MnSO_4 + K_2SO_4 + H_2O$

(d) $AsH_3 + KClO_3 \longrightarrow H_3AsO_4 + KCl$

(e) $FeCr_2O_4 + K_2CO_3 + KClO_3 \longrightarrow Fe_2O_3 + K_2CrO_4 + KCl + CO_2$

(f) $Pb(N_3)_2 + Co(MnO_4)_3 \longrightarrow CoO + MnO_2 + Pb_3O_4 + NO$

Answers

1. (a) +8, (b) $-\frac{1}{2}$, (c) +6, (d) –2, (e) –1, (f) +3, (g) +8/3 (h) +5, (i) +3, (j) +2, (Ba shows only +2 state in combined form) ;

2. (i) Intermolecular redox: (f), (ii) Disproportionation: (a), (b), (c), (iii) Intramolecular redox: (d), (e)

3. $KMnO_4 : FeC_2O_4 :: 5 : 3$ or 1 mole $FeC_2O_4 = 0.6$ mole $KMnO_4$;

4. $HS^- < S_8 < S_2O_3^{2-} < S_4O_6^{2-} < SO_3^{2-} < HSO_4^- = S_2O_8^{2-}$;

5. $\frac{2}{5}$ mole $KMnO_4$;

6. Follow solved problem 11; **7.** 1 or 3 or 5 ;

8. (a) 8 electrons, (b) 3 electrons ; **9.** +5, –1, $6Cl_2 \longrightarrow 2Cl^{5+} + 10Cl^-$;

10. (a) $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(b) $2Cu^{2+} + 2I^- \longrightarrow 2Cu^+ + I_2$

11. (i) $2CrI_3 + 27H_2O_2 + 10OH^- \longrightarrow 2CrO_4^{2-} + 6IO_4^- + 32H_2O$

(ii) $258KOH + K_4Fe(CN)_6 + 61Ce(NO_3)_4 \longrightarrow 61Ce(OH)_3 + Fe(OH)_3 + 36H_2O + 6K_2CO_3 + 250KNO_3$

12. (a) $Cr_2O_7^{2-} + 3C_2H_4O + 8H^+ \longrightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$

(b) $3SbCl_3 + KIO_3 + 6HCl \longrightarrow 2SbCl_5 + ICl + 3H_2O + KCl$

(c) $10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 20CO_2 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$

(d) $3AsH_3 + 4KClO_3 \longrightarrow 3H_3AsO_4 + 4KCl$

(e) $6FeCr_2O_4 + 12K_2CO_3 + 7KClO_3 \longrightarrow 3Fe_2O_3 + 12K_2CrO_4 + 7KCl + 12CO_2$

(f) $30Pb(N_3)_2 + 44Co(MnO_4)_3 \longrightarrow 132MnO_2 + 44CoO + 180NO + 10Pb_3O_4$

6

Redox Titrations

Chapter at a Glance

1. **Normality** $= \dfrac{\text{Equivalent of solute}}{\text{Volume of solution in litre}}$
2. **Milliequivalent** $= N \times V_{\text{in mL}} = \dfrac{\text{wt.} \times 1000}{\text{E. wt.}}$
3. **Equivalent** $= N \times V_{\text{in L}} = \dfrac{\text{wt.}}{\text{E. wt.}}$
4. **Molarity** $= \dfrac{\text{Moles of solute}}{\text{Volume of solution in litre}}$
5. **Milli-moles** $= M \times V_{\text{in mL}} = \dfrac{\text{wt.}}{\text{M. wt.}} \times 1000$
6. **Moles** $= M \times V_{\text{in L}} = \dfrac{\text{wt.}}{\text{M. wt.}}$
7. **Molarity × Valence factor** = Normality
8. **Valence factor** = No. of electrons lost or gained by one molecule of reductant or oxidant
9. **Equivalent wt. of reductant or oxidant**

$$= \frac{\text{M. wt. of reductant or oxidant}}{\text{No. of electrons lost or gained by one molecule of reductant or oxidant}}$$

Note: Never use any other formula for eq. wt. if change is redox one.

The Basic Problems with Solution

➤ Problem 1. Evaluate equivalent weight of reductant or oxidant given on left hand side of each reaction :

(a) $As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e$

(b) $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

(c) $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

(d) $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e$

(e) $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e$

(f) $2CuSO_4 + 2e \longrightarrow Cu_2^{1+} + SO_4^{2-}$

➤ Problem 2. 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 0.060 *M* solution of NaBr. What volume of a 0.050 *M* solution of Cl_2 is needed to react completely with the Br?

➤ Problem 3. What mass of $Na_2S_2O_3.5H_2O$ is needed to make 500 cm^3 of 0.200 *N* solution for the reaction :

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

➤ Problem 4. How many equivalents are there per mole of H_2S in its oxidation to SO_2?

➤ Problem 5. 12.53 mL of 0.0509 *M* SeO_2 reacted with 25.52 mL 0.1 *M* $CrSO_4$ solution. In the reaction Cr^{2+} was oxidized to Cr^{3+}. To what oxidation state selenium was converted in the reaction? Write the redox change for SeO_2.

➤ Problem 6. In a reaction, $Cr_2O_7^{2-}$ is reduced to Cr^{3+}. What is concentration of 0.1 *M* $K_2Cr_2O_7$ in equivalent per litre?

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

➤ Problem 7. What is molarity and normality of a MnO_4^- solution if 32.00 mL of the solution is required to titrate 40.00 mL of 0.400 *N* Fe^{2+}?

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

➤ Problem 8. Mn^{2+}(aq) can be determined by titration with MnO_4^-(aq)

$$3Mn^{2+} + 2MnO_4^- \longrightarrow 6MnO_2 + 2H_2O$$

A 25.00 mL sample of Mn^{2+} (aq) requires 34.77 mL of 0.05876 *M* $KMnO_4$ (aq) for its titration. What is the molarity of the Mn^{2+}(aq)?

➤ Problem 9. A 1.100 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 0.10 *M* $Na_2S_2O_3$ solution for titration. What is % copper by mass in the ore?

➤ **Problem 10.** What mass of N_2H_4 can be oxidised to N_2 by 24.0 g K_2CrO_4, which is reduced to $Cr(OH)_4^-$.

➤ **Problem 11.** It requires 40.0 mL of 0.50 *M* Ce^{4+} to titrate 10.0 mL of 1.0 *M* Sn^{2+} to Sn^{4+}. What is the oxidation state of cerium in the reduced product.

➤ **Problem 12.** Calculate the mass of oxalic acid ($H_2C_2O_4$) which can be oxidised to CO_2 by 100.0 mL of MnO_4^- solution, 10 mL of which is capable of oxidising 50.0 mL of 1.0 *N* I^- to I_2.

➤ **Problem 13.** A $KMnO_4$ solution can be standarised by titration against As_2O_3 (s). A 0.1156 g sample of As_2O_3 requires 27.08 mL of the $KMnO_4$ (aq) for its titration. What is the molarity of the $KMnO_4$ (aq) [As = 75].

$$5As_2O_3 + 4MnO_4^- + 9H_2O + 12H^+ \longrightarrow 10H_2AsO_4 + 4Mn^{2+}$$

➤ **Problem 14.** A particular acid-rain water has SO_3^{2-}. If a 25.00 mL sample of this water requires 34.08 mL of 0.01964 *M* $KMnO_4$ for its titration, what is the molarity of SO_3^{2-} in acid-rain?

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$$

➤ **Problem 15.** A solution containing 1.984 g of crystalline $Na_2S_2O_3.xH_2O$ in water required 40 mL of *N*/5 iodine solution for complete reaction. Calculate the value of *x*.

➤ **Problem 16.** If 10.00 g V_2O_5 is dissolved in acid and reduced to V^{2+} by treatment with Zn metal, how many mole I_2 could be reduced by the resulting V^{2+} solution as it is oxidised to V^{4+}. At. weight of V = 51.

➤ **Problem 17.** A 0.56 g sample of limestone is dissolved in acid and the calcium is precipitated as calcium oxalate. The precipitate is filtered, washed with water and dissolved in dil. H_2SO_4. The solution required 40 mL of 0.25*N* $KMnO_4$ solution for titration. Calculate percentage of CaO in limestone sample.

➤ **Problem 18.** How many mL of aqueous solution of $KMnO_4$ containing 158 g/L must be used to complete the conversion of 75.0 g of KI to iodine by the reaction :

$$KMnO_4 + KI + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + I_2 + 6H_2O$$

➤ **Problem 19.** What is the maximum weight of Cl_2 obtained by the action of 1 g HCl on 1 g MnO_2.

➤ **Problem 20.** 25 mL of 0.017 H_2SO_3 in strongly acidic medium required 16.9 mL of 0.01 *M* $KMnO_4$ and in neutral medium required 28.6 mL of 0.01*M* $KMnO_4$ for complete conversion of SO_3^{2-} to SO_4^{2-}. Assign the oxidation no. of Mn in the product formed in each case.

Answers

1. See solution ;
2. 300 mL;
3. 24.8 g ;
4. 6 equivalents ;
5. $Se^{4+} + 4e \longrightarrow Se^0$
6. 0.6 N;
7. 0.1 M, 0.5 N;
8. 0.1226 M;
9. 7.00% ;
10. 2.97 g ;
11. +3 ;
12. 22.5 g ;
13. 0.0172 M;
14. 0.1339 N, 0.0669 M;
15. $x = 5$;
16. 0.1098 ;
17. 50% ;
18. 90.36 mL;
19. 0.4792 g ;
20. Mn^{2+}, Mn^{4+}

Solution

Solution 1.

$$E_{red./oxi.} = \frac{\text{Mol. weight of reductant or oxidant}}{\text{Number of electrons gained or lost by one molecule of reductant or oxidant or valence factor}}$$

(a) $E_{As_2O_3} = \frac{M_{As_2O_3}}{4}$ $(As_2^{3+} \longrightarrow 2As^{5+} + 4e)$

(b) $E_{MnO_4^-} = \frac{M_{MnO_4^-}}{5}$ $(Mn^{7+} + 5e \longrightarrow Mn^{2+})$

(c) $E_{Cr_2O_7^{2-}} = \frac{M_{Cr_2O_7^{2-}}}{6}$ $(Cr_2^{6+} \longrightarrow 2Cr^{3+} + 6e)$

(d) $E_{C_2O_4^{2-}} = \frac{M_{C_2O_4^{2-}}}{2}$ $(C_2^{3+} \longrightarrow 2C^{4+} + 2e)$

(e) $E_{FeC_2O_4} = \frac{M_{FeC_2O_4}}{3}$ $(Fe^{2+} + C_2^{3+} \longrightarrow Fe^{3+} + 2C^{4+} + 3e)$

(f) $E_{CuSO_4} = \frac{M_{CuSO_4}}{1}$ $(2Cu^{2+} + 2e \longrightarrow Cu_2^{+})$

Solution 2.

$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$

or $2Br^- \longrightarrow Br_2^0 + 2e$ (Valence factor for $Br^{-1} = 1$)

$Cl_2^0 + 2e \longrightarrow 2Cl^-$ (Valence factor for $Cl_2 = 2$)

$\text{Meq. of } Cl_2 = \text{Meq. of } Br^-$

$0.05 \times 2 \times V = 50 \times 0.60 \times 1$

∴ $\mathbf{V = 300\ mL}$

Solution 3.

$\text{Meq. of } Na_2S_2O_3 = 0.2 \times 500 = 100$ $(\because \text{Meq.} = N \times V_{(in\ mL)})$

∴ $\frac{w}{M/1} \times 1000 = 100$ $(\because \text{Meq.} = \frac{\text{wt}}{\text{E.wt}} \times 1000)$

or $\frac{w}{248} \times 1000 = 100$ (Mol.wt. $Na_2S_2O_3.5H_2O = 248$)

$\mathbf{w = 24.8\ g}$

Solution 4.

$H_2S \longrightarrow SO_2$

or $S^{2-} \longrightarrow S^{4+} + 6e$

$N_{H_2S} = M_{H_2S} \times 6$

$$\because \quad \frac{\text{Moles}}{\text{Equivalent}} = \frac{N}{M} = 6$$

Thus one mole of H_2S has **6 equivalent** in it.

Solution 5. $Se^{4+} + (a-4)e \longrightarrow Se^{a+}$

$n = a - 4$ (where n is valence factor)

or $Cr^{2+} \longrightarrow Cr^{3+} + e$

Meq. of SeO_2 = Meq. of $CrSO_4$

$0.0509 \times n \times 12.53 = 0.1 \times 1 \times 25.52$

$\therefore \quad n = 4$

$a - 4 = 4$

or $a = 0$

Thus redox change is : $\mathbf{Se^{4+} + 4e \longrightarrow Se^{0}}$

Solution 6. $N = M \times \text{valence factor}$

$\therefore \quad N = 0.1 \times 6 \qquad (Cr_2^{6+} + 6e \longrightarrow 2Cr^{3+})$

or $N_{K_2Cr_2O_7} = \mathbf{0.6\ N}$

Solution 7. Meq. of MnO_4^- = Meq. of Fe^{2+} $\qquad (Mn^{7+} + 5e \longrightarrow Mn^{2+})$

$\therefore \quad N \times 32 = 40 \times 0.400 \qquad (Fe^{2+} \longrightarrow Fe^{3+} + e)$

$N = 0.5$

or $M_{KMnO_4} = N_{KMnO_4}/\text{valence factor}$

Also, $M_{KMnO_4} = \frac{0.5}{5} = \mathbf{0.1\ M}$

Solution 8. $Mn^{2+} \longrightarrow Mn^{4+} + 2e$

$Mn^{7+} + 3e \longrightarrow Mn^{4+}$

Also, Meq. of MnO_4^- = Meq. of Mn^{2+}

$0.05876 \times 3 \times 34.77 = M \times 2 \times 25$

$M_{Mn^{2+}} = \mathbf{0.1226\ M}$

Solution 9. $Cu^{2+} + e \longrightarrow Cu^{1+}$

$2I^- \longrightarrow I_2 + 2e$

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$

Meq. of Cu^{2+} = Meq. of liberated I_2 = Meq. of $Na_2S_2O_3$

$= 12.12 \times 0.1 \times 1 = 1.212$

$$\therefore \quad \frac{w_{Cu^{2+}}}{M/1} \times 1000 = 1.212$$

$$\therefore \quad w_{Cu^{2+}} = \frac{1.212 \times M}{1000} = \frac{1.212 \times 63.6}{1000} = 0.077\ \text{g}$$

$$\therefore \quad w_{Cu} = w_{Cu^{2+}} = 0.077 \text{ g}$$

$$\therefore \quad \% \text{ Cu} = \frac{0.077}{1.100} \times 100 = \mathbf{7.00\%}$$

Solution 10.

$$N_2^{2-} \longrightarrow N_2^0 + 4e$$

$$Cr^{6+} + 3e \longrightarrow Cr^{3+}$$

$$\text{Meq. of } N_2H_4 = \text{Meq. of } K_2CrO_4$$

$$\frac{w}{32/4} \times 1000 = \frac{24}{194.2/3} \times 1000 \qquad \left(\text{E.wt.} = \frac{\text{M. wt.}}{\text{Valence factor}}\right)$$

$$w_{N_2H_4} = \mathbf{2.97 \text{ g}}$$

Solution 11.

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e$$

$$ne + Ce^{4+} \longrightarrow Ce^{(4-n)+}$$

$$\text{Meq. of } Ce^{4+} = \text{Meq. of } Sn^{2+}$$

$$40 \times 0.5 \times n = 1 \times 2 \times 10.0$$

$$\therefore \quad n = 1$$

$$\therefore \quad Ce^{4+} + e \longrightarrow Ce^{3+}$$

Thus oxidation state of Ce in reduced state is **+3.**

Solution 12.

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$$2I^- \longrightarrow I_2 + 2e$$

$$\text{Meq. of } I^- = \text{Meq. of } MnO_4^-$$

$$50 \times 1.0 = 10 \times N$$

$$N_{MnO_4^-} = 5$$

Now

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$$C_2^{3+} \longrightarrow 2C^{4+} + 2e$$

$$\text{Meq. of } H_2C_2O_4 = \text{Meq. of } MnO_4^-$$

$$\frac{w}{90/2} \times 1000 = 5 \times 100$$

$$w = \mathbf{22.5 \text{ g}}$$

Solution 13.

$$\text{Meq. of } As_2O_3 = \text{Meq. of } KMnO_4 \qquad (As_2^{3+} \longrightarrow 2As^{5+} + 4e)$$

$$\frac{0.1156}{198/4} \times 1000 = M \times 5 \times 27.08 \qquad (Mn^{7+} + 5e \longrightarrow Mn^{2+})$$

$$\therefore \quad M = 0.0172$$

$$\therefore \quad M_{MnO_4^-} = \mathbf{0.0172}\ M$$

Solution 14.

$$\text{Meq. of } SO_3^{2-} = \text{Meq. of } KMnO_4$$

$$\therefore \quad N \times 25 = 34.08 \times 0.01964 \times 5$$

$$N = 0.1339$$

$$\therefore \quad M = \frac{0.1339}{2} = 0.0669$$

$$S^{4+} \longrightarrow S^{6+} + 2e$$

$$N_{SO_3^{2-}} = \mathbf{0.1339}\ N$$

$$M_{SO_3^{2-}} = \frac{0.1339}{2} = \mathbf{0.0669}\ M$$

Solution 15.

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

$$2e + I_2 \longrightarrow 2I^-$$

Also $\quad$ Meq. of I_2 = Meq. of $Na_2S_2O_3.xH_2O$

$$40 \times \frac{1}{5} = \frac{1.984}{M/1} \times 1000$$

$$\therefore \quad M_{Na_2S_2O_3.xH_2O} = 248$$

$$2 \times 23 + 2 \times 32 + 16 \times 3 + 18x = 248$$

or $\quad x = 5$

$$\mathbf{Na_2S_2O_3.5H_2O}$$

Solution 16.

$$V_2^{5+} + 6e \longrightarrow 2V^{2+}$$

$$Zn \longrightarrow Zn^{2+} + 2e$$

$$V^{2+} \longrightarrow V^{4+} + 2e$$

$$I_2 + 2e \longrightarrow 2I^-$$

and $\quad$ Meq. of V^{2+} (v.f. = 3) = Meq. of V_2O_5 (v.f. = 6)

$$= \frac{10}{182/6} \times 1000$$

$$\text{Meq. of } V^{2+} \text{ (v.f. = 2)} = \frac{10}{182/6} \times 1000 \times \frac{2}{3}$$

Meq. of V^{2+} (v.f. = 2) = Meq. of I_2

$$\frac{10 \times 6}{182} \times 1000 \times \frac{2}{3} = \text{Meq. of } I_2$$

or $\quad$ Meq. of I_2 = 219.78

$$m \text{ Mole of } I_2 = \frac{219.78}{2} = 109.89$$

$$\text{Mole of } I_2 = \frac{109.89}{1000}$$

$$\text{Mole of } I_2 = \mathbf{0.1098}$$

Solution 17. $$CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + CO_2 + H_2O$$

$$Ca^{2+} + C_2O_4^{\;2-} \longrightarrow CaC_2O_4$$

CaC_2O_4 + $KMnO_4$ in presence of H_2SO_4 show the following redox changes:

$$C_2^{\;3+} \longrightarrow 2C^{4+} + 2e$$

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

The above set of reaction shows :

Meq. of CaO = Meq. of CaC_2O_4 = Meq. of $KMnO_4$

(Valence factor is two for Ca throughout the changes)

$$\frac{w_{CaO}}{56/2} \times 1000 = 40 \times 0.25$$

$$\therefore \quad w_{CaO} = 0.28$$

$$\therefore \quad \% \text{ of CaO} = \frac{0.28}{0.56} \times 100 = \mathbf{50\%}$$

Solution 18. $$N_{KMnO_4} = \frac{158}{31.6 \times 1} = 5.0$$

$$\left(Mn^{7+} + 5e \longrightarrow Mn^{2+} \therefore E = \frac{M}{5} = \frac{158}{5} = 31.6\right)$$

$$\text{Meq. of KI} = \frac{75 \times 1000}{166} = 451.8 \quad \left(2I^- \longrightarrow I_2 + 2e \therefore E = \frac{M}{1} = \frac{166}{1}\right)$$

Now Meq. of $KMnO_4$ = Meq. of KI

$$5 \times V = 451.8$$

$$\therefore \quad \mathbf{V = 90.36\ mL}$$

Solution 19. $$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

	MnO_2	$4HCl$	$MnCl_2$	Cl_2	$2H_2O$
Initial mole	$\frac{1}{87}$ $= 0.011$	$\frac{1}{36.5}$ 0.027	—	—	—
Final mole	$\left[0.011 - \frac{0.027}{4}\right]$		$\frac{0.027}{4}$	$\frac{0.027}{4}$	

$$\therefore \quad \text{Mole of } Cl_2 \text{ formed} = \frac{0.027}{4}$$

$$\therefore \quad \text{wt. of } Cl_2 \text{ formed} = \frac{0.027}{4} \times 71 = \mathbf{0.4792\ g}$$

Solution 20. $SO_3^{2-} \longrightarrow SO_4^{2-}$

$$S^{4+} \longrightarrow S^{6+} + 2e$$

$\therefore$ Valence factor of $SO_3 = 2$

In acid medium :

$$\text{Meq. of } SO_3^{2-} = \text{Meq. of } MnO_4^-$$

$$25 \times 0.017 \times 2 = 16.9 \times 0.01 \times n_1$$

$$\therefore \quad n_1 = 5$$

$$\therefore \quad Mn^{7+} + 5e \longrightarrow \mathbf{Mn^{2+}}$$

In neutral medium :

$$\text{Meq. of } SO_3^{2-} = \text{Meq. of } MnO_4^-$$

$$25 \times 0.017 \times 2 = 28.6 \times 0.01 \times n_2$$

$$\therefore \quad n_2 = 3$$

$$\therefore \quad Mn^{7+} + 3e \longrightarrow \mathbf{Mn^{4+}}$$

Selected Problems with Solutions

➤ **Problem 1.** Calculate the equivalent weight of each oxidant and reductant in:

(a) $FeSO_4 + KClO_3 \longrightarrow KCl + Fe_2(SO_4)_3$

(b) $Na_2SO_3 + Na_2CrO_4 \longrightarrow Na_2SO_4 + Cr(OH)_3$

(c) $Fe_3O_4 + KMnO_4 \longrightarrow Fe_2O_3 + MnO_2$

(d) $KI + K_2Cr_2O_7 \longrightarrow Cr^{3+} + 3I_2$

(e) $Mn^{4+} \longrightarrow Mn^{2+}$

(f) $NO_3^- \longrightarrow N_2$

(g) $N_2 \longrightarrow NH_3$

(h) $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

(i) $FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$

➤ **Problem 2.** 20 mL of 0.2 *M* $MnSO_4$ are completely oxidized by 16 mL of $KMnO_4$ of unknown normality, each forming Mn^{4+} oxidation state. Find out the normality and molarity of $KMnO_4$ solution.

➤ **Problem 3.** An element *A* in a compound *ABD* has an oxidation no. A^{n-}. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In an experiment 1.68×10^{-3} mole of $K_2Cr_2O_7$ was required for 3.26×10^{-3} mole of the compound *ABD*. Calculate new oxidation state of *A*.

➤ **Problem 4.** $KMnO_4$ oxidizes X^{n+} ion to XO_3^-, itself changing to Mn^{2+} in acid solution. 2.68×10^{-3} mole of X^{n+} requires 1.61×10^{-3} mole of MnO_4^-. What is the value of *n*? Also calculate the atomic mass of *X*, if the weight of 1 g equivalent of XCl_n is 56.

➤ **Problem 5.** Mg can reduce NO_3^- to NH_3 in basic solution:

$$NO_3^- + Mg(s) + H_2O \longrightarrow Mg(OH)_2(s) + OH^-(aq) + NH_3(g)$$

A 25.0 mL sample of NO_3^- solution was treated with Mg. The $NH_3(g)$ was passed into 50 mL of 0.15 *N* HCl. The excess HCl required 32.10 mL of 0.10 *M* NaOH for its neutralisation. What was the molarity of NO_3^- ions in the original sample.

➤ **Problem 6.** Hydroxylamine reduces iron III according to the equation $4Fe^{3+} + 2NH_2OH \rightarrow N_2O + H_2O + 4Fe^{2+} + 4H^+$. Iron II thus produced is estimated by titration with standard $KMnO_4$ solution. The reaction is $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$. A 10 mL of hydroxylamine solution was diluted to one litre. 50 mL of this diluted solution was boiled with an excess of Fe^{3+} solution. The resulting solution required 12 mL of 0.02 *M* $KMnO_4$ solution for complete oxidation of Fe^{2+}. Calculate the weight of NH_2OH in one litre of original solution.

➤ **Problem 7.** A solution is containing 2.52 g litre^{-1} of a reductant. 25 mL of this solution required 20 mL of 0.01 *M* $KMnO_4$ in acid medium for oxidation. Find the mol. wt. of reductant. Given that each of the two atoms which undergo oxidation per molecule of reductant, suffer an increase in oxidation state by one unit.

➤ **Problem 8.** Two solutions of 0.1 *M* $Cr_2O_7^{2-}$(aq) and 0.1 *M* MnO_4^-(aq) are to be used to titrate Fe^{2+}(aq) separately:

(a) With which solution, $Cr_2O_7^{2-}$(aq) or MnO_4^-(aq), would the greater volume of titrant (titrating solution) be required for a given solution of Fe^{2+}(aq).

(b) If a given titration requires 24.50 mL of 0.100 *M* $Cr_2O_7^{2-}$(aq), how many mL of 0.100 *M* MnO_4^-(aq) would have been required if it had been used instead?

➤ **Problem 9.** $KMnO_4$ solution is to be standardised by titration against As_2O_3(s). A 0.1097 g sample of As_2O_3 requires 26.10 mL of the $KMnO_4$ solution for its titration. What are the molarity and normality of the $KMnO_4$ solution?

➤ **Problem 10.** A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment the Cr is oxidised to $Cr_2O_7^{2-}$ and the Mn to MnO_4^-. A 10.00 g sample of steel is used to produce 250.0 mL of a solution containing $Cr_2O_7^{2-}$ and MnO_4^-.

(a) A 10.00 mL portion of this solution is added to a $BaCl_2$ solution and by proper adjustment of the acidity, the chromium is completely precipitated as 0.0549 g $BaCrO_4$.

(b) A second 10.00 mL portion of this solution requires exactly 15.95 mL of 0.0750 *M* standard Fe^{2+} solution for its titration (in acid solution). Calculate the % of Mn and % of Cr in the steel sample. (Cr = 52, Mn = 55, Ba = 137)

➤ **Problem 11.** A 200 mL sample of a citrus fruit drinks containing ascorbic acid (vitamin C, mol. wt. 176.13) was acidified with H_2SO_4 and 10 mL of 0.0250 *M* I_2 was added. Some of the iodine was reduced by the ascorbic acid to I^-. The excess of I_2 required 4.6 mL of 0.01 *M* $Na_2S_2O_3$ for reduction. What was the vitamin C content of the drink in mg vitamin per mL drink? The reactions are:

$$C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2HI$$

$$5H_2O + S_2O_3^{2-} + 4I_2 \longrightarrow 2SO_4^{2-} + 8I^- + 10H^+$$

➤ **Problem 12.** An acid solution of $KReO_4$ sample containing 26.83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution including the washings from the column, was then titrated with 0.05 *N* $KMnO_4$. 11.45 mL of the standard $KMnO_4$ was required for the reoxidation of all the rhenium to the perrhenate ion

ReO_4^-. Assuming that rhenium was the only element reduced, what is the oxidation state to which rhenium was reduced by the zinc column.

➤ Problem 13. 2.480 g of $KClO_3$ are dissolved in conc. HCl and the solution was boiled. Chlorine gas evolved in the reaction was then passed through a solution of KI and liberated iodine was titrated with 100 mL of hypo. 12.3 mL of same hypo solution required 24.6 mL of 0.5 *N* iodine for complete neutralization. Calculate % purity of $KClO_3$ sample.

➤ Problem 14. 1 g of moist sample of KCl and $KClO_3$ was dissolved in water to make 250 mL solution, 25 mL of this solution was treated with SO_2 to reduce chlorate to chloride and excess of SO_2 was removed by boiling. The total chloride was precipitated as silver chloride. The weight of precipitate was 0.1435 g. In another experiment, 25 mL of original solution was heated with 30 mL of 0.2 *N* ferrous sulphate solution and unreacted ferrous sulphate required 37.5 mL of 0.08 *N* solution of an oxidant for complete oxidation. Calculate the molar ratio of chlorate to chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to equation.

$$ClO_3 + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{3+} + 3H_2O$$

➤ Problem 15. 0.84 g iron ore containing *X* per cent of iron was taken in a solution containing all the iron in ferrous state. The solution required *X* mL of a potassium dichromate solution for oxidation of iron content to ferric state. Calculate the strength of potassium dichromate solution.

➤ Problem 16. 0.5 g sample of iron containing mineral mainly in the form of $CuFeS_2$ was reduced suitably to convert all the ferric ions into ferrous ions ($Fe^{3+} \rightarrow Fe^{2+}$) and was obtained as solution. In the absence of any interferring radical, the solution required 42 mL of 0.01 *M* $K_2Cr_2O_7$ for titration. Calculate % of $CuFeS_2$ in sample.

➤ Problem 17. 0.2828 g of iron wire was dissolved in excess dilute H_2SO_4 and the solution was made upto 100 mL. 20 mL of this solution required 30 mL of *N*/30 $K_2Cr_2O_7$ solution for exact oxidation. Calculate % purity of Fe in wire.

➤ Problem 18. A substance of crude copper is boiled in H_2SO_4 till all the copper has reacted. The impurities are inert to acid. The SO_2 liberated in the reaction is passed into 100 mL of 0.4 *M* acidified $KMnO_4$. The solution of $KMnO_4$ after passage of SO_2 is allowed to react with oxalic acid and requires 23.6 mL of 1.2 *M* oxalic acid. If the purity of copper is 90%, what was the weight of sample.

➤ Problem 19. What mass of $K_2Cr_2O_7$ is required to produce 5.0 litre CO_2 at 75°C and 1.07 atm pressure from excess of oxalic acid. Also report the volume of 0.1 *N* NaOH required to neutralise the CO_2 evolved.

➤ Problem 20. Calculate the mass of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) which can be oxidised to CO_2 by 100 mL of MnO_4^- (acidic) solution, 10 mL of which are capable of oxidising 50.0 mL of 1.0 *M* I^- to I_2. Also calculate the weight of FeC_2O_4 oxidised by same amount of MnO_4^-.

➤ **Problem 21.** The calcium contained in a solution of 1.048 g of a substance being analysed was precipitated with 25 mL $H_2C_2O_4$. The excess of $C_2O_4^{2-}$ in one fourth of filtrate was back titrated with 5 mL of 0.1025*N* $KMnO_4$. To determine the conc. of $H_2C_2O_4$ solution, it was diluted four folds and titration of 25 mL of dilute solution used up 24.1 mL of same $KMnO_4$ solution. Calculate % of Ca in substance.

➤ **Problem 22.** 100 mL solution of FeC_2O_4 and $FeSO_4$ is completely oxidized by 60 mL of 0.02 *M* $KMnO_4$ in acid medium. The resulting solution is then reduced by Zn and dil. HCl. The reduced solution is again oxidized completely by 40 mL of 0.02 *M* $KMnO_4$. Calculate normality of FeC_2O_4 and $FeSO_4$ in mixture.

➤ **Problem 23.** 25 mL of a solution containing Fe^{2+} and Fe^{3+} sulphate acidified with H_2SO_4 is reduced by 3 g of metallic zinc. The solution required 34.25 mL of *N*/10 solution of $K_2Cr_2O_7$ for oxidation. Before reduction with zinc, 25 mL of the same solution required 22.45 mL of same $K_2Cr_2O_7$ solution. Calculate the strength of $FeSO_4$ and $Fe_2(SO_4)_3$ in solution.

➤ **Problem 24.** A sample of ferrous sulphate and ferrous oxalate was dissolved in dil. H_2SO_4. The complete oxidation of reaction mixture required 40 mL of *N*/15 $KMnO_4$. After the oxidation, the reaction mixture was reduced by Zn and H_2SO_4. On again oxidation by same $KMnO_4$, 25 mL were required . Calculate the ratio of Fe in ferrous sulphate and oxalate.

➤ **Problem 25.** A solution contains mixture of H_2SO_4 and $H_2C_2O_4$. 25 mL of this solution requires 35.5 mL of *N*/10 NaOH for neutralization and 23.45 mL of *N*/10 $KMnO_4$ for oxidation. Calculate:

(i) Normality of $H_2C_2O_4$ and H_2SO_4,

(ii) Strength of $H_2C_2O_4$ and H_2SO_4.

Assume molecular weight of $H_2C_2O_4 = 126$

➤ **Problem 26.** A compound is known to be hydrated double salt of potassium oxalate and oxalic acid of the type $aK_2C_2O_4 . bH_2C_2O_4 . cH_2O$, where *a*, *b* and *c* are unknown. When 1.613 g of this compound is dissolved in water and solution made upto 250 mL, it is found that 25.0 mL of this solution is neutralised by 19.05 mL of 0.1 *N* alkali and reduces 25.40 mL of 0.1 *N* $KMnO_4$ solution. What is the formula of the salt?

➤ **Problem 27.** 30 mL of a solution containing 9.15 g/litre of an oxalate $K_X H_Y (C_2O_4)_Z \cdot nH_2O$ are required for titrating 27 mL of 0.12 *N* NaOH and 36 mL of 0.12*N* $KMnO_4$ separately. Calculate *X*, *Y*, *Z* and *n*. Assume all H atoms are replaceable and *X*, *Y*, *Z* are in the simple ratio of g atoms.

➤ **Problem 28.** On ignition, Rochelle salt $NaKC_4H_4O_6{\cdot}4H_2O$ (mol. wt. 282) is converted into $NaKCO_3$ (mol. wt. 122). 0.9546 g sample of the Rachelle salt on ignition gives $NaKCO_3$ which is titrated with 41.72 mL H_2SO_4. From the following data, find the percentage purity of the Rochelle salt. The solution after neutralisation requires 1.91 mL of 0.1297 *N* NaOH. The H_2SO_4 used for the neutralisation requires its 10.27 mL against 10.35 mL of 0.1297 *N* NaOH.

➤ **Problem 29.** 25 mL of a solution of ferric alum $Fe_2(SO_4)_3\,(NH_4)_2SO_4{\cdot}24H_2O$ containing 1.25 g of the salt was boiled with iron when the reaction $Fe + Fe_2(SO_4)_3 \rightarrow 3FeSO_4$ occurred. The unreacted iron was filtered off and solution treated with 0.107*N* $KMnO_4$ in acid medium. What is titre value? If Cu had been used in place of Fe, what would have been titre value?

➤ **Problem 30.** A 2.5 g sample containing As_2O_5, Na_2HAsO_3 and inert substance is dissolved in water and the pH is adjusted to neutral with excess of $NaHCO_3$. The solution is titrated with 0.15 *M* I_2 solution, requiring 11.3 mL to just reach the end point, then the solution is acidified with HCl, KI is added and the liberated iodine requires 41.2 mL of 0.015 *M* $Na_2S_2O_3$ under basic conditions where it converts to SO_4^{2-}. Calculate per cent composition of mixture.

➤ **Problem 31.** Calculate the weight of MnO_2 and the volume of HCl of specific gravity 1.2 g mL^{-1} and 4% nature by weight, needed to produce 1.78 litre of Cl_2 at STP by the reaction:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

➤ **Problem 32.** Chile salt peter, a source of $NaNO_3$ also contains $NaIO_3$. The $NaIO_3$ can be used as a source of iodine, produced in the following reactions.

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-} \quad \ldots(1)$$

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_{2(s)} + 3H_2O \quad \ldots(2)$$

One litre of chile salt peter solution containing 5.80 g $NaIO_3$ is treated with stoichiometric quantity of $NaHSO_3$. Now an additional amount of same solution is added to reaction mixture to bring about the second reaction. How many grams of $NaHSO_3$ are required in step I and what additional volume of chile salt peter must be added in step II to bring in complete conversion of I^- to I_2?

➤ **Problem 33.** (a) $CuSO_4$ reacts with KI in acidic medium to liberate I_2

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(b) Mercuric per iodate $Hg_5(IO_6)_2$ reacts with a mixture of KI and HCl following the equation:

$$Hg_5(IO_6)_2 + 34KI + 24HCl \longrightarrow 5K_2HgI_4 + 8I_2 + 24KCl + 12H_2O$$

(c) The liberated iodine is titrated against $Na_2S_2O_3$ solution. One mL of which is equivalent to 0.0499 g of $CuSO_4{\cdot}5H_2O$. What volume in mL of $Na_2S_2O_3$ solution will be required to react with I_2 liberated from 0.7245 g of $Hg_5(IO_6)_2$? M. wt. of $Hg_5(IO_6)_2 = 1448.5$ and M. wt. of $CuSO_4 \cdot 5H_2O = 249.5$.

➤ **Problem 34.** Calculate the amount of SeO_3^{2-} in solution on the basis of following data. 20 mL of *M*/60 solution of $KBrO_3$ was added to a definite volume of SeO_3^{2-} solution. The bromine evolved was removed by boiling and excess of $KBrO_3$ was back titrated with 5.1 mL of *M*/25 solution of $NaAsO_2$. The reactions are given below:

(a) $SeO_3^{2-} + BrO_3^- + H^+ \longrightarrow SeO_4^{2-} + Br_2 + H_2O$

(b) $BrO_3^- + AsO_2^- + H_2O \longrightarrow Br^- + AsO_4^{3-} + H^+$

➤ **Problem 35.** A mixture containing As_2O_3 and As_2O_5 required 20.10 mL of 0.05*N* iodine for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.1113 g hypo ($Na_2S_2O_3 \cdot 5H_2O$) for complete reaction. Calculate mass of mixture. The reactions are:

$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4H^+ + 4I^-$$

$$As_2O_5 + 4H^+ + 4I^- \longrightarrow As_2O_3 + 2I_2 + 2H_2O$$

➤ **Problem 36.** In a quality control analysis for sulphur impurity 5.6 g steel sample was burnt in a stream of oxygen and sulphur was converted into SO_2 gas. The SO_2 was then oxidized to sulphate by using H_2O_2 solution to which has been added 30 mL of 0.04 *M* NaOH. The equation for the reaction is:

$$SO_{2(g)} + H_2O_{2(aq.)} + 2OH^-_{(aq.)} \longrightarrow SO^{2-}_{4(aq.)} + 2H_2O_{(l)}$$

22.48 mL of 0.024 *M* HCl was required to neutralize the base remaining after oxidation reaction. Calculate % of sulphur in given sample.

➤ **Problem 37.** 0.108 g of finely divided copper was treated with an excess of ferric sulphate solution until copper was completely dissolved. The solution after the addition of excess dilute sulphuric acid required 33.7 mL of 0.1 *N* $KMnO_4$ for complete oxidation. Find the equation which represents the reaction between metallic copper and ferric sulphate solution. At. wt. of Cu = 63.6; Fe = 56.

➤ **Problem 38.** 1.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil HCl and it evolved 168 mL of CO_2 at NTP. From this solution $BaCrO_4$ was precipitated, filtered and washed. The dry precipitate was dissolved in dilute H_2SO_4 and diluted to 100 mL. 10 mL of this solution when treated with KI solution liberated iodine which required exactly 20 mL of 0.05 *N* $Na_2S_2O_3$. Calculate percentage of CaO in the sample.

➤ **Problem 39.** A 10 g mixture of Cu_2S and CuS was treated with 200 mL of 0.75 *M* MnO_4^- in acid solution producing SO_2, Cu^{2+} and Mn^{2+}. The

SO_2 was boiled off and the excess of MnO_4^- was titrated with 175 mL of 1 *M* Fe^{2+} solution. Calculate % of CuS in original mixture.

➤ **Problem 40.** For estimating ozone in the air, a certain volume of air is passed through an acidified or neutral KI solution when oxygen is evolved and iodide is oxidised to give iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution. In an experiment 10 litre of air at 1 atm and 27°C were passed through an alkaline KI solution, at the end, the iodine entrapped in a solution on titration as above required 1.5 mL of 0.01*N* $Na_2S_2O_3$ solution. Calculate volume % of O_3 in sample.

➤ **Problem 41.** A forensic chemist needed to determine the concentration of HCN in the blood of a suspected homicide victim and decided to titrate a diluted sample of the blood with iodine, using the reaction,

$$HCN_{(aq)} + I_3^- \longrightarrow ICN_{(aq)} + 2I^-_{(aq)} + H^+_{(aq)}$$

A diluted blood sample of volume 15 mL was titrated to the stoichiometric point with 5.21 mL of an I_3^- solution. The molarity of I_3^- in the solution was determined by titrating it against arsenic (III) oxide, which in solution forms arsenious acid, H_3AsO_3. It was found that 10.42 mL of the tri-iodide solution was needed to reach the stoichiometric point with a 10 mL sample of 0.1235 *M* H_3AsO_3 in the reaction.

$$H_3AsO_{3(aq)} + I^-_{3(aq)} + H_2O_{(l)} \longrightarrow H_3AsO_{4(aq)} + 3I^-_{(aq)} + 2H^+_{(aq)}$$

(a) What is the normality of 0.1185 *M* tri-iodide ions in the initial solution?

(b) What is the molar concentration of 0.0412 *M* HCN in the blood sample?

➤ **Problem 42.** A mixture of two gases, H_2S and SO_2 is passed through three beakers successively. The first beaker contains Pb^{2+} ions, which absorbs all H_2S to form PbS. The second beaker contains 25 mL of 0.0396 *N* I_2, which oxidises all SO_2 to SO_4^{2-}. The third contains 10 mL of 0.0345 *N* thiosulphate solution to retain any I_2 carried over from the second absorber. The solution from first absorber was made acidic and treated with 20 mL of 0.0066 *M* $K_2Cr_2O_7$, which converted S^{2-} to SO_2. The excess dichromate was reacted with solid KI and the liberated iodine required 7.45 mL of 0.0345 *N* $Na_2S_2O_3$ solution. The solution in the second and third absorbers were combined and the resultant iodide was treated with 2.44 mL of the same solution of thiosulphate. Calculate the concentrations of SO_2 and H_2S in mg/litre of the sample.

➤ **Problem 43.** A 0.141 g sample of phosphorus containing compound was digested in a mixture of HNO_3 and H_2SO_4 which resulted in formation of CO_2, H_2O and H_3PO_4. Addition of ammonium molybdate yielded a solid having the composition $(NH_4)_3PO_4 \cdot 12MoO_3$. The precipitate was filtered, washed and dissolved in 50.0 mL of 0.20 *M* NaOH.

$$(NH_4)_3PO_4\cdot 12MoO_{3(s)} + 26OH^- \longrightarrow HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_{3(g)}$$

After boiling the solution to remove the NH_3, the excess of NaOH was titrated with 14.1 mL of 0.174 *M* HCl. Calculate the percentage of phosphorus in the sample.

➤ Problem 44. 1 g of a sample of NaOH was dissolved in 50 mL 0.33 *M* alkaline solution of $KMnO_4$ and refluxed till all the cyanide was converted into OCN^-. The reaction mixture was cooled and its 5mL portion was acidified by adding H_2SO_4 in excess and then titrated to end point against 19.0 mL of 0.1 *M* $FeSO_4$ solution. Calculate % purity of NaCN sample.

Answers

1. (a) 152, 20.42, (b) 63, 54, (c) 232, 52.67, (d) 166, 49, (e) 27.5, (f) 12.4, (g) 4.67, (h) 158, 127, (i) 48 ;

2. 0.5 *N*, 0.167 *M* ;

3. 3 − *n* ;

4. 2, 97 ;

5. 0.1716 ;

6. 39.6 g/litre ;

7. 126 ;

8. (a) See solution, (b) 29.4 mL ;

9. 0.085 *N*, 0.017 *M* ;

10. Cr = 2.821%, Mn = 1.496% ;

11. 0.058 mg/mL ;

12. +3 ;

13. 82.32% ;

14. $\frac{1}{2}, \frac{1}{2}$;

15. 7.35 g/litre ;

16. 92.48% ;

17. 99% ;

18. 5.06 g ;

19. $K_2Cr_2O_7 = 9.18$ g, $V = 3.746$ litre ;

20. $H_2C_2O_4 = 31.5$ g, $FeC_2O_4 = 24$ g ;

21. 14.94% ;

22. $FeC_2O_4 = 0.03\ N$, $FeSO_4 = 0.03\ N$;

23. $FeSO_4 = 13.64$ g/litre, $Fe_2(SO_4)_3 = 9.45$ g/litre ;

24. 7/3 ;

25. (i) $H_2C_2O_4 = 0.0938\ N$, $H_2SO_4 = 0.0482\ N$,
(ii) $H_2C_2O_4 = 5.909$ g/litre, $H_2SO_4 = 2.362$ g/litre ;

26. $K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 4H_2O$;

27. $X = 1$, $Y = 3$, $Z = 2$, $n = 2$;

28. 76.87% ;

29. 36.36 mL, 24.24 mL ;

30. $Na_2HAsO_3 = 11.53\%$, $As_2O_5 = 3.57\%$, inert material = 84.9% ;

31. HCl = 241.7 mL , $MnO_2 = 6.9134$ g ;

32. 9.14 g, 200 mL ;

33. 40 mL ;

34. 0.084 g ;

35. 0.2496 g ;

36. 0.1875% ;

37. See solution ;

38. 14.09% ;

39. 57.94% ;

40. $1.847 \times 10^{-3}\%$;

41. (a) 0.1185, (b) 0.412 ;

42. $SO_2 = 0.72$ mg/litre, $H_2S = 0.125$ mg/litre ;

43. 6.4%.

44. 93%

Problems for self Assessment

1. Find out the equivalent of the species written below taking their molecular weight as M.
(a) Na_2CrO_4 in $Na_2SO_3 + Na_2CrO_4 \longrightarrow Na_2SO_4 + Cr(OH)_3$
(b) As_2S_3 in $As_2S_3 + 10NO_3^- + 4H^+ \longrightarrow 10NO_2 + 2AsO_4^{3-} + 3S + 2H_2O$
(c) H_3PO_3 in $H_3PO_3 \longrightarrow H_3PO_4 + PH_3$
(d) MnO_4 in $MnO_2 \xrightarrow{OH^-} MnO_4^- + Mn^{2+}$
(e) KHC_2O_4 in $KHC_2O_4 + KOH \longrightarrow K_2C_2O_4 + H_2O$
(f) SO_2 in $SO_2 + H_2S \longrightarrow 3S + 2H_2O$
(g) CO_2 in $C + O_2 \longrightarrow CO_2$
(h) SO_2 in $5SO_2 + 2KMnO_4 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$
(i) Cu_2S in $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + SO_2 + Mn^{2+}$
(j) BiO_3^- in $BiO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$

2. If 10 g of V_2O_5 is dissolved in acid and is reduced to V^{2+} by zinc metal, how many moles of I_2 could be reduced by the resulting solution if it is further oxidised to VO^{2+} ions? (V = 51 , O = 16, I = 127).

3. 30 mL of an acidified solution 1.5 N MnO_4^- ions, 15 mL of 0.5 N oxalic acid and 15 mL of 0.4 N ferrous salt solution are added together. Find the molarities of MnO_4^- and Fe^{3+} ions in the final solution?

4. 0.518 g sample of limestone is dissolved and then Ca is precipitated as CaC_2O_4. After filtering and washing the precipitate, it requires 40 mL of 0.25N $KMnO_4$ solution to equivalence point. What is percentage of CaO in limestone?

5. What volume of H_2 at NTP is needed to reduce 125 g of MoO_3 to metal?

6. What weight of pyrolusite containing 89.21% of MnO_2 will oxidize the same amount of oxalic acid as 37.12 mL of $KMnO_4$ solution of which 1.0 mL will liberate 0.0175 g of I_2 from KI?

7. 9.824 g of $FeSO_4(NH_4)_2SO_4 \cdot xH_2O$ were dissolved in 250 mL of solution. 20 mL of this solution required 20 mL of $KMnO_4$ containing 3.52 g of 90% by weight $KMnO_4$ dissolved per litre. Calculate value of x.

8. Sufficient amount of H_2S gas is passed through 5 mL solution of tincture of iodine to convert its all iodine into iodide ion. The sulphur precipitated is filtered off and the solution is made upto 1 litre and acidified with HCl. 250 mL of this solution requires 28 mL of 0.05 N Ce^{4+} for the conversion of entire I^- into ICl only. 2 ml of same sample of tincture of iodine gave 0.0313 g of yellow precipitate in another experiment when treated with $AgNO_3$ solution. What weight per cent of iodine is present in the form of iodine. (Tincture of iodine contains I^- and I_2 both).

9. 9.55 g of a sample of bleaching powder was extracted with water and the solution was made up to one litre. 25 mL of this solution was added to 50 mL solution of $FeSO_4$ having 5.6 g Fe^{2+} ions per litre and acidified with dilute H_2SO_4. After the completion of the reaction, 29.9 mL of 0.1*N* $KMnO_4$ were needed to oxidize the excess of Fe^{2+} ions. Calculate % of available Cl_2 in bleaching powder.

10. Hydrogen peroxide is rapidly reduced by Sn^{2+}, the products being Sn^{4+} and H_2O. Hydrogen peroxide decomposed slowly at room temperature to produce O_2 and H_2O. Calculate the volume of O_2 produced at 20°C and 760 mm pressure when 100 g of 10% by mass of H_2O_2 in water is treated with 50 mL of 2.0 *M* Sn^{2+} and then the mixture is allowed to stand until no further reaction takes place.

11. In acidic solution, IO_3^- reacts with I^- to form I_2. What will be the final concentration of IO_3^-, I^- and I_2 in a solution prepared by mixing 64.8 mL of 10^{-2} *M* KIO_3 with 35.2 mL of 6×10^{-3} *M* KI?

12. Calculate the mass of oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, which can be oxidised to CO_2 by 100 mL of an MnO_4^- solution, 10 mL of which is capable of oxidising 50.0 mL of 1.00 *N* I^- to I_2.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$H_2C_2O_4 \longrightarrow 2CO_2 + 2H^+ + 2e^-$$

$$2I^- \longrightarrow I_2 + 2e^-$$

13. A compound on analysis gave 73.4% Pb and 3.2% H_2O. 0.235 g of the substance when treated with an excess of KI solution acidified with HCl, liberated I_2 equivalent to 25 mL of *N*/20 $Na_2S_2O_3$ solution. On igniting the substance a residue of PbO and Cr_2O_3 was left behind. Calculate the per cent of Cr in the compound. The compound was insoluble in water but on digestion with Na_2SO_4 solution gave strongly alkaline and yellow coloured solution with white precipitate. Derive the formula of compound.

14. 5 g of a copper alloy was dissolved in one litre of dil. H_2SO_4. 20 mL of this solution was titrated iodometrically and it required 20 mL of hypo solution. 20 mL of $K_2Cr_2O_7$ which contained 2.4 g/litre in presence of H_2SO_4 and excess of KI, required 30 mL of the same hypo solution. Calculate the % purity of copper in the alloy.

15. A solution of $Na_2S_2O_3$ is to be standardised by titrating against iodine liberated from standard KIO_3 solution. The later is made up by dissolving 2.03 g of KIO_3 in water and making up to 250 mL. 10.0 mL of this solution are then mixed with excess KI solution and the following reaction occurs:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

The resulting iodine is titrated with the $Na_2S_2O_3$ solution according to:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

and it is found that 24.4 mL are needed. What is the molarity of the $Na_2S_2O_3$ solution?

16. Iodic acid reacts with an aqueous solution of sulphur dioxide according to the reaction:

$$2HIO_3 + 5SO_2 + 4H_2O \longrightarrow 5H_2SO_4 + I_2$$

20 mL of a solution of iodic acid of unknown normality was allowed to react with an excess of an aqueous solution of SO_2. The excess of SO_2 and I_2 formed were removed by heating the solution. For the remaining solution 35.5 mL of 0.16 *N* sodium hydroxide was used for neutralisation. Calculate the amount of HIO_3 present in one litre of the solution.

17. 0.1 g sample of chromite was fused with excess of Na_2O_2 and brought into solution according to reaction:

$$2Fe(CrO_2)_2 + 7Na_2O_2 \longrightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$$

The solution was acidified with dil. HCl and 1.2 g mohr salt (M. wt. 392) added. The excess of Fe^{2+} required 24 mL of 0.05 *N* $K_2Cr_2O_7$ for titration. What is % of Cr in sample?

18. A 1.0 g sample of $KClO_3$ was heated under such condition that a part of it decomposed according to equation:

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

and the remaining underwent a change according to the equation $4KClO_3 \rightarrow 3KClO_4 + KCl$. If the amount of oxygen evolved was 146.8 mL at STP, calculate the % by weight of $KClO_4$ in residue.

19. One litre of O_2 at STP was passed through an ozonizer when the resulting volume was 888 mL at STP. This quantity of ozonized oxygen was passed through excess of KI solution. Calculate the weight of I_2 liberated.

$$O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$$

20. A mixture of 4.94 g of 85% pure phosphine, PH_3, and 0.110 kg of $CuSO_4{\cdot}5H_2O$ (of molar mass 249.68 g/mol) is placed in a reaction vessel.

(a) Balance the chemical equation for the reaction that takes place, given the skeletal form,

$$CuSO_4{\cdot}5H_2O_{(s)} + PH_{3(g)} \longrightarrow Cu_3P_{2(s)} + H_2SO_{4(aq)} + H_2O_{(l)}$$

(b) Calculate the mass (in grams) of Cu_3P_2 (of molar mass 252.56 g/mol) formed if a 6.31% yield were produced in the reaction.

(c) Point out the limiting reagent.

21. Chrome alum $K_2SO_4\,Cr_2(SO_4)_3{\cdot}24H_2O$ is prepared by passing SO_2 gas through an aqueous solution of $K_2Cr_2O_7$ acidified with dilute sulphuric acid till the reduction is complete. The alum is crystallised followed by filteration/centrifugation. If only 90% of the alum can be recovered from the above process, how much alum can be prepared from 10 kg of K_2CrO_4. How many mole of electrons supplied by SO_2 for reducing one mole of $K_2Cr_2O_7$.

22. Oxygen, potassium chromate and Cr_2O_3 are obtained by decomposing $K_2Cr_2O_7$. Oxygen evolved reacted completely with 20.4 g of chromium. CrO_3 was obtained when potassium chromate is treated with conc. H_2SO_4. How much CrO_3 and Cr_2O_3 are obtained assuming the oxygen evolved is measured at STP.

23. For complete oxidation of 60 mL of a ferrous sulphate solution with $KMnO_4$ in acid medium, the volume of 0.01 *M* $KMnO_4$ required was 12 mL. What would have the volume of 0.01 *M* $K_2Cr_2O_7$ required for the same oxidation?

24. A mixture $K_2Cr_2O_7$ and $KMnO_4$ weighing 0.561 g was treated with excess of KI in acid medium. Iodine liberated required 100 mL of 0.15 *N* hypo solution for exact oxidation. What is the percentage of each in the mixture? Reactions involved are:

$$2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

25. O_2 liberated during decomposition of $KMnO_4$ and measured at STP was all used for converting MnO_2 to K_2MnO_4 in basic medium. Find the masses of $KMnO_4$ decomposed and K_2MnO_4 produced, if 50 mL of KOH solution having a density of 1.2 g/cc containing 22% by mass of KOH is used for above conversion. [Mn = 55, K = 39]

$$2KMnO_4 \longrightarrow K_2MnO_4 + O_2 + MnO_2$$

$$MnO_2 + 2KOH + \frac{1}{2}O_2 \longrightarrow K_2MnO_4 + H_2O$$

Answers

1. (a) $M/3$, (b) $M/10$, (c) $M/2$, (d) $M/3$, (e) $M/1$, (f) $M/4$, (g) $M/4$, (h) $M/2$, (i) $M/8$, (j) $M/6$;

2. 0.11 mole I_2 ;

3. $[Fe^{3+}] = 0.1\ M$, $[MnO_4^-] = 0.105\ M$;

4. 54.05% ;

5. 58.3 litre ;

6. 0.2494 g ;

7. 6 ;

8. 88.2% ;

9. 29.89% ;

10. 2.33 litre ;

11. $2.26 \times 10^{-4}\ M$, 0, $1.26 \times 10^{-3}\ M$;

12. 31.5 g ;

13. $PbCrO_4 \cdot Pb(OH)_2$;

14. 42% ;

15. $0.093\ M$;

16. 10 g $litre^{-1}$;

17. 32.24% ;

18. 49.83% ;

19. 2.54 g ;

20. (a) $3CuSO_4 \cdot 5H_2O_{(s)} + 2PH_3 \longrightarrow Cu_3P_{2(s)} + 3H_2SO_4 + 5H_2O_{(l)}$

(b) 2.33 g , (c) PH_3 ;

21. 30.55 kg, 6 N electrons ;

22. $Cr_2O_3 = 61.98$ g, $CrO_3 = 39.23$ g ;

23. 10 mL

24. 43.65%, 56.35%

25. 18.62 g $KMnO_4$, 23.22 g K_2MnO_4

7

Electrochemistry

Chapter at a Glance

Faraday's laws of electrolysis

1. $w = Z \times i \times t$

   where w is amount discharged or deposited during the passage of i ampere current for t second.

2. $\frac{w}{E}$ = constant

Nernst equation for electrode potential

3. $E_{OP} = E^\circ_{OP} - \frac{0.059}{n} \log_{10} \frac{[O.S.]}{[R.S.]}$

4. $E_{RP} = E^\circ_{RP} + \frac{0.059}{n} \log_{10} \frac{[O.S.]}{[R.S.]}$

   E_{OP} and E_{RP} are oxidation and reduction electrode potentials respectively. E°_{OP} and E°_{RP} are standard oxidation and reduction potentials respectively. [O.S.] is concentration of oxidised state and [R.S.] is concentration of reduced state.

5. $E_{OP} = - E_{RP}$
6. $E^\circ_{OP} = - E^\circ_{RP}$
7. $E_{cell} = E_{OP} + E_{RP}$
8. $E^\circ_{cell} = E^\circ_{OP} + E^\circ_{RP}$
   (i) E°_{OP} and E_{OP} of one showing oxidation and E°_{RP} and E_{RP} of other showing reduction.
   (ii) The electrode having more or +ve E_{OP} shows oxidation and the other shows reduction.
9. $E^\circ_{Cl^-/AgCl/Ag} = E^\circ_{Ag^+/Ag} + (0.059/1) \log K_{SP_{AgCl}}$

   K_{SP} is solubility product.

10. $-\Delta G^\circ = RT \log_e K = 2.303\, RT \log_{10} K$
11. $E^\circ = \frac{0.059}{n} \log_{10} K$

    K is equilibrium constant.

12. $\Delta H = nF\,[T(\delta E/\delta T)_P - E]$

    ΔH is heat of reaction and $\left(\frac{\delta E}{\delta T}\right)_P$ temperature coefficient of e.m.f. of cell.

The Basic Problems with Solution

➤ **Problem 1.** Write equations for the electrolysis of CaH_2 in fused state.

➤ **Problem 2.** How much electricity in terms of Faraday is required to produce :
(a) 20.0 g of Ca from molten $CaCl_2$;
(b) 40.0 g of Al from molten Al_2O_3.

➤ **Problem 3.** How much electricity is required in coulomb for the oxidation of :
(a) 1 mole of H_2O to O_2; (b) 1 mole of FeO to Fe_2O_3.

➤ **Problem 4.** Calculate the number of electrons lost or gained during electrolysis of :
(a) 2g Br^- ions, (b) 1g Cu^{2+} ions.

➤ **Problem 5.** A metal wire carries a current of 4 ampere. How many electrons pass through a point in the wire in one second?

➤ **Problem 6.** Calculate current strength in ampere required to deposit 10 g Zn in 2 hrs. At. wt. of Zn = 65.

➤ **Problem 7.** How many hour are required for a current of 3.0 ampere to decompose 18 g water.

➤ **Problem 8.** Calculate the Avogadro's number using the charge on the electron 1.60×10^{-19} C and the fact that 96500 C deposits 107.9 g silver from its solution.

➤ **Problem 9.** Three electrolytic cells *A*, *B*, *C* containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. *A* steady current of 1.5 ampere was passed through them until 1.45 g of silver deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and of zinc were deposited?

➤ **Problem 10.** Calculate the volume of gases liberated at anode and cathode at NTP from the electrolysis of Na_2SO_4(aq.) solution by a current of 2 ampere passed for 10 minute.

➤ **Problem 11.** A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 minute. What mass of Ni is deposited at the cathode?

➤ **Problem 12.** A current of 3.7 ampere is passed for 6 hrs. between Ni electrodes in 0.5 litre of 2 *M* solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

➤ **Problem 13.** A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing $CdSO_4$ solution. What weight of Cd will be deposited by current flowing for 10 hr.? At.wt. of Cd = 112.4

➤ **Problem 14.** Calculate the volume of Cl_2 at 27°C and 2 atm produced during electrolysis of $MgCl_2$ which produces 6.50 g Mg.
(At. wt. of Mg = 24.3)

➤ **Problem 15.** A metal is known to form fluoride MF_2. When 10 ampere electricity is passed through a molten salt for 330 sec, 1.95 g metal is deposited.

Find out the atomic weight of metal. What will be the quantity of charge required to deposit the same mass of Cu from $CuSO_{4\,(aq.)}$.
(At. wt. of Cu = 63.6)

➤ **Problem 16.** 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 thio-sulphate. Calculate equivalent weight of metal. Also calculate the total time to bring this change if 10 ampere current passed through solution of metal iodide.

➤ **Problem 17.** A current of 2.0 ampere is passed for 5.0 hour through a molten tin salt to deposit 22.2 g tin. What is the oxidation state of tin in salt. Atomic wt. of Sn = 118.69 g.

➤ **Problem 18.** Calculate the number of kw-h of electricity is necessary to produce 1.0 metric ton (1000 kg) of aluminium by the Hall process in a cell operating at 15.0 V.

➤ **Problem 19.** How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with a thickness of 0.005 mm? Density of Ag is 10.5 g cm^{-3}.

➤ **Problem 20.** Write the nernst equation and e.m.f. of the following cells at 298 K :

(a) $Mg(s) \mid Mg^{2+}\ (0.001\ M) \parallel Cu^{2+}\ (0.0001\ M) \mid Cu(s)$

(b) $Fe(s) \mid Fe^{2+}\ (0.001\ M) \parallel H^+\ (1\ M) \mid H_2(g)\ (1\ \text{bar}) \mid Pt(s)$

(c) $Sn(s) \mid Sn^{2+}\ (0.050\ M) \parallel H^+\ (0.020\ M) \mid H_2(g)\ (1\ \text{bar}) \mid Pt(s)$

(d) $Pt(s) \mid Br_2(l) \mid Br^-(0.010\ M) \parallel H^+(0.030\ M) \mid H_2(g)(1\ \text{bar}) \mid Pt(s)$

Given : E°_{OP} Mg = 2.36 V, E°_{OP} Cu = – 0.34 V, E°_{OP} Fe = 0.44 V, E°_{OP} Sn = 0.14 V and E°_{OP} Br_2 = – 1.09 V respectively.

➤ **Problem 21.** Calculate e.m.f. of half cells given below :

(a) $\begin{array}{c|c} Pt_{H_2} & H_2SO_4 \\ 4\ \text{atm} & 0.02\ M \end{array}$ $\quad E^\circ_{OP} = 0$ V

(b) $\begin{array}{c|c} Fe & FeSO_4 \\ & 0.2\ M \end{array}$ $\quad E^\circ_{OP} = 0.44$ V

(c) $\begin{array}{c|c} Pt_{Cl_2} & HCl \\ 10\ \text{atm} & 0.02\ M \end{array}$ $\quad E^\circ_{OP} = -1.36$ V

➤ **Problem 22.** For the cell :

$$Zn \left| \begin{array}{c} Zn^{2+}_{aq.} \\ 1\,M \end{array} \right\| \begin{array}{c} Cu^{2+}_{aq.} \\ 2\,M \end{array} \Bigg| \ Cu$$

Calculate the values for ;

(a) cell reaction,

(b) E°_{cell},

(c) E_{cell}

(d) the minimum concentration of Cu^{2+} at which cell reaction is spontaneous if Zn^{2+} is 1 *M*,

(e) does the displacement of Cu^{2+} goes almost to completion.

Given : $E^\circ_{RP_{Cu^{2+}/Cu}} = +0.35$ V

$E^\circ_{RP_{Zn^{2+}/Zn}} = -0.76$ V

➤ **Problem 23.** Calculate the pH of the following half cells solutions and also the molarity of acids :

(a) $\underset{1\ \text{atm}}{Pt_{H_2}} \mid H_2SO_4$ $\qquad E = 0.05$ V

(b) $\underset{1\ \text{atm}}{Pt_{H_2}} \mid HCl$ $\qquad E = 0.4$ V

➤ **Problem 24.** The e.m.f. of a cell corresponding to the reaction :

$$Zn(s) + 2H^+(aq) \longrightarrow \underset{(0.1M)}{Zn^{2+}} + \underset{(1\ \text{atm})}{H_2(g)}$$

is 0.28 V at 25°C and $E^\circ_{Zn/Zn^{2+}} = 0.76$ V.

(i) Write half cell reactions.

(ii) Calculate pH of the solution at H electrode.

➤ **Problem 25.** The e.m.f. of the cell $M \mid M^{n+}$ (0.02 *M*) ∥ H^+ (1*M*) $H_{2(g)}$ (1 atm) Pt at 25°C is 0.81 V. Calculate the valence of metal if $E^\circ_{M/M^{n+}} = 0.76$ V.

➤ **Problem 26.** The e.m.f. of cell Ag | $AgI_{(s)}$, 0.05 *M* KI ∥ 0.05 *M* $AgNO_3$ | Ag is 0.788 V. Calculate solubility product of AgI.

➤ **Problem 27.** E° of some oxidants are given as :

$$I_2 + 2e \longrightarrow 2I^- \qquad E^\circ = +0.54\ \text{V}$$

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \qquad E^\circ = +1.52\ \text{V}$$

$$Fe^{3+} + e \longrightarrow Fe^{2+} \qquad E^\circ = +0.77\ \text{V}$$

$$Sn^{4+} + 2e \longrightarrow Sn^{2+} \qquad E^\circ = +0.1\ \text{V}$$

(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below :

(i) $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$

(ii) $2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$

(iii) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$

(iv) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

➤ **Problem 28.** Given the standard electrode potentials;

$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V.

Arrange these metals in their increasing order of reducing power.

➤ **Problem 29.** Two metals *A* and *B* have $E°_{RP} = +0.76$ V and -0.80 V respectively. Which will liberate H_2 from H_2SO_4?

➤ **Problem 30.** Calculate the standard cell potentials of galvanic cell in which the following reactions take place :

(Given $E°_{OP}$ Cr, Cd, Fe^{2+}, Ag are 0.74 V, 0.40 V, – 0.77 V and – 0.80 V respectively)

(a) $2Cr_{(s)} + 3Cd^{2+}_{(aq.)} \longrightarrow 2Cr^{3+}_{(aq.)} + 3Cd$

(b) $Fe^{2+}_{(aq.)} + Ag^{+}_{(aq.)} \longrightarrow Fe^{3+}_{(aq.)} + Ag_{(s)}$

Calculate the $\Delta_rG°$ and equilibrium constant of the reactions.

Answers

1. See solution; **2.** (a) 1 F, (b) 4.44 F;
3. (a) 2 F, (b) 1 F;
4. (a) 1.51×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained;
5. 2.5×10^{19} electrons; **6.** 4.12 ampere;
7. 17.87 hr; **8.** 6.03×10^{23} electrons;
9. 14.4 minute, Zn = 0.437 g, Cu = 0.427 g;
10. 0.0696 litre O_2, 0.139 litre H_2; **11.** 1.825 g;
12. 2 *M*; **13.** 19.06 g ;
14. 3.29 litre; **15.** 5917.45 coulomb;
16. 107.47, 55.4 second; **17.** +2;
18. 4.47×10^4 kw-h; **19.** 125.09 sec.;
20. (a) 2.67 V, (b) 0.53 V, (c) 0.08 V, (d) –1.06 V;
21. (a) +0.100 V, (b) +0.4606 V, (c) –1.49 V;
22. (a) See solution, (b) 1.1 V, (c) 1.109 V, (d) $> 5.13 \times 10^{-38}$, (e) yes;
23. (a) pH = 0.8475, 0.071 *M*, (b) pH = 1.6949, 0.020 *M*;
24. pH = 8.635 ; **25.** 2;
26. 1.10×10^{-16};
27. (a) Strongest reductant = Sn^{2+}, weakest oxidant = Sn^{4+},
(b) Strongest oxidant = MnO_4^-, weakest reductant = Mn^{2+},
(c) (i) non-spontaneous, (ii) non-spontaneous,
(iii) non-spontaneous, (iv) spontaneous;
28. Ag < Hg < Cr < Mg < K; **29.** *B* will liberate H_2 from H_2SO_4;
30. (a) 3.17×10^{34}, (b) 3.22

Solutions

Solution 1. At cathode : $Ca^{2+} + 2e \longrightarrow Ca;$

At anode : $2H^{-} \longrightarrow H_2 + 2e$

Solution 2. **(a)** (w/E) Eq. of Ca $= \dfrac{i.t}{96500}$

$(Ca^{2+} + 2e \longrightarrow Ca)$ $\therefore$ Eq.wt. of Ca $= \dfrac{40}{2}$

or $\dfrac{20}{40/2} = \dfrac{i.t}{96500}$

or $i.t = 1 \times 96500 = \mathbf{1\ F}$

(b) Eq. of Al $= \dfrac{i.t}{96500}$

$(6e + Al_2^{3+} \longrightarrow 2Al)$ $\therefore$ Eq.wt. of Al $= \dfrac{27}{6/2}$

or $\dfrac{40}{27/3} = \dfrac{i.t}{96500}$

or $i.t = \dfrac{120}{27} \times 96500 = \mathbf{4.44\ F}$

Solution 3. **(a)** Eq. of $H_2O = \dfrac{i.t}{96500}$

1 mole H_2O = 2 eq.

$[2H_2O \longrightarrow 4H^{+} + 4e + O_2 \ \therefore\ E_{H_2O} = \dfrac{M_{H_2O}}{2}]$

$$2 = \frac{i.t}{96500}$$

$i.t = 96500 \times 2C = \mathbf{2\ F}$

(b) Eq. of FeO $= \dfrac{i.t}{96500}$

$[2Fe^{2+} \longrightarrow Fe_2^{3+} + 2e \ \therefore\ E_{FeO} = M_{FeO}]$

Valence factor for FeO = 1

or $1 = \dfrac{i.t}{96500}$

$i.t = 96500\ C = \mathbf{1\ F}$

Solution 4. (a) Eq. of Br^- used = $\frac{2}{80}$ for $2Br^- \longrightarrow Br_2 + 2e$

$\because$ 1 eq. of an element involve = 1 Faraday charge

$= 6.023 \times 10^{23}$ electrons

$$\therefore \quad \frac{2}{80} \text{ eq. of } Br^- \text{ involve} = \frac{6.023 \times 10^{23} \times 2}{80}$$

$$= \mathbf{1.51 \times 10^{22}} \textbf{ electrons lost}$$

(b) Similarly, calculate for $Cu^{2+} + 2e \longrightarrow Cu$

No. of electrons gained = 1.89×10^{22}

Solution 5. Total charge passed in 1 sec. = 4 × 1 = 4 coulomb ($\because$ $Q = i \times t$)

$\therefore$ 1 Faraday or 96500 C current carried by = 6.023×10^{23} electrons

$$\therefore \quad 4 \text{ coulomb current carried by} = \frac{6.023 \times 10^{23} \times 4}{96500}$$

$$= \mathbf{2.5 \times 10^{19}} \textbf{ electrons}$$

Solution 6. $\because \quad w = \frac{E.i.t.}{96500}$; $\therefore \quad i = \frac{96500 \times w}{E.t.}$

$$\left[\begin{array}{l} \because Zn^{2+} + 2e \longrightarrow Zn \\ \therefore E = \frac{\text{At. wt.}}{2} = \frac{65}{2} \end{array}\right]$$

$$i = \frac{96500 \times 10 \times 2}{65 \times 2 \times 60 \times 60} = \mathbf{4.12} \textbf{ ampere}$$

Solution 7. $H_2O \longrightarrow H_2 + ½O_2$

$$\left[\begin{array}{l} 2H^+ + 2e \longrightarrow H_2 \\ O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e \end{array}\right]$$

$$\therefore \quad \text{Eq. of } H_2O = \frac{i.t}{96500}$$

Equivalent weight of H_2O = 18/2 as two electrons are used for 1 mole H_2O to decompose in H_2 and O_2.

$$\frac{18}{18/2} = \frac{3 \times t}{96500}$$

t = 64333.3 sec = 1072.2 minute = **17.87 hr**

Solution 8. $\because$ 96500 coulomb deposits 107.9 g Ag or *E* g Ag or *A* g Ag, where *E* and *A* are equivalent weight and atomic weight of Ag respectively. *E* = *A* because Ag is monovalent. Thus 96500 coulomb charge means charge on *N* electrons where *N* in Av. no.

Thus $N \times e = 96500$

$$N = \frac{96500}{1.60 \times 10^{-19}} = \mathbf{6.03 \times 10^{23}} \textbf{ electrons}$$

Solution 9. $(Ag^+ + e \longrightarrow Ag \;\therefore\; E_{Ag} = \frac{108}{1})$

$$\text{Eq. of Zn} = \text{Eq. of Cu} = \text{Eq. of Ag} = \frac{i.t}{96500}$$

or $$\frac{1.45}{108/1} = \frac{1.5 \times t}{96500}$$

$$\mathbf{t = 864\ sec = 14.4\ min}$$

$(Zn^{2+} + 2e \longrightarrow Zn \;\therefore\; E_{Zn} = \frac{65}{2})$

Now $$\text{Eq. of Zn} = \frac{w}{E} = \frac{1.5 \times 864}{96500} = 0.0134$$

$$w_{Zn} = \frac{65 \times 0.0134}{2} = \mathbf{0.437\ g}$$

$(Cu^{2+} + 2e \longrightarrow Cu \;\therefore\; E_{Cu} = \frac{63.6}{2})$

Also Eq. of Cu = 0.0134

$$\therefore \quad w_{Cu} = \frac{0.0134 \times 63.6}{2} = \mathbf{0.427\ g}$$

Solution 10. At cathode : $2H_2O + 2e \longrightarrow H_2 + 2OH^-$

At anode : $2H_2O \longrightarrow 4H^+ + 4e + O_2$

$\therefore$ **At anode** $E_{O_2} = \frac{32}{4} = 8$

$$\therefore \quad w_{O_2} = \frac{E.i.t.}{96500} = \frac{32 \times 2 \times 10 \times 60}{4 \times 96500} = 0.0995\ g$$

At NTP : Volume of $O_2 = \frac{0.0995 \times 22.4}{32} = \mathbf{0.0696\ litre}$

Similarly **at cathode** $w_{H_2} = \frac{E.i.t.}{96500} = \frac{2 \times 2 \times 10 \times 60}{2 \times 96500} = 0.0124\ g$

At NTP : Volume of $H_2 = \frac{0.0124 \times 22.4}{2} = \mathbf{0.139\ litre}$

Solution 11. Eq. of Ni deposited $\frac{w}{E} = \frac{i.t}{96500} = \frac{5 \times 20 \times 60}{96500} = 0.0622$

or $$w_{Ni} = 0.0622 \times 58.71/2 = \mathbf{1.825\ g}$$

$(Ni^{2+} + 2e \longrightarrow Ni)$

Solution 12. The electrolysis of $Ni(NO_3)_2$ in presence of Ni electrode will bring in following changes:

At anode : $$Ni \longrightarrow Ni^{2+} + 2e$$

At cathode : $$Ni^{2+} + 2e \longrightarrow Ni$$

$$\text{Eq. of } Ni^{2+} \text{ formed} = \text{Eq. of } Ni^{2+} \text{ lost}$$

Thus, there will be no change in conc. of $Ni(NO_3)_2$ solution during electrolysis *i.e.*,

It will remain 2 *M*.

Solution 13. $$\text{Current Strength} = \frac{\text{Watt}}{\text{Volt}} = \frac{100}{110} = 0.909 \text{ ampere}$$

Given, $t = 10 \times 60 \times 60$ sec., $E_{Cd} = \frac{112.4}{2}$ $\quad (Cd^{2+} + 2e \longrightarrow Cd)$

$$w = \frac{E.i.t.}{96500}$$

$$w = \frac{112.4 \times 0.909 \times 10 \times 60 \times 60}{2 \times 96500}$$

$$= \mathbf{19.06\ g}$$

Solution 14. **At cathode :** $$Mg^{2+} + 2e \longrightarrow Mg$$

At anode : $$2Cl^- \longrightarrow Cl_2 + 2e$$

$\because$ Equivalent of Mg formed at cathode = Equivalent of Cl_2 formed at anode

$$\therefore \quad \frac{6.5}{24.3/2} = \frac{w_{Cl_2}}{35.5}$$

$$\therefore \quad w_{Cl_2} = 18.99 \text{ g}$$

At NTP, $$PV = \frac{w}{m} RT$$

$$\therefore \quad 2 \times V = \frac{18.99}{71} \times 0.0821 \times 300$$

$\therefore$ Volume of Cl_2 = **3.29 litre**

Solution 15. $$\text{Eq. of metal} = \frac{i.t}{96500}$$ $(i = 10 \text{ ampere}, t = 330 \text{ sec.})$

$$\frac{1.95}{E} = \frac{10 \times 330}{96500}$$

$$E_{\text{metal}} = 57.0$$

$$\text{At. wt. of metal} = 57.0 \times 2$$ (metal is bivalent as salt is MF_2)

$$= 114.0$$

Also, if $w_{Cu} = 1.95$ g, then

$$\text{Eq. of Cu} = \frac{i.t}{96500}$$

or $$\frac{1.95}{63.6/2} = \frac{i.t}{96500}$$

$\therefore$ $$i.t. = Q = \mathbf{5917.45\ coulomb}$$

Solution 16. $$\text{Eq. of metal} = \text{Eq. of iodine} = \text{Eq. of hypo} = \frac{i.t.}{96500}$$

$\therefore$ $$\frac{0.617}{E} = \frac{46.3}{1000} \times 0.124 \times 1$$

$$[\text{For hypo}: 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e;\ E = \frac{M}{1}]$$

$\therefore$ $$E = 107.47$$

Also, $$\frac{10 \times t}{96500} = \frac{46.3}{1000} \times 0.124 \times 1$$

$\therefore$ $$t = \mathbf{55.4\ second}$$

Solution 17. $$\text{Eq. of tin} = \frac{i.t}{96500}$$

$$\frac{22.2}{E} = \frac{2\times5\times60\times60}{96500}$$

$$E_{tin} = 59.5$$

$\therefore$ $$\text{Valence of tin} = \frac{A}{E} = \frac{118.69}{59.5} = 2 \text{ (an integer)}$$

Thus $Sn^{2+} + 2e \longrightarrow Sn$ or tin is in **+2 oxidation state.**

Solution 18. $$Al^{3+} + 3e \longrightarrow Al$$

$$\text{Eq. of Al, } \frac{w}{E} = \frac{i.t}{96500}$$

$$i.t = \frac{1000\times10^3\times96500}{27/3} \qquad [E_{Al} = 27/3]$$

$$i.t = 107.22 \times 10^8 \text{ ampere-sec or coulomb}$$

$$E = \text{Coulomb} \times \text{volt} = 107.22 \times 10^8 \times 15.0 = 1.61 \times 10^{11} \text{ J-sec}$$

or $$E = 1.61 \times 10^{11} \text{ watt-sec}$$

$$= \frac{1.61\times10^{11}}{10^3} \times \frac{1}{3600} \text{ kw-hr}$$

$$= \mathbf{4.47 \times 10^4\ kw\text{-}h}$$

Solution 19. Given, $i = 3$ ampere

Also Volume covered by Ag = $80 \times 0.005 \times 10^{-1}\ cm^3 = 0.04\ cm^3$

$$\therefore \quad \text{Weight of Ag used} = 0.04 \times 10.5 \text{ g}$$

$$w_{Ag} = \frac{E.i.t.}{96500}$$

$$0.04 \times 10.5 = \frac{108 \times 3 \times t}{96500}$$

$$\therefore \quad t = \mathbf{125.09 \text{ sec.}}$$

Solution 20. (a)

$$E_{Cell} = E^\circ_{OP_{Mg/Mg^{2+}}} + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Mg^{2+}]}$$

$$= 2.36 + 0.34 + \frac{0.059}{2}\log\frac{10^{-4}}{10^{-\text{[illegible]}}} = \mathbf{2.67 \text{ V}}$$

(b)

$$E_{Cell} = E^\circ_{OP_{Fe/Fe^{2+}}} + E^\circ_{RP_{2H^+/H_2}} + \frac{0.059}{2}\log\frac{[H^+]^2}{[P_{H_2}][Fe^{2+}]}$$

$$= 0.44 + 0 + \frac{0.059}{2}\log\frac{(1)^2}{(1)\times(0.001)} = \mathbf{0.53 \text{ V}}$$

(c)

$$E_{Cell} = E^\circ_{OP_{Sn/Sn^{2+}}} + E^\circ_{RP_{2H^+/H_2}} + \frac{0.059}{2}\log\frac{[H^+]^2}{(P_{H_2})\times[Sn^{2+}]}$$

$$= 0.14 + 0 + \frac{0.059}{2}\log\frac{(0.02)^2}{1\times 0.05} = \mathbf{0.08 \text{ V}}$$

(d)

$$E_{Cell} = E^\circ_{OP_{Br_2/Br^-}} + E^\circ_{RP_{2H^+/H_2}} + \frac{0.059}{2}\log\frac{[H^+]^2}{(P_{H_2})\times[Br^-]^2}$$

$$= -1.09 + 0 + \frac{0.059}{2}\log\frac{(0.03)^2}{1\times(0.01)^2} = \mathbf{-1.06 \text{ V}}$$

Solution 21. (a) $H_2 \longrightarrow 2H^+ + 2e$

$$\therefore \quad E_{OP} = E^\circ_{OP} - \frac{0.059}{2}\log\frac{[H^+]^2}{P_{H_2}} \qquad [H^+ = 0.02 \times 2M]$$

$$= 0 - \frac{0.059}{2}\log\frac{(0.02\times 2)^2}{4}$$

$$E_{OP_{H_2/H^+}} = \mathbf{+\,0.100 \text{ V}}$$

(b) $Fe \longrightarrow Fe^{2+} + 2e$

$$\therefore \quad E_{OP} = E^\circ_{OP} - \frac{0.059}{2}\log[Fe^{2+}]$$

$$= 0.44 - \frac{0.059}{2} \log [0.2]$$

$$E_{OP_{Fe/Fe^{2+}}} = \mathbf{+\,0.4606\ volt}$$

(c) $2Cl^- \longrightarrow Cl_2 + 2e$

$$\therefore \quad E_{OP} = E^\circ_{OP} - \frac{0.059}{2} \log \frac{P_{Cl_2}}{[Cl^-]^2}$$

$$= -1.36 - \frac{0.059}{2} \log \frac{10}{(0.02)^2}$$

$$E_{OP_{Cl^-/Cl_2}} = \mathbf{-1.49\ volt}$$

Solution 22. **(a)** E°_{OP} for $Cu/Cu^{2+} = -\,0.35$ V

E°_{OP} for $Zn/Zn^{2+} = +\,0.76$ V

More is E°_{OP}, more is tendency to show oxidation and thus Zn will oxidize and Cu^{2+} will reduce.

Anode : $Zn \longrightarrow Zn^{2+} + 2e$

Cathode : $Cu^{2+} + 2e \longrightarrow Cu$

Cell reaction : $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(b) Also, $E^\circ_{Cell} = E^\circ_{OP_{Zn/Zn^{2+}}} + E^\circ_{RP_{Cu^{2+}/Cu}} = 0.76 + 0.35 = \mathbf{1.1\ V}$

(c) Also, $E_{Cell} = E^\circ_{Zn/Zn^{2+}} + E_{Cu^{2+}/Cu}$

$$E_{Cell} = E^\circ_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2} \log [Zn^{2+}] + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2} \log [Cu^{2+}]$$

$$E_{Cell} = E^\circ_{OP_{Zn/Zn^{2+}}} + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= 0.76 + 0.35 + \frac{0.059}{2} \log \frac{2}{1}$$

$$E_{Cell} = \mathbf{1.109\ V}$$

(d) Also, $E_{Cell} = 1.1 + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$

Thus if E_{Cell} is +ve for $[Zn^{2+}] = 1$

$$\frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]} > -1.1$$

or $$\log \frac{[Cu^{2+}]}{[Zn^{2+}]} > -\frac{1.1 \times 2}{0.059}$$

$$> -37.29$$

or $$\log \frac{[Cu^{2+}]}{1} > -37.29$$

or $$[Cu^{2+}] > \mathbf{5.13 \times 10^{-38}}$$

(e) Yes, the displacement almost goes to completion.

Solution 23. (a) $H_2 \longrightarrow 2H^+ + 2e$

$$\therefore \quad E_{OP_{H/H^+}} = E^\circ_{OP_{H/H^+}} - \frac{0.059}{2} \log \frac{[H^+]^2}{P_{H_2}}$$

$$0.05 = 0 - \frac{0.059}{2} \log \frac{[H^+]^2}{1}$$

$$\therefore \quad -\log [H^+] = 0.8475$$

$$\therefore \quad pH = \mathbf{0.8475}$$

$$\therefore \quad [H^+] = 0.1420\ M$$

$$\therefore \quad \text{Molarity of } H_2SO_4 = \tfrac{1}{2}[H^+]$$

$$\therefore \quad = \tfrac{1}{2} \times 0.1420 = \mathbf{0.071\ M}$$

(b) Solve accordingly : pH = **1.6949**

$$\therefore \quad [H^+] = 0.020\ M$$

$$\therefore \quad \text{Molarity of HCl} = [H^+] = \mathbf{0.020\ M}$$

No change in calculation if any strong acid producing H^+ is given.

Solution 24. **(i) Anode :** $Zn \longrightarrow Zn^{2+} + 2e$

Cathode : $2H^+ + 2e \longrightarrow H_2$

(ii) $$E_{cell} = E^\circ_{OP_{Zn}} - \frac{0.059}{2} \log[Zn^{2+}] + E^\circ_{RP} \frac{0.059}{2} \log \frac{[H^+]^2}{P_{H_2}}$$

or $$E_{cell} = E^\circ_{OP_{Zn}} + 0 + \frac{0.059}{2} \log \frac{[H^+]^2}{P_{H_2} \times [Zn^{2+}]}$$

$$0.28 = 0.76 + \frac{0.059}{2} \log \frac{[H^+]^2}{0.1 \times 1}$$

or $$\log \frac{[H^+]^2}{0.1} = -\frac{0.48 \times 2}{0.059} = -16.271$$

or $$\frac{[H^+]^2}{0.1} = 5.3556 \times 10^{-17}$$

or $$[H^+] = 2.3142 \times 10^{-9}$$

$$\therefore \quad pH = -\log [H^+] = \mathbf{8.635}$$

Solution 25.

$$M \longrightarrow M^{n+} + ne$$

$$nH^+ + ne \longrightarrow \frac{n}{2}H_2$$

$$E_{Cell} = E_{OP_{M/M^{n+}}} + E_{RP_{H^+/H_2}}$$

$$= E^\circ_{OP_{M/M^{n+}}} - \frac{0.059}{n}\log[M^{n+}] + E^\circ_{RP_{H^+/H_2}} + \frac{0.059}{n}\log\frac{[H^+]^n}{[P_{H_2}]^{n/2}}$$

$$= 0.76 + \frac{0.059}{n}\log\frac{[H^+]^n}{[P_{H_2}]^{n/2}[M^{n+}]}$$

$$0.81 = 0.76 + \frac{0.059}{n}\log\frac{[1]^n}{[1]^{n/2}[0.02]}$$

or $n = 2$

Solution 26.

$$K_{sp} \text{ of AgI} = [Ag^+][I^-] = [Ag^+][0.05]$$

For given cell

$$E_{Cell} = E_{OP_{Ag}} + E_{RP_{Ag}} \qquad ...(1)$$

$$= E_{OP_{Ag/Ag^+}} - \frac{0.059}{1}\log[Ag^+]_{L.H.S.} + E_{RP_{Ag^+/Ag}} + \frac{0.059}{1}\log[Ag^+]_{R.H.S.}$$

$$E_{Cell} = \frac{0.059}{1}\log\frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}} \qquad \left[\because E^\circ_{OP_{Ag/Ag^+}} = E^\circ_{RP_{Ag^+/Ag}}\right]$$

$$0.788 = \log\frac{0.05}{[Ag^+]_{L.H.S.}}$$

$$\therefore \quad [Ag^+]_{L.H.S.} = 2.203 \times 10^{-15}$$

By eq. (1) $\quad K_{sp} = [2.203 \times 10^{-15}][0.05]$

$$K_{sp_{AgI}} = \mathbf{1.10 \times 10^{-16}}$$

Solution 27. (a) More or +ve the E°_{OP}, more is the tendency for oxidation or stronger is reductant. Therefore, since maximum E°_{OP} stands for :

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e \qquad E^\circ_{OP} = -0.1 \text{ V}$$

$\therefore$ strongest reductant : **Sn^{2+}**

and weakest oxidant : **Sn^{4+}**

(b) More or +ve is E°_{RP}, more is the tendency for reduction or stronger is oxidant. Therefore, since maximum E°_{RP} stands for :

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \qquad E^\circ_{RP} = +1.52 \text{ V}$$

∴ strongest oxidant : MnO_4^-
and weakest reductant : Mn^{2+}

Note: Stronger is oxidant, weaker is its conjugate reductant and *vice-versa.*

(c) For (i) $E^\circ_{Cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Sn^{2+}/Sn^{3+}}} = -0.77 + 0.1$

∵ Fe^{2+} oxidizes and Sn^{4+} reduces in change.

$E^\circ_{Cell} = \mathbf{-0.67\ V}$

E°_{Cell} is negative.

∴ **(i) Is non-spontaneous change.**

For (ii) $E^\circ_{Cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{I_2/I^-}}$

$= -0.77 + 0.54 = \mathbf{-0.23\ V}$

∴ **(ii) Is non-spontaneous change.**

For (iii) $E^\circ_{Cell} = E^\circ_{OP_{I^-/I_2}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}}$

$= -0.54 + 0.1 = \mathbf{-0.44\ V}$

∴ **(iii) Is non-spontaneous change.**

For (iv) $E^\circ_{Cell} = E^\circ_{OP_{Sn^{2+}/Sn^{4+}}} + E^\circ_{RP_{I_2/I^-}}$

$= -0.1 + 0.54 = \mathbf{+0.44\ V}$

(iv) Is spontaneous change.

Solution 28. More is E°_{RP}, more is the tendency to get reduced or more is the oxidising power or lesser is reducing power.

Ag < Hg < Cr < Mg < K

Solution 29. Given,

For A $A^{n+} + ne \longrightarrow A$ $E^\circ_{RP} = +0.76V$

For B $B^{n+} + ne \longrightarrow B$ $E^\circ_{RP} = -0.80\ V$

We have, for H $H^+ + e \longrightarrow ½H_2$ $E^\circ_{RP} = 0$

Now coupling A with H_2SO_4 :

$$2A + nH_2SO_4 \longrightarrow A_2(SO_4)_n + nH_2$$

$$E^\circ_{Cell} = E^\circ_{OP_A} + E^\circ_{RP_H} = -0.76 + 0.0 = -0.76\ V$$

Since E° is +ve,

Reaction $2A + nH_2SO_4 \longrightarrow A_2(SO_4)_n + nH_2$ is non-spontaneous

***A* will not liberate H_2 from H_2SO_4**

Now coupling B with H_2SO_4

$$2B + nH_2SO_4 \longrightarrow B_2(SO_4)_n + nH_2$$

$$E^\circ_{Cell} = E^\circ_{OP_B} + E^\circ_{RP_H} = +0.80 + 0 = +0.80$$

Since E° is +ve;

∴ $2B + nH_2SO_4 \longrightarrow B_2(SO_4)_n + nH_2$

Reaction will be spontaneous.

***B* will liberate H_2 from H_2SO_4.**

Solution 30. **(a)** $E^\circ_{Cell} = E^\circ_{OP_{Cr/Cr^{3+}}} + E^\circ_{RP_{Cd^{2+}/Cd}}$

$[2Cr \longrightarrow 2Cr^{3+} + 6e; \quad 3Cd^{2+} + 6e \longrightarrow 3Cd]$

$= 0.74 + (-0.40) = +0.34$ V

Six electrons ($n = 6$) are used in redox change.

$-\Delta_r G^\circ = nE^\circ F = 6 \times 0.34 \times 96500 \text{ J} = 196860 \text{ J}$

or $\Delta_r G^\circ = -196.86 \text{ kJ}$

Also $-\Delta_r G^\circ = 2.303\, RT \log K$

$\therefore$ $196860 = 2.303 \times 8.314 \times 298 \log K$

$K = 3.17 \times 10^{34}$

(b) $E^\circ_{Cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Ag^+/Ag}}$

$[Fe^{2+} \longrightarrow Fe^{3+} + e; \quad Ag^+ + e \longrightarrow Ag]$

$= -0.77 + 0.80 = 0.03$ V

Also $-\Delta_r G^\circ = nE^\circ F = 1 \times 0.03 \times 96500$

or $\Delta_r G^\circ = -2895 \text{ J}$

Also $-\Delta_r G^\circ = 2.303\, RT \log K$

$2895 = 2.303 \times 8.314 \times 298 \log K$

$K = 3.22$

Selected Problems with Solutions

➤ **Problem 1.** A current of 0.5 A is passed through acidulated water for 30 minute. Calculate weight of H_2 and O_2 evolved. Also calculate the volume of O_2 produced at 25°C and 760 mm of Hg if the gas is:
(a) dry
(b) saturated with water vapour (aqueous tension is 23.0 mm at 25°C).

➤ **Problem 2.** Find the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 25°C and 1 atm.

➤ **Problem 3.** A copper cell containing 5% solution of $CuSO_4 \cdot 5H_2O$ and a silver cell containing a 2% solution of $AgNO_3$ by weight are connected in series. A current of 0.01 ampere was passed through the cells for 30 minute. What was the ratio of mass of Cu and Ag deposited at the cathode of cell. At. wt. of Cu and Ag are 63.6 and 108 respectively.

➤ **Problem 4.** Calculate the mass of benzene that would be required to produce a current of one ampere (Assume current efficiency 50%) for three hours from the following data:

$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$$

➤ **Problem 5.** Same quantity of electricity being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x liberated at cathode is 0.617 g and the liberated iodine completely reduced by 46.3 mL of 0.124 M sodium thio-sulphate solution. What is equivalent weight of metal.

➤ **Problem 6.** A test for complete removal of Cu^{2+} ions from a solution of Cu^{2+}(aq.) is to add NH_3(aq.). A blue colour signifies the formation of complex $[Cu(NH_3)_4]^{2+}$ having $K_f = 1.1 \times 10^{13}$ and thus confirms the presence of Cu^{2+} in solution. 250 mL of 0.1 M $CuSO_4$(aq.) is electrolysed by passing a current of 3.512 ampere for 1368 second. After passage of this charge sufficient quantity of NH_3(aq.) is added to electrolysed solution maintaining $[NH_3] = 0.10\ M$. If $[Cu(NH_3)_4]^{2+}$ is detectable upto its concentration as low as 1×10^{-5}, would a blue colour be shown by the electrolysed solution on addition of NH_3.

➤ **Problem 7.** A Zn rod weighing 25 g was kept in 100 mL of 1 M $CuSO_4$ solution. After a certain time the molarity of Cu^{2+} in solution was 0.8. What was molarity of SO_4^{2-}? What was the weight of Zn rod after cleaning? At. weight of Zn = 65.4.

➤ **Problem 8.** Assume that impure copper contains only Fe, Au and Ag as impurities. After passage of 140 ampere for 482.5 sec, the mass of anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Calculate the percentage of iron and percentage of copper originally present.

► **Problem 9.** 50 mL of 0.1 *M* $CuSO_4$ solution is electrolysed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate $[Cu^{2+}]$, $[H^+]$ and $[SO_4^{2-}]$ after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes?

► **Problem 10.** An oxide of metal (at. wt. = 112) contains 12.5% O_2 by weight. The oxide was converted into chloride by treatment with HCl and electrolysed. Calculate the amount of metal that would be deposited at cathode if a current of 0.965 ampere was passed for a period of 5 hr. What is valency of metal?

► **Problem 11.** 19 g fused $SnCl_2$ was electrolysed using inert electrodes. 0.119 g Sn was deposited at cathode. If nothing was given out during electrolysis, calculate the ratio of weight of $SnCl_2$ and $SnCl_4$ in fused state after electrolysis (at. wt. Sn = 119).

► **Problem 12.** A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g mL^{-1} at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. How many faraday have left the anode of battery? Note the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is:

$$Pb_{(s)} + PbO_2 + 2H_2SO_{4(l)} \longrightarrow 2PbSO_{4\,(s)} + 2H_2O$$

► **Problem 13.** Two litre solution of a buffer mixture containing 1.0 *M* NaH_2PO_4 and 1.0 *M* Na_2HPO_4 is placed in two compartments (one litre in each) of an electrolytic cell. The platinum electrodes are inserted in each compartment and 1.25 ampere current is passed for 212 minute. Assuming electrolysis of water only at each compartment. What will be pH in each compartment after passage of above charge? pK_a for $H_2PO_4^- = 2.15$.

► **Problem 14.** A current of 40 microampere is passed through a solution of $AgNO_3$ for 32 minute using Pt electrodes. An uniform single atom thick layer of Ag is deposited covering 43% cathode surface. What is the total surface area of cathode if each Ag atom covers 5.4×10^{-16} cm^2?

► **Problem 15.** Suppose a fully charged battery contains 1.50 litre of 5.0 *M* H_2SO_4. What will be the concentration of H_2SO_4 left in battery after 2.50 ampere current is drawn from the battery for 6.0 hours. Assume volume of solution remains constant.

► **Problem 16.** In an analytical determination of arsenic, a solution containing arsenious acid, H_3AsO_3, KI and a small amount of starch is electrolysed. The electrolysis produces free I_2 from I^- ion and the I_2 immediately oxidises the arsenious acid to hydrogen arsenate ion, $HAsO_4^{2-}$,

$$I_{2(aq)} + H_3AsO_{3(aq)} + H_2O_{(l)} \longrightarrow 2I^-_{(aq)} + HAsO^{2-}_{4(aq)} + 4H^+_{(aq)}$$

When the oxidation of arsenic is complete, the free iodine combines with the starch to give a deep blue colour. If during a particular run, it takes 65.3 s for a current of 10.5 mA to give an end point (indicated by the blue colour), how many grams of arsenic and H_3AsO_3 are present in the solution. (As = 75)?

➤ **Problem 17.** The half cell potentials of a half cell $A^{(x+n)+}, A^{x+} \mid Pt$ were found to be as follows:

% of reduced form	24.4	48.8
Half cell potential (V)	0.101	0.115

Determine the value of *n*.

➤ **Problem 18.** Find the e.m.f. of the following cell at 18°C taking the degree of dissociation of 0.2 *N* $AgNO_3$ and 0.05 $AgNO_3$ solution as 0.75 and 0.95 respectively.

$$Ag \mid 0.2\,N\,AgNO_3 \mid\mid 0.05\,AgNO_3 \mid Ag$$

➤ **Problem 19.** If $NO_3^- \longrightarrow NO_2$ (acid medium) ; $E° = 0.790$ V

and $NO_3^- \longrightarrow NH_2OH$ (acid medium) ; $E° = 0.731$ V

At what pH the above two half reactions will have same *E* values. Assume the concentrations of all other species be unity.

➤ **Problem 20.** If it is desired to construct the following voltaic cell to have $E_{cell} = 0.0860$ V, what $[Cl^-]$ must be present in the cathodic half cell to achieve the desired e.m.f. Given K_{SP} of AgCl and AgI are 1.8×10^{-10} and 8.5×10^{-17} respectively?

$$Ag(s) \mid Ag^+ \text{ [Sat. AgI(aq.)]} \parallel Ag^+ \text{ [Sat. } AgCl \cdot xMCl^- \mid Ag(s)]$$

➤ **Problem 21.** The e.m.f. of the cell obtained by combining Zn and Cu electrodes of a Daniel cell with N calomel electrodes are 1.083 V and − 0.018 V respectively at 25°C. If the potential of N calomel electrode is − 0.28 V, find e.m.f. of Daniel cell.

➤ **Problem 22.** Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1 *M* MnO_4^- and 0.8 *M* H^+ and which was treated with Fe^{2+} necessary to reduce 90% of MnO_4 to Mn^{2+}. $E°_{MnO_4/Mn^{2+}} = 1.51$ V.

➤ **Problem 23.** An electrode is prepared by dipping a silver strip into a solution saturated with AgSCN and containing 0.10 *M* SCN^-. The e.m.f. of voltaic cell constructed by connecting this, as the cathode, to the standard hydrogen half-cell as anode was found to be 0.45 V. What is the solubility product of AgSCN. Given $E°_{Ag^+/Ag} = 0.80$ V.

➤ **Problem 24.** Calculate the minimum weight of NaOH required to be added in R.H.S. to consume all the H^+ present in R.H.S. of cell of e.m.f. + 0.701 V at 25°C before its use. Also report the e.m.f. of cell after addition of NaOH.

$$Zn \left| \begin{matrix} Zn^{2+} \\ 0.1\,M \end{matrix} \right\| \begin{matrix} HCl \\ 1 \text{ litre} \end{matrix} \left| \begin{matrix} Pt_{H_2(g)} \\ 1 \text{ atm} \end{matrix} \right. \qquad E°_{Zn/Zn^{2+}} = +0.760 \text{ V} ,$$

▶ **Problem 25.** Consider the cell $Ag \mid AgBr_{(s)}, Br^- \parallel AgCl_{(s)}, Cl^- \mid Ag$ at 25°C. The solubility product of AgCl and AgBr are 1×10^{-10} and 5×10^{-13} respectively. For what ratio of the concentrations of Br^- and Cl^- ions would the e.m.f. of the cell be zero.

▶ **Problem 26.** Calculate the half cell potential of a reaction $Ag_2S + 2e \longrightarrow 2Ag + S^{2-}$ in a solution buffered at pH = 3 and also saturated with 0.1 M H_2S. K_1 and K_2 for H_2S are 10^{-8} and 1.1×10^{-13} respectively, $K_{SP_{Ag_2S}} = 2 \times 10^{-49}$, $E^\circ_{Ag^+/Ag} = 0.8$ V.

▶ **Problem 27.** The standard electrode potentials are for the following reactions:

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e \quad ; \qquad E^\circ = 0.48 \text{ V}$$

$$Cr^{3+} + e \longrightarrow Cr^{2+}(aq) \quad ; \qquad E^\circ = -0.41 \text{ V}$$

If excess of Fe(s) is added to a solution in which $[Cr^{3+}] = 1M$, what will be maximum value of $[Fe^{2+}]$ when equilibrium is attained at 298 K.

▶ **Problem 28.** The pK_{SP} of AgI is 16.07. If the E° value for Ag^+/Ag is 0.7991 V, find the E° for half cell reaction: $AgI_{(s)} + e \longrightarrow Ag + I^-$

▶ **Problem 29.** The e.m.f. of cell $Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$ at 25°C is 0.03 V and the temperature coefficient of e.m.f. is -1.4×10^{-4} V per degree. Calculate heat of reaction for the change taking place inside the cell.

▶ **Problem 30.** EMF diagram for some ions is given as:

$$FeO_4^{2-} \xrightarrow{E^\circ = +2.20 \text{ V}} Fe^{3+} \xrightarrow{E^\circ = +0.77 \text{ V}} Fe^{2+} \xrightarrow{E^\circ = -0.445 \text{ V}} Fe^0$$

Determine the value of $E_{FeO_4^{2-}/Fe^{2+}}$.

▶ **Problem 31.** For the cell $Mg_{(s)} \left| Mg^{2+}_{(aq.)} \right| \left| Ag^{+}_{(aq.)} \right| Ag(s)$, calculate the equilibrium constant at 25°C and the maximum work that can be obtained during operation of cell. Given,

$$E^\circ_{Mg/Mg^{2+}} = +2.37 \text{ V} \quad \text{and} \quad E^\circ_{Ag^+/Ag} = +0.80 \text{ V}, \quad R = 8.314 \text{ J}$$

▶ **Problem 32.** The standard reduction potential of $E^\circ_{Bi^{3+}/Bi}$ and $E^\circ_{Cu^{2+}/Cu}$ are 0.226 V and 0.344 V respectively. A mixture of salts of Bi and Cu at unit concentration each is electrolysed at 25°C. To what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit during electrolysis.

▶ **Problem 33.** Show that the potentials are additive for the process in which half reactions are added to yield an overall reaction but they are not additive when added to yield a third half reaction.

▶ **Problem 34.** The reduction potential diagram for Cu in acid solution is:

$$\begin{tikzcd} Cu^{2+} \arrow[r, "+0.15 \text{ volt}"] \arrow[rr, bend right, "E^\circ = X \text{ volt}"'] & Cu^{+} \arrow[r, "+0.50 \text{ volt}"] & Cu \end{tikzcd}$$

Calculate X. Does Cu^+ disproportionate in solution?

➤ Problem 35. An alloy weighing 1.05 g of Pb — Ag was dissolved in desired amount of HNO_3 and the volume was made 350 mL. An Ag electrode was dipped in solution and E_{cell} of the cell $Pt\ \underset{1\ atm}{H_2} \mid \underset{1M}{H^+} \parallel Ag^+ \mid Ag$ was 0.503V at 298K.

Calculate the percentage of lead in alloy. Given $E^\circ_{Ag^+/Ag} = 0.80$ V.

➤ Problem 36. The following galvanic cell was

$$Zn \left| \begin{array}{c} Zn(NO_3)_{2(aq)} \\ 100\ mL,\ 1\ M \end{array} \right\| \begin{array}{c} Cu(NO_3)_{2(aq)} \\ 100\ mL,\ 1\ M \end{array} \right| Cu$$

operated as an electrolytic cell using Cu as anode and Zn as cathode. A current of 0.48 ampere was passed for 10 hour and then the cell was allowed to function as galvanic cell. What would be the e.m.f of the cell at 25°C? Assume that the only electrode reactions occurring were those involving Cu/Cu^{2+} and Zn/Zn^{2+}. Given $E^\circ_{Cu^{2+}/Cu} = +0.34$ V and $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

➤ Problem 37. At 25°C, the free energy of formation of $H_2O_{(l)}$ is −56700 cal/mol while that of its ionisation to H^+ and OH^- is 19050 cal mol^{-1}. What is the e.m.f. of cell at 25°C.

➤ Problem 38. Peroxodisulphate salts (*e.g.*, $Na_2S_2O_8$) are strong oxidising agents used as bleaching agents for fats, oils and fabrics. Can oxygen gas oxidise sulphate ion to peroxodisulphate ion ($S_2O_8^{2-}$) in acidic solution, with the O_2 (g) being reduced to water?

Given $O_2(g) + 4H^+(aq) + 4e \longrightarrow 2H_2O$; $E^\circ = 1.23$ V

$S_2O_8^{2-}(aq) + 2e \longrightarrow 2SO_4^{2-}(aq)$; $E^\circ = 2.01$ V

➤ Problem 39. When silver chloride is dissolved in a large excess of ammonia, practically all silver ion can be assumed to exist in form of a single ionic species $[Ag_x(NH_3)_y]^{x+}$. Compute the values of x and y using the following two cells.

(a) $Ag \mid 0.4 \times 10^{-3}\ M\ AgCl,\ 1M\ NH_3 \parallel 40 \times 10^{-3}\ M\ AgCl,\ 1M\ NH_3 \mid Ag$

$E_{cell} = 0.1185$ V at 298 K

(b) $Ag \mid 3 \times 10^{-3}\ M\ AgCl,\ 1M\ NH_3 \parallel 3.0 \times 10^{-3}\ M\ AgCl,\ 0.1M\ NH_3 \mid Ag$

$E_{cell} = 0.1263$ V at 298 K.

➤ Problem 40. Dissociation constant for $Ag(NH_3)_2^+$ into Ag^+ and NH_3 is 6×10^{-14} Calculate E° for the half reaction,

$$Ag(NH_3)_2^+ + e \longrightarrow Ag + 2NH_3$$

Given, $Ag^+ + e \longrightarrow Ag$ has $E^\circ = 0.799$ V.

➤ Problem 41. Estimate the cell potential of a Daniel cell having 1.0 M Zn^{2+} and originally having 1.0 M Cu^{2+} after sufficient ammonia has been added to the cathode compartment to make the NH_3 concentration 2.0 M. Given $E^\circ_{Zn/Zn^{2+}}$ and $E_{Cu/Cu^{2+}}$ are 0.76 and − 0.34 V respectively. Also equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ formation is 1×10^{12}.

► **Problem 42.** Two weak acid solutions HA_1 and HA_2 each with the same concentration and having p*K*a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25°C) and are interconnected through a salt bridge. Find. e.m.f. of cell.

► **Problem 43.** Calculate the e.m.f. of cell

$$\mathrm{Pt}_{H_2}\ \underset{1\ \text{atm}}{}\left|\ \underset{0.1\ M}{CH_3COOH}\ \right|\left|\ \underset{0.01\ M}{NH_4OH}\ \right|\ \underset{1\ \text{atm}}{\mathrm{Pt}_{H_2}}$$

K_a for $CH_3COOH = 1.8 \times 10^{-5}$, K_b for $NH_4OH = 1.8 \times 10^{-5}$.

► **Problem 44.** Calculate the degree of hydrolysis and hydrolysis constant of $M/32$ solution of aniline hydrochloride from the following cell data.

$$\mathrm{Pt}\ \left|\ \underset{1\ \text{atm}}{H_2}\ \right|\ \underset{1\ M}{H^+}\ \left|\right|\ \frac{M}{32}\ C_6H_5NH_3^+Cl^-aq\ \left|\ \underset{1\ \text{atm}}{H_2}\ \right|\ \mathrm{Pt}\ ;\quad E_{cell} = -0.188\ \text{V}$$

Answers

1. $H_2 = 9.33 \times 10^{-3}$ g, $O_2 = 7.46 \times 10^{-2}$ g, (a) 5.7×10^{-2} litre, (b) 5.88×10^{-2} litre ;
2. 1.762 litre ; 3. 1/3.372
4. 0.582 g ; 5. 107.47 ;
6. Show blue colour ; 7. 23.692 g, no change molarity ;
8. Cu = 98.88%, Fe = 0.85% ;
9. $[Cu^{2+}] = 0.094\ M$, $[H^+] = 0.012\ M$, $[SO_4^{2-}] = 0.1\ M$;
10. 10.08 g, 2 ; 11. 71.34 ;
12. 1.255 Faraday ; 13. 2.005, 2.295 ;
14. 601.65 cm^3 ; 15. 4.63 ;
16. $As = 2.66 \times 10^{-4}$ g, $H_3AsO_3 = 5.0 \times 10^{-4}$ g ;
17. $n = 2$; 18. − 0.029 V ;
19. pH = 1.192 ; 20. $6.8 \times 10^{-4}\ M$;
21. 1.101 volt ; 22. 1.41 V ;
23. 1.169×10^{-7} ; 24. 1.264 g , 0.3765 V ;
25. $\frac{1}{200}$; 26. − 0.1658 V ;
27. 0.48 ; 28. − 0.1490 V ;
29. 13.842 kJ mol^{-1} ; 30. 1.84 V ;
31. 107.457, 3.17 V, 6.118×10^2 kJ ; 32. $10^{-4}\ M$;
33. See solution ; 34. X = +0.325 volt, +0.35 volt ;
35. 99.967% ; 36. 1.137 V ;
37. 0.892 V ; 38. O_2 will not oxidise ;
39. $x = 1$, $y = 2$; 40. +0.019 V ;
41. 0.71 V ; 42. +0.059 V ;
43. −0.4575 volt ; 44. 2.08×10^{-2}, 1.352×10^{-5}

Problems for Self Assessment

1. Calculate the quantity of charge required to reduce 16.2 g of *o*-benzoquinone ($C_6H_4O_2$) to hydroquinone ($C_6H_6O_2$) if current efficiency is 75%. If the potential drop across the cell is 2 volt, how much energy will be consumed.
2. Lactic acid, $HC_3H_5O_3$, produced in 1 g sample of muscle tissue was titrated using phenolphthalein as indicator against OH^- ions which were obtained by the electrolysis of water. As soon as OH^- ions are produced, they react with lactic acid and at complete neutralisation immediately a pink colour is noticed. If electrolysis was made for 115 second using 15.6 mA current to reach the end point, what was the percentage of lactic acid in muscle tissue.
3. Calculate the quantity of electricity in coulomb which liberates enough hydrogen at the cathode during electrolysis of acidified water so that it can fill a balloon of capacity 10 litre at a pressure of 1.5 atmosphere at 27°C. If the oxygen liberated is completely used in burning methane, calculate the volume of methane at STP which is burnt.
4. Anthracene ($C_{14}H_{10}$) can be oxidised anodically to anthraquinone ($C_{14}H_8O_2$). What weight of anthraquinone can be produced by passage of a current of 1 ampere for 60 minute if current efficiency in 80%?
5. Per di-sulphuric acid ($H_2S_2O_8$) can be prepared by electrolytic oxidation of H_2SO_4 as $2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e$. O_2 and H_2 are by-products. In such an electrolysis 0.87 g of H_2 and 3.36 g O_2 were generated at STP. Calculate the total quantity of current passed through solution to carry out electrolysis. Also report the weight of $H_2S_2O_8$ formed.
6. The electrode reactions for charging of a lead storage battery are

$$PbSO_4 + 2e \rightleftharpoons Pb + SO_4^{2-}$$

$$PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + SO_4^{2-} + 4H^+ + 2e$$

The electrolyte in the battery is an aqueous solution of sulphuric acid. Before charging, the specific gravity of liquid was found to be 1.11 g mL^{-1} (15.7% H_2SO_4 by weight). After charging for 100 hour, the specific gravity of liquid was found to be 1.28 g mL^{-1} (36.9% H_2SO_4 by weight). If the battery holds two litre liquid, calculate average current used for charging battery. Assume that volume remains constant during charging.

7. How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with a thickness of 0.005 mm? Density of Ag is 10.5 g cm^{-3}.

8. H_2O_2 can be prepared by successive reactions,

$$2NH_4HSO_4 \longrightarrow H_2 + (NH_4)_2S_2O_8$$
$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$$

The first reaction is an electrolytic reaction and second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 g pure H_2O_2 per hr? Assume current efficiency 50%.

9. A current of 15 ampere is used to plate Ni from $NiSO_4$ bath. Both H_2 and Ni are formed at cathode. The current efficiency of Ni formation is 60%.

(a) How many g of Ni is plated per hr?

(b) What is the thickness of plating if the cathode consists of a sheet of 4 cm^2 which is coated on both sides? The density of Ni is 8.9 g mL^{-1}.

(c) What volume of H_2 is formed per hr at STP?

(d) What volume of O_2 is formed per hr at STP?

10. A solution of a salt of a metal of atomic weight 'm' was electrolysed for 150 minute by passing a current of 0.15 ampere. The weight of metal deposited was 0.783 g. Find atomic weight of metal. Given specific heat of metal is 0.057 cal/g.

11. In a zinc-manganese dioxide cell, the anode is made up of Zn and cathode of carbon rod surrounded by a mixture of MnO_2, carbon, NH_4Cl and $ZnCl_2$ in aqueous base. The cathodic reaction is,

$$2MnO_{2(s)} + Zn^{2+} + 2e \longrightarrow ZnMn_2O_{4(s)}$$

If 8 g MnO_2 is present in cathodic compartment, how many day the dry cell will continue to give a current of 4×10^{-3} ampere?

12. A battery available for the electrode reaction involves the use of 25% of the Pb and PbO_2 available in it for reaction. What should be the minimum mass of lead in the free and combined states in a battery designed to deliver 50 ampere hour? What is the standard free energy change for the reaction? Average voltage of lead storage battery is 2.0 V.

13. Calculate the number of coulombs derived by a Daniel cell, initially containing 1.0 litre each of 1.0 *M* Cu^{2+} ion and 1.0 *M* Zn^{2+} ion, which is operated untill its potential drops to 1.0 V.

14. Calculate the degree of dissociation and concentration of Ag ions in left hand side from the following data:

$$Ag \mid 0.01\,N\,AgNO_3 \mid\mid NH_4NO_3 \text{ saturated} \mid 0.001\,N\,AgNO_3 \mid Ag$$

The emf of cell is – 0.0579 V at 25°C and 0.00 *N* $AgNO_3$ is completely ionised.

15. Calculate the potential of iron-cadmiun cell after the reaction has proceeded to 80% completion. Initially 1 *M* of Fe^{2+} and Cd^{2+} were taken.

$E^\circ_{Fe/Fe^{2+}} = 0.44$ V ; $E^\circ_{Cd/Cd^{2+}} = 0.40$ V.

16. Determine the e.m.f. of the following cell:

$$Pb \mid PbSO_4 \text{ (saturated)}, SO_4^{2-} (1.0\,M) \mid\mid H^+ (1.0\,M) \mid H_2(1.0 \text{ atm}) \text{ Pt}$$

K_{SP} of $PbSO_4$ is 1.7×10^{-8}, $E^\circ_{Pb/Pb^{2+}} = 0.126$ V

17. Calculate the e.m.f. of the cell at 25°C,

$$\begin{array}{c|c||c|c} \text{Pb} & \text{PbSO}_4 & \text{PbI}_2 & \text{Pb} \\ & \text{Saturated} & \text{Saturated} & \\ & \text{solution} & \text{solution} & \end{array}$$

K_{SP} of $PbSO_4 = 1.6 \times 10^{-8}$ and K_{SP} of $PbI_2 = 8 \times 10^{-9}$.

18. Suppose that the standard hydrogen electrode was arbitrarily asigned a value of 0.1 volt for : $2e + 2H^+ \longrightarrow H_{2(g)}$. What will be the effect on the observed voltage under standard conditions for each of the following:

Zn — H_2 cell, Cu — H_2 cell, Zn — Cu cell

19. For a cell consisting of an inert electrode in a solution containing 0.10 M $KMnO_4$, 0.20 M $MnCl_2$ and 1.0 M HCl suitably connected to another inert electrode in a solution containing 0.1 M $K_2Cr_2O_7$, 0.20 M $CrCl_3$ and 0.70 M HCl. Calculate (Given, $E^\circ_{Mn^{7+}/Mn^{2+}} = 1.51$ V and $E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V)

(a) E for each half cell.
(b) E for cell.
(c) The overall redox change.

20. Write the cell reactions and calculate the e.m.f. of the cell given below if, $E^\circ_{Co^{2+}/Co^{3+}} = -1.82$ V and $E^\circ_{Cr_2^{6+}/Cr^{3+}} = 1.33$ V

$Pt \mid H^+ (1.5\ M), Cr^{3+} (0.5M), Cr_2O_7^{2-} (4.0\ M) \mid\mid Co^{2+} (2.0\ M), Co^{3+} (0.010\ M) \mid Pt$

21. Consider the following cell reactions in two different cells.

(I) $A + B \rightleftharpoons C + D$
(II) $2A + 2B \rightleftharpoons 2C + 2D$

How are the values of E° and K are related in there two cells.

22. How much Cu^{2+} ions are present at equilibrium when finely divided Ni is mixed with 0.05 M solution of $CuSO_4$? Given $Cu/Cu^{2+} = -0.337$ V and $Ni/Ni^{2+} = 0.25$ V.

23. For the reaction $Fe^{3+} + 3e \rightleftharpoons Fe$, E° is –0.036 V and the standard electrode potential for $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ is 0.771 V. Calculate the E° for $Fe^{2+} + 2e \rightleftharpoons Fe$.

24. From the following informations, calculate the overall stability constant K_{SP} of $Ag(S_2O_3)_2^{3-}$ at 25°C.

$Ag^+ + e \longrightarrow Ag$; $E^\circ = 0.799$ V
$Ag(S_2O_3)_2^{3-} + e \longrightarrow Ag + 2S_2O_3^{2-}$; $E^\circ = 0.017$ V

25. A cell designed below contains one litre of buffer mixture of CH_3COOH and CH_3COONa each 1 M in two compartments using platinum electrodes. pK_a for $CH_3COOH = 4.74$.

$$\begin{array}{c|c||c|c} \text{Pt} & CH_3COOH + CH_3COONa & CH_3COOH + CH_3COONa & \text{Pt} \\ H_2 & 1M \qquad 1M & 1M \qquad 1M & H_2 \\ 1\ \text{atm} & & & 1\ \text{atm} \end{array}$$

Calculate:

(i) The pH in each compartment,

(ii) The e.m.f. of cell,

(iii) The pH and e.m.f. of cell of each compartment after passage of 1.25 A current for 241.25 minute.

26. Calculate the e.m.f. of the cell at 18°C for:

$$\underset{1\text{ atm}}{\text{Pt H}_2} \left| N/10\text{ HCl} \right|\left| N\text{ KOH} \right| \underset{1\text{ atm}}{\text{Pt H}_2}$$

HCl is 90% dissociated and KOH is 75% ionised.

27. The e.m.f. of the cell Ag | AgCNS, KCNS(0.1*M*) || $AgNO_3$ (0.1 *M*) | Ag is 0.586 V. Neglecting the liquid junction potential calculate the $[Ag^+]$ in thiocyanate solution. Also report K_{SP} of AgCNS.

28. At what potential should a solution containing 1 *M* CuSO, 1 *M* $NiSO_4$ and 2*M* H_2SO_4 be electrolysed so as to deposit essentially none of the nickel and all of the copper leaving 1.0×10^{-9} Cu^{2+}. $E^{\circ}_{Cu/Cu^{2+}} = -0.34$ V ; $E^{\circ}_{Ni/Ni^{2+}} = 0.25$ V.

Answers

1. 0.428 F , 82714 J ;
2. 0.1673% ;
3. 1.175×10^5 C, 3.41 litre CH_4 ;
4. 1.0346 g ;
5. 83955 C , 43.65 g ;
6. 1.63 ampere ;
7. 125.09 second ;
8. 315.35 ampere ;
9. (a) 9.85 g , (b) 0.138 cm, (c) 2.51 litre, (d) 3.13 litre ;
10. 111.94 ;
11. 25.675 day ;
12. 1544 g, –386 kJ ;
13. ≈ 193000 C ;
14. $[Ag^+] = 9.58 \times 10^{-3}\,M$, $\alpha = 9.58 \times 10^{-1}$;
15. 0.0577 V ;
16. 0.585 V ;
17. 0.0295 V ;
18. Increase, Decrease, No change ;
19. (a) 1.31 V, 0.20 V (b) 1.51 V ,

(c) $6MnO_4^- + \underset{1M}{48H^+} + 10Cr^{3+} + 35H_2O \longrightarrow 6Mn^{2+} + 24H_2O + S$;

20. 0.32 V, $6Co^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 6Co^{3+} + 2Cr^{3+} + 7H_2O$;
21. $E^{\circ}_{\text{I cell}} = E^{\circ}_{\text{II cell}}$, $K_{\text{I cell}} = \sqrt{K_{\text{II cell}}}$;
22. 6.33×10^{-22} *M* ;
23. –0.4395 V ;
24. 1.8×10^{13} ;
25. (i) pH = 4.74, (ii) 0.0 V, (iii) Anode pH = 4.5752, Cathode pH = 4.9048, e.m.f. = –0.019 V ;
26. –0.756 V ;
27. 1.17×10^{-11} *M*, $K_{SP} = 1.17 \times 10^{-12}$;
28. 0.07 V.

8

Dilute Solutions and Colligative Properties

Chapter at a Glance

Laws of Osmotic pressure $\pi = h \times d \times g$ ...(1)

where h is height developed in column, d is density of fluid in column at equilibrium, g is gravity.

$$\pi \propto (n/v) \propto \text{concentration} \quad \text{...(2)}$$

$$\pi V = (w/m)\,ST = nST \quad \text{...(3)}$$

π is osmotic pressure, n is mole of solute present in V litre solution, w is weight of solute, m is mol. wt. of solute S is solution constant and T is temperature in K.

Isotonic solution $\pi_1 = \pi_2$ ...(4)

(for solutes neither showing association nor dissociation)

$$C_1 = C_2 \quad \text{...(5)}$$

C is concentration of solute.

Vapour pressure variation with temperature: $2.303 \log_{10}\dfrac{P_2}{P_1} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$ ...(6)

P_1 and P_2 are vapour pressures at temperature T_1 and T_2. ΔH is heat of vaporisation.

Raoult's Law

For liquid liquid systems

$$P_m = P'_A + P'_B + \ldots \quad \text{...(7)}$$

P_m is vapour pressure of mixture and P' is partial vapour pressure of each component.

$$P_m = P^\circ_A X_A + P^\circ_B X_B \quad \text{...(8)}$$

$$P_m = P^\circ_A \frac{n_A}{n_A + n_B + \ldots} + P^\circ_B \frac{n_B}{n_A + n_B + \ldots} + \ldots \quad \text{...(9)}$$

P° are vapour pressure of component in pure state.

$$P_m = P^\circ_A \frac{w_A/m_A}{w_A/m_A + w_B/m_B + \ldots} + P^\circ_B \frac{w_B/m_B}{w_A/m_A + w_B/m_B + \ldots} + \ldots \quad \text{...(10)}$$

$$P_m . X'_{A\,(\text{G.P.})} = P^\circ_A . X_{A(\text{L.P.})} \quad \text{...(11)}$$

X'_A and X_A are mole fractions in gaseous phase (G.P.) and liquid phase (L.P.) respectively.

For solid-liquid system

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{n+N} = \frac{w/m}{w/m + W/M} \qquad \ldots(12)$$

$\dfrac{P^\circ - P_s}{P^\circ}$ is relative lowering in vapour pressure.

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{N} = \frac{w \times M}{m \times W} \qquad \text{(For dilute solutions)} \qquad \ldots(13)$$

$$\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{w \times M}{m \times W} \qquad \text{(Alternative form of Raoult's law)} \qquad \ldots(14)$$

Elevation in boiling point : $\Delta T_b \propto \dfrac{P^\circ - P_s}{P^\circ} \approx \dfrac{n}{N} \approx \dfrac{w \times M}{m \times W} \propto \dfrac{w \times 1000}{m \times W} \propto \text{molality}$ ...(15)

$$\Delta T_b = K_b \times \text{molality} = \frac{K_b \times w \times 1000}{m \times W} \qquad \ldots(16)$$

ΔT_b is elevation in boiling point and K_b is molal elevation constant of solvent.

Depression in freezing point : $\Delta T_f \propto \dfrac{P^\circ - P_s}{P^\circ} \approx \dfrac{n}{N} \approx \dfrac{w \times M}{m \times W} \propto \dfrac{w \times 1000}{m \times W}$ ...(17)

$$\Delta T_f = K_f \times \text{molality} = \frac{K_f \times w \times 1000}{m \times W} \qquad \ldots(18)$$

ΔT_f is depression in freezing point and K_f is molal depression constant.

or $$K = \frac{RT^2}{1000\, l} \qquad \ldots(19)$$

or $$K_f = \frac{RT_f^2}{1000\, l_f} \qquad \ldots(20)$$

or $$K_b = \frac{RT_b^2}{1000\, l_v} \qquad \ldots(21)$$

l_f and l_v are latent heat of fusion and vaporisation in cal/g respectively.

or $$K_b = \frac{RT_b^2 \cdot M}{1000\, \Delta H_v} = \frac{RT_b \cdot M}{1000\, \Delta S_v} \qquad \left(\because\ \Delta S_v = \frac{\Delta H_v}{T}\right) \qquad \ldots(22)$$

where ΔH_v and ΔS_v are latent heat of vaporisation in cal/mol and entropy change for vaporisation in cal/mol respectively.

Abnormal Colligative Properties

For solutes undergoing dissociation :

Experimental colligative property > normal colligative property
(O.P., ΔP, ΔT_b, ΔT_f)

Experimental molecular wt. < normal molecular wt.

For solute : $A_xB_y \longrightarrow xA^{y+} + yB^{x-}$

$$i = \frac{\text{Exp C.P.}}{\text{Normal C.P.}} = 1 - \alpha + x\alpha + y\alpha \qquad \ldots(23)$$

α is degree of dissociation

$$i > 1 \qquad \ldots(24)$$

$$i = \frac{\text{Normal mol. wt.}}{\text{Exp. mol. wt.}} = 1 - \alpha + x\alpha + y\alpha \qquad \ldots(25)$$

$$\text{van't Hoff Coefficient } (g) = \frac{i}{(x+y)} \qquad \ldots(26)$$

For solutes undergoing association :

Exp. C.P. < Normal C.P.

Exp. mol. wt. > normal mol. wt.

For solute : $nA \rightleftharpoons (A)_n$

$$i = \frac{\text{Exp. C.P.}}{\text{Normal C.P.}} = 1 - \alpha + \frac{\alpha}{n} \qquad \ldots(27)$$

or

$$i = \frac{\text{Normal mol. wt.}}{\text{Exp. mol. wt.}} = 1 - \alpha + \frac{\alpha}{n} \qquad \ldots(28)$$

α is degree of association and n is no. of molecules undergoing association.

The Basic Problems with Solution

➤ **Problem 1.** Arginine vasopressin is a pituitary harmone. It helps to regulate the amount of water in the blood by reducing the flow of urine from the kidneys. An aqueous solution containing 21.6 mg of vasopressin in 100 mL of solution had an osmotic pressure of 3.70 mm Hg at 25°C. What is the molecular weight of the harmone?

➤ **Problem 2.** A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50.0 cm^3 of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K.

(a) What is the molar mass of the albumin?

(b) What is the height of water column placed in solution? $d(H_2O) = 1 \text{ g cm}^{-3}$.

➤ **Problem 3.** The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per litre for an intravenous injection that is to have the same osmotic pressure as blood.

➤ **Problem 4.** At 25°C, a solution containing 0.2 g of polyisobutylene in 100 mL of benzene developed a rise of 2.4 mm at osmotic equilibrium. Calculate the molecular weight of polyisobutylene if the density of solution is 0.88 g/mL.

➤ **Problem 5.** At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of solution is 1.52 bar at the same temperature, what would be its concentration?

➤ **Problem 6.** At 20°C, the osmotic pressure of urea solution is 400 mm. The solution is diluted and the temperature is raised to 35°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

➤ **Problem 7.** At 27°C, a 5% solution (wt./vol.) of cane-sugar is isotonic with 8.77 g/litre of urea solution. Find m.wt. of urea, if m.wt. of sugar is 342. Also report the osmotic pressure of solution if 100 mL each are mixed at 27°C.

➤ **Problem 8.** An aqueous solution of 2 per cent (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?

➤ **Problem 9.** The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a solute in it.

➤ **Problem 10.** Calculate the mass of a non-volatile solute (molecular mass 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

➤ **Problem 11.** A solution containing 30 g of a non-volatile solute exactly in 90 g water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is then added to solution, the new vapour pressure becomes 2.9 kPa at 298 K. Calculate :

(i) Molecular mass of the solute,

(ii) vapour pressure of water at 298 K.

► **Problem 12.** Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water.

► **Problem 13.** Dry air was successively passed through a solution of 5 g solute in 80 g water and then through pure water. The loss in weight of solution was 2.5 g and that of pure water was 0.04 g. What is mol. wt. of solute?

► **Problem 14.** Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure, in bar, of a mixture of 25.0 g of heptane and 35.0 g of octane?

► **Problem 15.** The vapour pressures of ethanol and methanol are 44.5 and 88.7 mm of Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol and 40 g of methanol. Calculate the total vapour pressure of solution and mole fraction of methanol in vapour phase.

► **Problem 16.** 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 temperature, if one mole of *B* is added to this solution, the vapour pressure of solution increases by 10 mm of Hg. Calculate the V.P. of *A* and *B* in their pure state.

► **Problem 17.** In a cold climate water gets frozen causing damage to the radiators of car. Ethylene glycol is used as an antifreeze agent. Calculate the amount of ethylene glycol to be added to 4 kg water to prevent it from freezing at −6°C. K_f for water is 1.85 K mol^{-1} kg.

► **Problem 18.** 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.

► **Problem 19.** A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of a 5% glucose (by mass) in water. The freezing point of pure water is 273.15 K.

► **Problem 20.** Butylated hydroxytoluene (BHT) is used as an antioxidant in processed foods (it prevents fats and oils from becoming rancid). A solution of 2.5 g of BHT in 100 g of benzene has a freezing point of 4.88 K. What is the molecular weight of BHT? K_f (benzene) = 5.12 K mol^{-1} kg, freezing point of benzene = 5.45 K?

► **Problem 21.** An aqueous solution of glucose containing 12 g in 100 g of water was found to boil at 100.34°C. Calculate K'_b for water in K mol^{-1} kg.

➤ **Problem 22.** The boiling point of $CHCl_3$ was raised by 0.323°C when 0.37 g of naphthalene was dissolved in 35 g $CHCl_3$. Calculate the molecular weight of naphthalene. K'_b for $CHCl_3 = 3.9$ K mol^{-1} kg.

➤ **Problem 23.** What will be the boiling point of bromine when 174.5 mg of octa-atomic sulphur is added to 78 g of bromine. K'_b for Br_2 is 5.2 K mol^{-1} kg and b.pt. of Br_2 is 332.15 K.

➤ **Problem 24.** What is the depression in freezing point of a solution of non-electrolyte if elevation in boiling point is 0.13 K, $K_b = 0.52$ K mol^{-1} kg; $K_f = 1.86$ K mol^{-1} kg?

➤ **Problem 25.** Pure benzene boiled at 80°C. The boiling point of a solution containing 1 g of substance dissolved in 83.4 g of benzene is 80.175°C. If latent heat of vaporization of benzene is 90 cal per g, calculate the molecular weight of solute.

➤ **Problem 26.** Calculate the osmotic pressure of 20% (wt./vol.) anhydrous $Ca(NO_3)_2$ solution at 0°C assuming 100% ionisation.

➤ **Problem 27.** The vapour pressure of a solution containing 2 g of NaCl in 100 g water, which dissociated in one Na^+ and one Cl^- ion in water, is 751 mm, at 100°C. Calculate the degree of ionisation of NaCl.

➤ **Problem 28.** What is osmotic pressure of the aq. solution of the given solute at 27°C if depression in freezing point is 0.93°? Molal depression constant of water is 1.86 K mol^{-1} kg? Assume molality as molarity.

➤ **Problem 29.** 17.4% (wt./vol.) K_2SO_4 solution at 27°C is isotonic to 5.85% (wt./vol.) NaCl solution at 27°C. If NaCl is 100% ionised, what is % ionisation of K_2SO_4 in aq. solution?

➤ **Problem 30.** The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas.

➤ **Problem 31.** Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 4 atm over the liquid at 25°C. The Henry's law constant for CO_2 in water at 25°C is 3.1×10^{-2} mol/litre-atm.

Answers

1. 1085 g mol^{-1};
2. (a) 68655 g/mol, (b) 7.958 cm;
3. 54.10 g;
4. 2.39×10^5;
5. 0.061 molar;
6. 4 times;
7. 59.99, 3.60 atm;
8. 40.97 g mol^{-1};
9. 12.08 kPa;
10. 10 g;
11. (i) 23 g mol^{-1}, (ii) 3.53 kPa;
12. 1.1334;
13. 70.31;
14. 73.08 kPa;
15. 66.13 mm, 0.344, 0.656 ;
16. A = 460 mm, B = 610 mm;
17. 804.12 g ;
18. 110 mm;
19. 269.06 K;
20. 224.56 g/mol;
21. 0.51 K mol^{-1} kg;
22. 127.6;
23. 312.195 K;
24. 0.465 K;
25. 189.72;
26. 82.0 atm;
27. 94.74%;
28. 12.315 atm;
29. 50% K_2SO_4;
30. 0.762 bar;
31. 0.12 mol $litre^{-1}$

Solutions

Solution 1. Given, vasopressin = 21.6 mg = 21.6×10^{-3} g;

$$V_{\text{solution}} = 100 \text{ mL} = \frac{100}{1000} \text{ litre}; \quad \pi = 3.70 \text{ mm} = \frac{3.70}{760} \text{ atm};$$

$$T = 25 + 273 = 298 \text{ K}$$

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

$$\frac{3.70}{760} \times \frac{100}{1000} = \frac{21.6 \times 10^{-3}}{m} \times 0.0821 \times 298$$

Mol. weight (m) = **1085 g mol^{-1}**

Solution 2. Given, $w_{\text{albumin}} = 1.08$ g, $V_{\text{solution}} = 50 \text{ cm}^3 = \frac{50}{1000}$ litre;

$$\pi = 5.85 \text{ mm} = \frac{5.85}{760} \text{ atm}; \quad T = 298 \text{ K}$$

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

$$\frac{5.85}{760} \times \frac{50}{1000} = \frac{1.08}{m} \times 0.0821 \times 298$$

m = **68655 g/mol**

Also, $\pi = h.d.g$

$$\frac{5.85}{760} \times 1.01325 \times 10^5 = h \times 1 \times 10^{-3} \times 9.8 \quad (\pi \text{ in N/m}^2, d \text{ in kg/m}^3)$$

$h = 7.958 \times 10^{-2}$ m = **7.958 cm**

Solution 3.

$$\pi_{\text{blood}} = \pi_{\text{glucose}} = \frac{w}{mV} ST$$

or

$$7.65 = \frac{w}{180 \times 1} \times 0.0821 \times 310$$

w_{glucose} = **54.10 g**

Solution 4. Height developed = 2.4 mm

$$\text{Osmotic pressure} = h.d.g = \frac{2.4}{10} \times 0.88 \times 981$$

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

Now $\pi V = nST$

$$207.187 \times 100 = \frac{0.2}{m} \times 8.314 \times 10^7 \times 298$$

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

$$\mathbf{m = 2.39 \times 10^5}$$

Solution 5. Given : O.P. = 4.98 bar, $w = 36$ g, $V = 1$ litre (case I)

O.P. = 1.52 bar, (case II)

For I : $$\pi V = \frac{w}{m} S \times T$$

$$\therefore \quad 4.98 \times 1 = \frac{36}{180} \times S \times T \quad \text{...(1)}$$

For II : $$1.52 = C \times S \times T \left(C = \frac{w}{m \times V}\right) \quad \text{...(2)}$$

By eq. (1) and (2);

$$\mathbf{C = 0.061\ molar}$$

Solution 6. For initial solution, $\pi = \frac{400}{760}$ atm, $T = 293$ K

$$\frac{400}{760} \times V_1 = n \times S \times 293 \quad \text{...(1)}$$

After dilution, let volume becomes V_2 and temperature is raised to 35°C, *i.e.* 308 K.

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

$$\frac{105.3}{760} \times V_2 = n \times S \times 308 \quad \text{...(2)}$$

By eqs. (1) and (2) we get

$$\frac{V_1}{V_2} = \frac{293}{308} \times \frac{105.3}{400}$$

$$\frac{V_1}{V_2} = \frac{1}{4}$$

$$\mathbf{V_2 = 4V_1}$$

i.e., Solution was **diluted to 4 times.**

Solution 7. For isotonic solutions, having neither dissociation nor association nature of solutes.

$$C_1 = C_2$$

or $$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

For sugar For urea

$$\frac{5}{342\times\frac{100}{1000}} = \frac{8.77}{m\times\frac{1000}{1000}}$$

$$\therefore \qquad m = \frac{8.77\times342}{5\times10} = \mathbf{59.99}$$

On mixing 100 mL of cane sugar with 100 mL urea solution, the total volume now contains 200 mL in which 5 g cane sugar and 0.877 g urea is present.

$$\text{Thus} \qquad \pi\times\frac{200}{1000} = \left[\frac{5}{342}+\frac{0.877}{60}\right]\times0.0821\times300$$

$$\therefore \qquad \pi = \mathbf{3.60\ atm}$$

Solution 8. Given $P_S = 1.004$ bar, $P^\circ = 1.013$ bar (at boiling point $P^\circ = 1.013$ bar = 1 atm), $w = 2$ g,

$$\therefore \qquad W = 100 - 2 = 98\text{ g}$$

From Raoult's law : $$\frac{P^\circ - P_S}{P_S} = \frac{w\times M}{m\times W}$$

$$\frac{1.013-1.004}{1.004} = \frac{2\times18}{m\times98}$$

$$\therefore \qquad m = \mathbf{40.97\ g\ mol^{-1}}$$

Solution 9. $$\frac{P^\circ - P_S}{P_S} = \frac{n}{N}$$

(Given $n = 1$ and $N = 1000/18$; assuming molarity = molality)

$$\therefore \qquad \frac{12.3 - P_S}{P_S} = \frac{1}{1000/18}$$

$$\therefore \qquad P_S = \mathbf{12.08\ kPa}$$

Solution 10. $$\frac{P^\circ - P_S}{P_S} = \frac{n}{N} = \frac{wM}{m\times W};$$ octane is C_8H_{18}

(Given $m = 40$, $W = 114$ g, $M_{octane} = 114$)

$$\frac{100-80}{80} = \frac{w\times114}{40\times114}$$

$$w = \mathbf{10\ g}$$

Note : By $\frac{P^\circ - P_S}{P^\circ} = \frac{n}{N}$ (Only for dilute solution, the answer comes 8 g.)

Solution 11.

$$\frac{P^\circ - P_S}{P_S} = \frac{w \times M}{m \times W}$$

For I case : $$\frac{P^\circ - 2.8}{2.8} = \frac{30 \times 18}{m \times 90} = \frac{6}{m} \qquad \text{...(1)}$$

For II case : $$\frac{P^\circ - 2.9}{2.9} = \frac{30 \times 18}{m \times 108} = \frac{5}{m} \qquad \text{...(2)}$$

By eq. (1) and (2) $\mathbf{P^\circ = 3.53\ kPa}$

$\mathbf{m = 23\ g\ mol^{-1}}$

Note : Answers will be 3.4 kPa and 34 g mol^{-1} if $\frac{P^\circ - P_S}{P^\circ} = \frac{n}{N}$ is used which is only valid for dilute solutions.

Solution 12. Given, $$P_S = \frac{98}{100} P^\circ$$

Now $$\frac{P^\circ - P_S}{P_S} = \frac{w \times M}{m \times W} = \frac{w}{m \times W} \times 1000 \times \frac{M}{1000}$$

$$\left\{\frac{P^\circ - \frac{98}{100} . P^\circ}{\frac{98}{100} . P^\circ}\right\} = \text{molality} \times \frac{18}{1000}$$

$$\text{Molality} = \left\{\frac{2P^\circ}{100 \times \frac{98}{100} P^\circ}\right\} \times \frac{1000}{18} = \mathbf{1.1334}$$

Solution 13. Loss in weight of solution $\propto P_S$

Loss in weight of solvent $\propto P^\circ - P_S$

$$\frac{P^\circ - P_S}{P_S} = \frac{\text{Loss in wt. of solvent}}{\text{Loss in wt. of solution}} = \frac{0.04}{2.5} \qquad \text{...(1)}$$

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

$\therefore$ $$\frac{0.04}{2.5} = \frac{5 \times 18}{80 \times m}$$

or $\mathbf{m = 70.31}$

Solution 14. $$P_M = P'_{\text{Heptanes}} + P'_{\text{Octane}} = P^\circ_{\text{Heptane}} \times \frac{n}{n+N} + P^\circ_{\text{Octane}} \times \frac{N}{n+N}$$

(mol. wt. of C_7H_{16} = 100; mol. wt. of C_8H_{18} = 114)

$$= 105.2 \times \frac{25/100}{\frac{25}{100}+\frac{35}{114}} + 46.8 \times \frac{35/114}{\frac{25}{100}+\frac{35}{114}} = \mathbf{73.08\ kPa}$$

Solution 15.

$$P_M = P^\circ_{EtOH} \times X_{EtOH} + P^\circ_{MeOH} \times X_{MeOH}$$

$$P_M = 44.5 \times \frac{60/46}{\frac{60}{46}+\frac{40}{32}} + 88.7 \times \frac{40/32}{\frac{60}{46}+\frac{40}{32}}$$

$$= 22.72 + 43.41 = \mathbf{66.13\ mm}$$

Also we have :

$$P^\circ_{EtOH} \times X_{EtOH(l)} = P_M \times X_{EtOH(v)}$$

$$44.5 \times \frac{60/46}{\frac{60}{46}+\frac{40}{32}} = 66.13 \times X_{EtOH(v)}$$

$$\therefore \quad X_{EtOH(v)} = \mathbf{0.344}$$

$$\therefore \quad X_{MeOH(v)} = \mathbf{0.656}$$

Solution 16. Initially,

$$P_M = P^\circ_A . X_A + P^\circ_B . X_B$$

$$550 = P^\circ_A . \left(\frac{2}{2+3}\right) + P^\circ_B . \left(\frac{3}{2+3}\right)$$

or $\quad 2P^\circ_A + 3P^\circ_B = 2750 \qquad$ ...(1)

When 1 mole of B is further added to it,

$$P_M = P^\circ_A X_A + P^\circ_B X_B$$

$$560 = P^\circ_A . \left(\frac{2}{2+4}\right) + P^\circ_B . \left(\frac{4}{2+4}\right)$$

$\therefore \quad 2P^\circ_A + 4P^\circ_B = 3360 \qquad$ ...(2)

By eq. (1) and (2);

$$P^\circ_A = \mathbf{460\ mm}; \quad P^\circ_B = \mathbf{610\ mm}$$

Solution 17.

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

Given, $\Delta T_f = 6°$; $w = ?$, $W = 4 \times 10^3$ g H_2O; $K_f = 1.85$ K mol^{-1} kg

$m_{glycol} = 62$

$$\therefore \quad 6 = \frac{1000 \times 1.85 \times w}{4 \times 10^3 \times 62}$$

$$\therefore \quad w_{glycol} = \mathbf{804.32\ g}$$

Solution 18. According to Raoult's law for liquid mixtures,

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

$$= 105.2 \times \frac{25/100}{\frac{25}{100}+\frac{35}{114}} + 46.8 \times \frac{35/114}{\frac{25}{100}+\frac{35}{114}} = \mathbf{73.08\ kPa}$$

Solution 15.

$$P_M = P^\circ_{EtOH} \times X_{EtOH} + P^\circ_{MeOH} \times X_{MeOH}$$

$$P_M = 44.5 \times \frac{60/46}{\frac{60}{46}+\frac{40}{32}} + 88.7 \times \frac{40/32}{\frac{60}{46}+\frac{40}{32}}$$

$$= 22.72 + 43.41 = \mathbf{66.13\ mm}$$

Also we have :

$$P^\circ_{EtOH} \times X_{EtOH(l)} = P_M \times X_{EtOH(v)}$$

$$44.5 \times \frac{60/46}{\frac{60}{46}+\frac{40}{32}} = 66.13 \times X_{EtOH(v)}$$

$\therefore$ $X_{EtOH(v)} = \mathbf{0.344}$

$\therefore$ $X_{MeOH(v)} = \mathbf{0.656}$

Solution 16. Initially, $P_M = P^\circ_A.X_A + P^\circ_B.X_B$

$$550 = P^\circ_A \cdot \left(\frac{2}{2+3}\right) + P^\circ_B \cdot \left(\frac{3}{2+3}\right)$$

or $2P^\circ_A + 3P^\circ_B = 2750$ ...(1)

When 1 mole of B is further added to it,

$$P_M = P^\circ_A.X_A + P^\circ_B.X_B$$

$$560 = P^\circ_A \cdot \left(\frac{2}{2+4}\right) + P^\circ_B \cdot \left(\frac{4}{2+4}\right)$$

$\therefore$ $2P^\circ_A + 4P^\circ_B = 3360$ ...(2)

By eq. (1) and (2);

$$P^\circ_A = \mathbf{460\ mm}; \quad P^\circ_B = \mathbf{610\ mm}$$

Solution 17.

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

Given, $\Delta T_f = 6°$; $w = ?$, $W = 4 \times 10^3$ g H_2O; $K_f = 1.85$ K mol^{-1} kg

$m_{glycol} = 62$

$$\therefore \quad 6 = \frac{1000 \times 1.85 \times w}{4 \times 10^3 \times 62}$$

$$\therefore \quad w_{glycol} = \mathbf{804.32\ g}$$

Solution 18. According to Raoult's law for liquid mixtures,

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

$$\therefore \quad P_M = P^\circ_A \times \left\{ \frac{\frac{w_A}{m_A}}{\frac{w_A}{m_A} + \frac{w_B}{m_B}} \right\} + P^\circ_B \times \left\{ \frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A} + \frac{w_B}{m_B}} \right\}$$

Given that, $w_A = 28$ g, $w_{H_2O} = 72$ g, $P^\circ_A = ?$
$P^\circ_{H_2O} = 155$, $m_A = 56$ g, $m_{H_2O} = 18$ g, and $P_M = 150$ mm

$$\therefore \quad 150 = P^\circ_A \times \left\{ \frac{\frac{28}{56}}{\frac{28}{56} + \frac{72}{18}} \right\} + 155 \times \left\{ \frac{\frac{72}{18}}{\frac{28}{56} + \frac{72}{18}} \right\}$$

$$150 = P^\circ_A \times \frac{1}{2} \times \frac{2}{9} + 155 \times 4 \times \frac{2}{9}$$

$$\therefore \quad P^\circ_A = \mathbf{110\ mm}$$

Solution 19. $$\Delta T = \frac{1000 \times K \times w}{m \times W}$$

Assuming 5% weight per cent, we have
$w = 5$ g, $W = 100 - 5 = 95$ g; $\Delta T - 273.15 - 271 = 2.15$,
$m = 342$ (for sugar)

$$\therefore \quad 2.15 = \frac{1000 \times K \times 5}{342 \times 95} \qquad \text{...(1)}$$

For glucose $$\Delta T = \frac{1000 \times K \times 5}{180 \times 95} \qquad \text{...(2)}$$

By eq. (1) and (2); $\Delta T = 4.085$

$\therefore$ Freezing point = 273.15 – 4.09 = **269.06 K**

Solution 20. Given, $w_{BHT} = 2.5$ g, $W = 100$ g,

$\Delta T = 5.45 - 4.88 = 0.57$ K, $K_f = 5.12$ K molality^{-1}

$$\Delta T = \frac{1000 \times K_f \times w}{W \times m}$$

$$0.57 = \frac{1000 \times 5.12 \times 2.5}{100 \times m}$$

Mol. weight (m) = **224.56 g/mol**

Solution 21. Given, b.pt. of water = 100°C

b.pt. of solution = 100.34°C

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

$$\Delta T = \frac{1000 K_b w}{m W}$$

or
$$0.34 = \frac{1000 \times K_b \times 12}{180 \times 100}$$
$$K_b = \mathbf{0.51\ K\ mol^{-1}\ kg}$$

Solution 22. Given that, $w = 0.37$ g, $W = 35$ g, $K_b = 3.9$ K mol^{-1} kg, $\Delta T = 0.323°C$

$$\because \quad \Delta T = \frac{1000 K_b w}{mW}$$

$$\therefore \quad 0.323 = \frac{1000 \times 3.9 \times 0.37}{m \times 35}$$
$$m = \mathbf{127.6}$$

Solution 23. Given, $w = 174.5 \times 10^{-3}$ g, $W = 78$ g,

$m = 8 \times 32 = 256$ ($\because$ octa-atomic), $K_b = 5.2$

$$\because \quad \Delta T = \frac{1000 K_b w}{mW} = \frac{1000 \times 5.2 \times 174.5 \times 10^{-3}}{78 \times 256} = 0.045$$

$\therefore$ Boiling point of Br_2 solution $= 332.15 + \Delta T = 332.15 + 0.045$

$= \mathbf{332.195\ K}$

Solution 24. $\Delta T_b = 0.13$, $K_b = 0.52$

$\Delta T_f = ?$ $K_f = 1.86$

For a given solution $\Delta T_b \propto K_b$

$\Delta T_f \propto K_f$

$$\therefore \quad \frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b}$$

or
$$\Delta T_f = \Delta T_b \times \frac{K_f}{K_b} = \frac{0.13 \times 1.86}{0.52}$$
$$\Delta T_f = \mathbf{0.465\ K}$$

Solution 25. B.pt. of C_6H_6 $= 80 + 273 = 353$ K

Latent heat $(l_v) = 90$ cal/g

$\Delta T = 80.175 - 80 = 0.175$, $w = 1$ g, $W = 83.4$ g

$$\because \quad K_b = \frac{RT^2}{1000\ l_v}$$

(l_v is latent heat of vaporisation/g in the unit of R)

or
$$K_b = \frac{2 \times 353 \times 353}{1000 \times 90} = 2.769 \text{ K mol}^{-1} \text{ kg}$$

Now,
$$\Delta T_b = \frac{K_b \times 1000 \times w}{m.W}$$

$$0.175 = \frac{2.769 \times 1000 \times 1}{m \times 83.4}$$

$$\therefore \quad m = \mathbf{189.72}$$

Solution 26.

$$\begin{array}{lccc} & Ca(NO_3)_2 & \longrightarrow & Ca^{2+} + 2NO_3^- \\ \text{Before dissociation} & 1 & & 0 \qquad 0 \\ \text{After dissociation} & 1-\alpha & & \alpha \qquad 2\alpha \end{array}$$

Given, $w = 20$ g, $V = 100$ mL, $T = 273$ K,
Mol. wt. of $Ca(NO_3)_2 = 164$

$$\pi_N = \frac{w}{m.V} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{164 \times 100} = 27.33 \text{ atm}$$

Now, $$\frac{\pi_{exp}}{\pi_N} = 1 + 2\alpha = 1 + 2 = 3 \qquad \because \quad \alpha = 1$$

$$\therefore \quad \pi_{exp} = 27.33 \times 3 = \mathbf{82.0 \text{ atm}}$$

Solution 27. $\because$

$$\frac{P^\circ - P_S}{P_S} = \frac{w \times M}{m \times W}$$

$$\frac{760 - 751}{751} = \frac{2 \times 18}{m \times 100}$$

$$\therefore \quad m_{exp} = 30.04$$

$$\begin{array}{lccc} \text{For} & NaCl & \rightleftharpoons & Na^+ + Cl^- \\ \text{Before dissociation} & 1 & & 0 \qquad 0 \\ \text{After dissociation} & 1-\alpha & & \alpha \qquad \alpha \end{array}$$

Now $$\frac{m_N}{m_{exp}} = 1 + \alpha \quad \text{or} \quad \frac{58.5}{30.04} = 1 + \alpha$$

$$\therefore \quad \alpha = \mathbf{0.9474} \quad \text{or} \quad \mathbf{94.74\%}$$

Solution 28. $\Delta T_f = K_f \times$ molality, $\quad \pi =$ molarity $\times ST$

$$\frac{\Delta T_f}{\pi} = \frac{K_f}{ST} \qquad (\because \text{ molality} = \text{molarity})$$

$$\frac{0.93}{\pi} = \frac{1.86}{0.0821 \times 300}$$

$$\therefore \quad \pi = \mathbf{12.315 \text{ atm}}$$

Solution 29. For

$$\begin{array}{ccc} K_2SO_4 & \rightleftharpoons & 2K^+ + SO_4^{2-} \\ 1 & & 0 \qquad 0 \\ 1-\alpha & & 2\alpha \qquad \alpha \end{array}$$

$$\because \quad \pi_1 = \frac{w}{m.V} ST \quad (1 + 2\alpha)$$

$$\pi_1 = \frac{17.4 \times 1000}{174 \times 100} \times ST\ (1 + 2\alpha) = ST \times (1 + 2\alpha)$$

For $NaCl \rightleftharpoons Na^+ + Cl^-$

$$\begin{array}{ccc} 1 & 0 & 0 \\ (1-\alpha_1) & \alpha_1 & \alpha_1 \end{array}$$

$\therefore$ $$\pi_2 = \frac{5.85 \times 1000}{58.5 \times 100} \times ST \times (1 + \alpha_1) \qquad \because \alpha_1 = 1$$

$\because$ $\pi_2 = ST \times 2$

Given $\pi_1 = \pi_2$ (isotonic solution)

$\therefore$ $ST \times 2 = ST \times (1 + 2\alpha)$

or $\alpha = 0.5$ or **50% ionisation of K_2SO_4**

Solution 30. $a \propto P$

$6.56 \times 10^{-2} \propto 1$ (P = 1 bar)

$5.00 \times 10^{-2} \propto P$

$\therefore$ $$P = \frac{1 \times 5.00 \times 10^{-2}}{6.56 \times 10^{-2}} = \mathbf{0.762\ bar}$$

Solution 31. According to Henry's law, $\frac{a}{p} = K$ or $a = K \times P$

$\therefore$ $a = 3.1 \times 10^{-2} \times 4 = \mathbf{0.12\ mol\ litre^{-1}}$

Selected Problems with Solutions

➤ Problem 1. If at a particular temperature, the density of 18 *M* H_2SO_4 is 1.8 g cm^{-3}, calculate:

(a) Molality,

(b) % concentration by weight of solution,

(c) Mole fraction of water and H_2SO_4,

(d) Relative decrease in vapour pressure with respect to H_2O solvent assuming H_2SO_4 almost unionised at this high concentration.

➤ Problem 2. At 25°C, a solution containing 0.2 g of polyisobutylene in 100 mL of benzene developed a rise of 2.4 mm at osmotic equilibrium. Calculate the molecular weight of polyisobutylene if the density of solution is 0.88 g/mL.

➤ Problem 3. Calculate O.P. of a solution obtained by mixing 100 mL of 3.4% solution (wt./vol.) of urea (m. wt. 60) and 100 mL of 1.6% solution (wt./vol.) of cane-sugar (m. wt. 342) at 20°C.

➤ Problem 4. A tube of uniform cross-sectional area 1 cm^2 is closed at one end with semipermeable membrane. A solution of 5 g glucose per 100 mL is placed inside the tube and is dipped in pure water at 27°C. When equilibrium is established calculate.

(a) Osmotic pressure of solution,

(b) Height developed in vertical column,

Assume density of final glucose solution 1 g/mL.

➤ Problem 5. A beaker containing 20 g sugar in 100 g water and another containing 10 g sugar in 100 g water are placed under a bell-jar and allowed to stand until equilibrium is reached. How much water will be transferred from one beaker to other?

➤ Problem 6. At 300 K, two solutions of glucose in water of concentration 0.01 *M* and 0.001 *M* are separated by semipermeable membrane with respect to water. On which solution, the pressure need be applied to prevent osmosis? Calculate magnitude of this applied pressure.

➤ Problem 7. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

➤ Problem 8. At 300 K, the vapour pressure of an ideal solution containing one mole of *A* and 3 mole of *B* is 550 mm of Hg. At the same temperature, if one mole of *B* is added to this solution, the vapour pressure of solution increases by 10 mm of Hg. Calculate the V.P. of *A* and *B* in their pure state.

➤ Problem 9. The vapour pressure of benzene and toluene at 20°C are 75 mm of Hg and 22 mm of Hg respectively. 23.4 g of benzene and 64.4 g of toluene are mixed. If two forms ideal solution, calculate the mole fraction of benzene in vapour phase when vapours are in equilibrium with liquid mixture.

➤ **Problem 10.** Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C are given by $P = 179\,X_B + 92$, where X_B is mole fraction of C_6H_6. Calculate (in mm):

(a) Vapour pressure of pure liquids.

(b) Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 and 736 g toluene.

(c) If the vapours are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in vapour state?

➤ **Problem 11.** Ideal mixture of two miscible liquids A and B is placed in a cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapours increases. When negligibly small amount of liquid was left, the mole fraction of A in vapour phase is 0.4. If $P_A^\circ = 0.4$ atm and $P_B^\circ = 1.2$ atm at the experimental temperature, calculate the total pressure at which the liquid is almost evaporated.

➤ **Problem 12.** A mixture of two immiscible liquids nitrobenzene and water boiling at 99°C has a partial vapour pressure of water 733 mm and that of nitrobenzene 27 mm. Calculate the ratio of the weights of nitrobenzene to the water in distillate.

➤ **Problem 13.** The vapour pressure of two pure liquids A and B that forms an ideal solution at 300 and 800 torr, respectively at temperature T. A mixture of the vapours of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate:

(a) The composition of the first drop of the condensate,

(b) The total pressure when this drop formed,

(c) The composition of the solution whose normal boiling point is T,

(d) The pressure when only the last bubble of vapour remains,

(e) Composition of the last bubble.

➤ **Problem 14.** The vapour pressure of water at 293 K is 2338 Pa and the vapour pressure of an aqueous solution is 2295.8 Pa. If solution density is 1010 kg/m^3 at 313 K, calculate the osmotic pressure at 313 K. Molecular weight of solute = 60.

➤ **Problem 15.** Calculate the vapour pressure of solution having 3.42 g of cane-sugar in 180 g water at 40°C and 100°C. Given that boiling point of water is 100°C and heat of vaporisation is 10 kcal mol^{-1} in the given temperature range. Also calculate the lowering in vapour pressure of 0.2 molal cane-sugar at 40°C.

➤ **Problem 16.** Calculate the vapour pressure lowering of a 0.10 *m* aqueous solution of non-electrolyte at 75°C.

➤ **Problem 17.** What weight of solute (M. wt. 60) is required to dissolve in 180 g of water to reduce the vapour pressure to 4/5th of pure water?

➤ **Problem 18.** Dry air was successively passed through a solution of 5 g solute in 80 g water and then through pure water. The loss in weight of solution was 2.5 g and that of pure water was 0.04 g. What is mol. wt. of solute?

➤ **Problem 19.** What will be the boiling point of bromine when 174.5 mg of octa-atomic sulphur is added to 78 g of bromine? K_b for Br_2 is 5.2 K mol^{-1} kg and b. pt. of Br_2 is 332.15 K.

➤ **Problem 20.** An aqueous solution containing 5% by weight of urea and 10% by weight of glucose. What will be its freezing point? K_f for H_2O is 1.86° mol^{-1} kg.

➤ **Problem 21.** Two elements A and B form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g C_6H_6, 1 g of AB_2 lowers the f. pt. by 2.3°C whereas 1.0 g of AB_4 lowers it by 1.3°C. The K_f for C_6H_6 is 5.1 K mol^{-1} kg. Calculate atomic weight of A and B.

➤ **Problem 22.** If boiling point of an aqueous solution is 100.1°C. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

➤ **Problem 23.** Calculate the freezing point of an aqueous solution having mole fraction of water 0.8. Latent heat of fusion of ice is 1436.3 cal mol^{-1}.

➤ **Problem 24.** 1000 g of 1 m sucrose solution in water is cooled to − 3.534°C. What weight of ice would be separated out at this temperature? K_f of H_2O = 1.86 K mol^{-1} kg.

➤ **Problem 25.** The osmotic pressure of an aqueous solution of sucrose is 2.47 atm at 303 K and the molar volume of the water present in solution is 18.10 cm^3. Calculate the elevation of boiling point of this solution. Given ΔH_{vap} = 540 cal/g. Assume volume of solvent equal to volume of solution.

➤ **Problem 26.** A dilute solution contains m mole of solute A in 1 kg of a solvent with molal elevation constant K_b. The solute A undergoes dimerization as $2A \rightleftharpoons A_2$. Show that equilibrium constant for dimer formation is given by:

$$K_c = \frac{K_b\,(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$

where ΔT_b is elevation in boiling point for given solution. Assume molarity = molality.

➤ **Problem 27.** A solution containing 0.1 mole of naphthalene and 0.9 mole of benzene is cooled out until some benzene freezes out. The solution is then decanted off from the solid and warmed upto 353 K where its vapour pressure was found to be 670 torr. The freezing point and boiling point of benzene are 278.5 K and 353 K respectively and its enthalpy of fusion is 10.67 kJ mol^{-1}. Calculate the temperature to which the solution was cooled originally and the amount of benzene that must have frozen out. Assume ideal behaviour.

➤ **Problem 28.** One mole of $(C_6H_5)_3C\,OH$ dissolved in 1000 g of 100% sulphuric acid lowers the freezing point of sulphuric acid twice as one mole of CH_3OH shows in 1000 g of 100% sulphuric acid. Comment on it assuming that CH_3OH is neither dissociated nor associated in sulphuric acid.

➤ **Problem 29.** Calculate the osmotic pressure of 20% (wt./vol.) anhydrous $CaCl_2$ solution at 0°C assuming 100% ionisation.

➤ **Problem 30.** A certain mass of a substance when dissolved in 100 g C_6H_6 lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100 g of water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely dissociated in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12 K mol^{-1} kg respectively.

➤ **Problem 31.** The vapour pressure of a solution containing 2 g of an electrolyte BA in 100 g water, which dissociates in one B^+ and one A^- ion in water, is 751 mm, at 100°C. Calculate degree of ionisation of BA if its mol. wt. is 56.

➤ **Problem 32.** Vapour pressure of a saturated solution of a sparingly soluble salt A_2B_3 is 31.8 mm of Hg at 40°C. If vapour pressure of pure water is 31.9 mm of Hg at 40°C, calculate K_{SP} of A_2B_3 at 40°C.

➤ **Problem 33.** 1 g of mono-basic acid in 100 g of water lowers the freezing point by 0.168°. If 0.2 g of same acid requires 15.1 mL of $N/10$ alkali for complete neutralization, calculate degree of dissociation of acid. K'_f for H_2O is 1.86 K mol^{-1} kg.

➤ **Problem 34.** What will be the osmotic pressure of 0.1 M monobasic acid if its pH is 2 at 25°C.

➤ **Problem 35.** A complex is represented as $CoCl_3 \cdot XNH_3$. Its 0.1 molal solution in aqueous solution shows $\Delta T_f = 0.558°$. K_f for H_2O is 1.86 K $molality^{-1}$. Assuming 100% ionisation of complex and co-ordination number of Co as six, calculate formula of complex.

➤ **Problem 36.** The freezing point of an aqueous solution of KCN containing 0.1892 mol kg^{-1} was –0.704°C. On adding 0.045 mole of $Hg(CN)_2$, the freezing point of the solution was –0.620°C. If whole of $Hg(CN)_2$ is used in complex formation according to the equation, $Hg(CN)_2 + m KCN \rightarrow K_m[Hg(CN)_{m+2}]$ what is the formula of the complex? Assume $[Hg(CN)_{m+2}]^{m-}$ is not ionised and the complex molecule is 100% ionised. K_f (H_2O) is 1.86 kg mol^{-1} K.

➤ **Problem 37.** A 0.001 molal solution of a complex represented as $Pt(NH_3)_4Cl_4$ in water had freezing point depression of 0.0054°C. Given K_f for H_2O = 1.86 K molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

➤ **Problem 38.** The freezing point of 0.08 *m* $NaHSO_4$ is – 0.345°C. Calculate the percentage of HSO_4^- ions that transfer a proton to water to form SO_4^{2-} ion. K_f of $H_2O = 1.86 \text{ mol}^{-1}$ kg. Assume HSO_4^- does not show hydrolysis

➤ **Problem 39.** The K_{SP} (25°C) of sparingly soluble salt XY_2 is 3.56×10^{-5} mol^3 litre^{-3} and at 30°C, the vapour pressure of its saturated solution in water is 31.78 mm of Hg. Calculate the enthalpy change of the reaction if the vapour pressure of H_2O at 30°C is 31.82 mm.

$$XY_2 + \text{Aq.} \rightleftharpoons X^{2+}_{(aq.)} + 2Y^-_{(aq.)} \qquad \text{(100\% ionisation)}$$

➤ **Problem 40.** An aqueous solution of an acid is so weak that it can be assumed to be practically unionised, boiled at 100.4°C. 25 mL of this solution was neutralised by 38.5 mL of 1 *N* solution of NaOH. Calculate basicity of the acid if K_b for water is 0.52 K mol^{-1} kg. Assume molality equal to molarity.

➤ **Problem 41.** The freezing point of 0.02 mole fraction of acetic acid in benzene is 277.4 K. Acetic acid exists partly as dimer. Calculate the equilibrium constant for dimerisation. Freezing point of benzene is 278.4 K and heat of fusion of benzene is 10.042 kJ mol^{-1}. Assume molarity equal to molality.

➤ **Problem 42.** What is the ratio by weight of NaF and NaI which when dissolved in water produces the same osmotic effects as 0.1 molar solution of urea in water at same temperature? The weight of residue obtained on evaporation of the salt solution is 0.48 gram per 100 mL of solution evaporated. Assume complete dissociation of the salts.

➤ **Problem 43.** Calculate the value of molal elevation constant for water if $\Delta S_{\text{vaporisation}}$ is 26.33 cal K^{-1} mol^{-1}.

Answers

1. (a) 500 molal, (b) 98%, (c) $H_2SO_4 = 0.9$, $H_2O = 0.1$, (d) 0.9 ;
2. 2.39×10^5 ; **3.** 7.38 atm ;
4. (a) 6.842 atm, (b) 70.43 m ; **5.** 33.3 g ;
6. See solution ; **7.** 5 times ;
8. $A = 400$ mm, $B = 600$ mm ; **9.** 0.59, 0.41 ;
10. (a) 92 mm, (b) 199.4 mm, (c) 0.815, 0.185, (d) 0.928, 0.072 ;
11. 0.667 atm ; **12.** 4 ;
13. (a) 0.47, 0.53, (b) 565 torr, (c) 0.08, 0.92, (d) 675 torr, (e) 0.889 ;
14. 2.53×10^6 Pa ; **15.** 759.2 mm, 0.21 mm ;
16. 0.53 mm ; **17.** 150 g ;
18. 70.31 ; **19.** 332.195 K ;
20. –3.04°C ; **21.** $A = 25.59$, $B = 42.65$;
22. –0.362°C ; **23.** –25.97°C ;
24. 352.98 ; **25.** 5.145×10^{-2} ;
26. See Solution **27.** 270.39 K , 12.14 g ;
28. See solution ; **29.** 121.14 atm ;
30. 3 ; **31.** 86.41% ;
32. 5.672×10^{-8} ; **33.** 19.6% ;
34. 2.69 atm ; **35.** See solution ;
36. $K_2[Hg(CN)_4]$; **37.** See solution ;
38. 31.85% ; **39.** 52.799 kJ ;
40. 2 ; **41.** 3.39 ;
42. 0.28 ; **43.** 0.5 K molality^{-1}.

Problems for Self Assessment

1. A beaker containing 0.01 mole of sugar in 100 g water and a beaker containing 0.02 mole of sugar in 100 g water are placed in a chamber and allowed to equilibriate. What is the mole fraction of sugar in the resulting solution?
2. Calculate the molecular weight of cellulose acetate if its 0.2% (wt/vol) solution in acetone (sp. gravity 0.8 g/cm^3) shows an osmotic rise of 23.1 mm against pure acetone at 27°C.
3. 5 g of a polymer of molecular weight 50 kg mol^{-1} is dissolved in 1 dm^3 solution. If the density of this solution is 0.96 kg dm^{-3} at 300 K, calculate the height of solution that will represent this pressure.
4. Calculate osmotic pressure of a solution containing 100 mL of 3.4% solution (by volume) of urea (m. wt. 60) and 50 mL of 1.6% solution (by volume) of cane-sugar (m. wt. 342) at 27°C.
5. Consider the following arrangement in which a solution containing 20 g of haemoglobin in 1 dm^3 of the solution is placed in a right hand compartment and pure water in left hand compartment. Both the compartments are separated through a semi-permeable membrane. At equilibrium, the height of water in the right hand column is 77.8 mm in excess of that in the left hand column at 298 K. Calculate the molecular mass of haemoglobin if $g = 981$ and density of right hand column be assumed 1g/cm^3.
6. Two liquids *A* and *B* are miscible over the whole range of composition and may be treated as ideal (obeying Raoult's Law). At 350 K the vapour pressure of pure *A* is 24.0 kPa and of pure *B* is 12.0 kPa. A mixture of 60% *A* and 40% *B* is distilled at this temperature; what is the pressure in a closed distillation apparatus from which air is excluded? A small amount of the distillate is collected and redistilled at 350 K; what is the composition of the second distillate?
7. A liquid mixture of benzene (B) and toluene (T) contains 1 mole each of B and T. If $P^\circ_T = 4.274$ kN m^{-2} and $P^\circ_B = 13.734$ kN m^{-2}:
   (a) Calculate the pressure at which vapour first appears if the pressure over the mixture above 300 K is reduced.
   (b) What is the composition of the first trace of vapour formed?
   (c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?
   (d) What is the composition the last trace of liquid?
8. Two liquids *A* and *B* are perfectly miscible. If *A* and *B* have molecular masses in the ratio 1 : 2, what would be the total vapour pressure of mixture of *A* and *B* in their mixture having 2 : 3 weight ratio. $P^\circ_A = 400$ torr, $P^\circ_B = 200$ torr.
9. A solution of 1-propanol and 2-propanol having ¾ by weight of 2-propanol has an equilibrium vapour pressure of 88.8 mm Hg. Another solution having ⅓ by weight of 2-propanol has an equilibrium vapour pressure of 68.3 mm Hg.

Calculate vapour pressure of pure alcohols at 40°C assuming ideal solution mixtures prepared at 40°C.

10. A certain liquid mixture of two liquids A and B (behaving ideally) has a vapour pressure 70 torr (1 torr = 1 mm) at 25°C for a certain mole fraction X of A. For the same mole fraction X for B in the mixture, the vapour pressure of mixture is 90 torr at 25°C. If $P^\circ_A - P^\circ_B = 40$ torr, calculate P°_A, P°_B and X.

11. A 6% (by weight) of non-volatile solute in isopentane at 300 K has a vapour pressure of 1426 mm Hg. 20 g of isopentane is now added to the solution. The resulting solution has a vapour pressure of 1445 mm of Hg at the same temperature. Calculate:

(a) Mol. wt. of solute.

(b) Vapour pressure of isopentane at 300 K.

12. The vapour pressure P in mm of $CH_3OH - C_2H_5OH$ binary solution, at a certain temperature is represented by the equation: $P = 254 - 119X$ where X is mole fraction of C_2H_5OH. Find the vapour pressure of pure components.

13. A current of dry N_2 was successively passed through two saturator, one containing a solution of 8 g of non-volatile solute in 312 g C_6H_6 and other through pure C_6H_6. The weight loss in first was found to be 1.023 g while that of second was 0.033 g. Calculate mol. wt. of solute.

14. A current of dry air was passed through a series of bulbs containing 1.25 g of a solute A_2B in 50 g of water and then through pure water. The loss in weight of the former series of bulbs was 0.98 g and in the later series 0.01 g. If the molecular weight of A_2B is 80 calculate degree of dissociation of A_2B.

15. Calculate the weight loss of the liquids that would result by passing 10 litre of dry air through a saturator containing 60 g of glucose in 1000 g of water at 20°C. Aqueous tension at 20°C = 17.45 mm.

16. An aqueous solution containing 288 g of a non-volatile solute $C_xH_{2x}O_x$ in 90 g water boils at 101.24°C at 1 atmospheric pressure. Calculate the molecular weight and molecular formula of solute. K_b for $H_2O = 0.512$ K mol^{-1} kg.

17. Calculate the density of glycol solution whose 2.976 litre on addition to 5 litre of water produce an antifreeze which protects automobile radiator down to –20°C. Also calculate the temperature at which this solution will boil. K'_f and K'_b for water are 1.86 and 0.51 K mol^{-1} kg respectively.

18. What approximate proportion by volume of water ($d = 1$ g mL^{-1}) and ethylene glycol ($d = 1.2$ g mL^{-1}) must be mixed to ensure protection of an automobile radiator to cooling –10°C. K'_f $H_2O = 1.86$ K mol^{-1} kg.

19. Two solvents A and B have K_f values 1.86 and 2.72 K mol^{-1} kg respectively. A given amount of substance when dissolved in 500 g of A, it completely dimerizes and when same amount of substance is dissolved in 500 g of B, the solute undergoes trimerization. What will be the ratio of observed lowering of freezing point in two cases?

20. Sea water is found to contain 5.85% solution by weight NaCl and 9.50% $MgCl_2$ solution by weight. Calculate the normal boiling point of sea water assuming 80% ionisation of NaCl and 50% ionisation $MgCl_2$. K_b for $H_2O = 5.1$ K mol^{-1} 100 g solvent.

21. Heavy water (D_2O) boils at 101.42°C and its molal elevation constant is 10% higher than that of pure water. Calculate the ratio of latent heat of heavy water and pure water.

22. A 10% solution of cane sugar has undergone partial inversion according to the equation: Sucrose + $H_2O \longrightarrow$ Glucose + Fructose

If the boiling point of solution is 100.27°C, calculate:

(a) Average molecular mass of the dissolved material.

(b) The fraction of sugar inverted.

23. The vapour pressure of water at 293 K is 2338 Pa and the vapour pressure of an aqueous solution is 2295.8 Pa. Determine its osmotic pressure at 313 K, if the solution density at this temperature is 1010 kg/m^3. The molecular weight of solute is 60.

24. The vapour pressure of a mixture of diethyl aniline and water is 1.013×10^5 Nm^{-2} at 99.4°C. The vapour pressure of water at this temperature is 0.992×10^5 Nm^{-2}. How many gram of steam are necessary to distill over 100 g of diethyl aniline?

25. Calculate the b. pt. of a solution having 6 g sugar (5% by weight NaCl) in one litre water. Assume latent heat of steam 2.25 kJ/g and complete dissociation of NaCl.

26. The average O.P. of human blood is 7.7 atm at 40°C. Calculate, assuming molarity and molality be same:

(a) Concentration of blood in molarity.

(b) Freezing point of blood. Given K_f' of $H_2O = 1.86$ K $molality^{-1}$

27. A solution of 6 g NaCl (5% by weight impurity of $CaCl_2$) in one litre of water has been prepared. Calculate its depression in freezing point. Assume complete dissociation of both. K_f' for $H_2O = 1.86$ K mol^{-1} Kg.

28. 1.1 g $CoCl_3 \cdot 6NH_3$ (mol. wt. = 267.5) was dissolved in 100 g of water. The freezing point of solution was –0.306°C. How many mole of solute particles exist in solution for each mole of solute introduced if 100% ionisation of complex is noticed. K_f for $H_2O = 1.86$ K mol^{-1} kg.

29. A solution containing 10 g of a dibasic acid in 1000 g water freezes at 272.85 K. 10 mL of this solution requires 12 mL of $N/10$ NaOH for complete neutralization. If K_f' for water is 1.86° mol^{-1} kg, calculate van't Hoff factor for acid.

30. Phenol associates in C_6H_6 to double molecules. A solution of 2 g of phenol in 100 g C_6H_6 has its f. pt. lowered by 0.72 K. K_f for C_6H_6 is 5.12 K mol^{-1} kg. Calculate degree of association of phenol.

31. A metal M of molar mass 96 g mol^{-1} reacts with fluorine to form a salt that can be represented as MF_x. In order to determine x, 9.18 g of the sample of the salt is dissolved in 100 g of water and its boiling point was determined to be 374.38 K. What is the chemical formula of the salt? Given K_b (water) = 0.512 kg mol^{-1} Assume complete dissociation of salt.

32. A solution of non-volatile solute in water freezes at –0.30°C. The vapour pressure of pure water at 298 K is 23.0 mm Hg and K_f of water is 1.8 K kg mol^{-1}. Calculate vapour pressure of the solution at 298 K.

Answers

1. 2.69×10^{-3} ;
2. 2.75×10^4
3. 26.52 mm ;
4. 9.704 atm ;
5. 6.49×10^7 ;
6. 21 kPa (II distillate), $n_A = 0.857$, $n_B = 0.143$;
7. (a) 9.004 k Nm^{-2}, (b) 0.2373, (c) 6.519 k Nm^{-2}, (d) 0.7626 ;
8. 371.42 torr ;
9. 2-propanol = 101.10 mm, 1-propanol = 51.9 mm ;
10. $P_A^\circ = 100$ torr, $P_B^\circ = 60$ torr, $X = 0.25$;
11. (a) 56.65 , (b) 1541.68 mm ;
12. 254 mm, 135 mm ;
13. 62 ;
14. 40.5% ;
15. 0.1708 g ;
16. 1321.3, $C_{44}H_{88}O_{44}$;
17. 1.12 g mL^{-1}, 105.48°C ;
18. 36 : 10 ;
19. $A : B :: 1 : 1$;
20. 102.29°C ;
21. 1.02 ;
22. (a) 213.99, (b) $\alpha = 0.60$;
23. 2.56×10^5 Pa ;
24. 570.66 g ;
25. 100.013°C ;
26. (a) 0.3 M, (b) –0.558°C ;
27. 0.377°C ;
28. $i = 4 \therefore [Co(NH_3)_6]Cl_3 \longrightarrow Co(NH_3)_6^{3+} + 3Cl^-$;
29. 1.344 ;
30. 67.78% ;
31. $x = 4$;
32. 22.93 mm.

(c) II order : When both the reactants have same concentration

$$K = \frac{1}{t.a}\frac{X}{(a-X)} \qquad \ldots(13)$$

When both the reactants have different concentration

$$K = \frac{2.303}{t(a-b)}\log\frac{b(a-X)}{a(b-X)} \qquad \ldots(14)$$

$$t_{1/2} = \frac{1}{K.a} \qquad \ldots(15)$$

$$\text{unit of } K = \text{litre mol}^{-1}\text{ time}^{-1} \qquad \ldots(16)$$

(d) III order :

$$K = \frac{1}{t.2a^2}\frac{X(2a-X)}{(a-X)^2} \qquad \ldots(17)$$

$$t_{1/2} = \frac{3}{2Ka^2} \qquad \ldots(18)$$

$$\text{unit of } K = \text{litre}^2\text{ mol}^{-2}\text{ time}^{-1} \qquad \ldots(19)$$

4. General formula for $t_{1/2}$:

$$t_{1/2} \propto (a)^{1-n} \qquad \ldots(20)$$

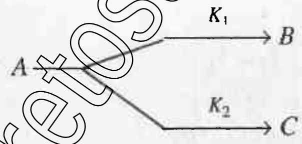
or

$$(1-n) = \frac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''} \qquad \ldots(21)$$

5. General formula for unit of K : $\text{litre}^{n-1}\text{ mol}^{1-n}\text{ time}^{-1}$ ...(22)

6. Parallel path reactions: A single reactant gives two products B, C simultaneously with different decay constants.

For a I order reaction :



$$-\frac{dA}{dt} = (K_1 + K_2)A = K_{av.}[A] \qquad \ldots(23)$$

where

$$K_{av.} = (K_1 + K_2) \qquad \ldots(24)$$

If after a time interval say x mol/litre of B are formed and y mol/litre of C are formed, then if reaction is carried out with A [at $t = 0$, $[B] = 0$ and $[C] = 0$]

$$\frac{x}{y} = \frac{K_1}{K_2} \qquad \ldots(25)$$

Also

$$\frac{d[B]}{dt}\Big/\frac{d[C]}{dt} = \frac{K_1}{K_2} \qquad \ldots(26)$$

Also

$$K_1 = [\text{Fractional yield of } B] \times K_{av.} \qquad \ldots(27)$$

$$K_2 = [\text{Fractional yield of } C] \times K_{av.} \qquad \ldots(28)$$

7. Sequential reactions: A reactant (A) decomposes to (B), which in turns decomposes to (C), *i.e.*, $(A) \xrightarrow{K_1} (B) \xrightarrow{K_2} (C)$

If $t = 0$, $[B] = 0$ and $K_1 < K_2$, then at $t = t$

$$[B]_t = \frac{K_1[A]_0}{K_2 - K_1}\left[e^{-K_1 t} - e^{-K_2 t}\right] \qquad \text{...(29)}$$

Also maximum conc. of $[B]$ at time t is given by

$$t_{\max} = \frac{2.303}{K_2 - K_1}\log_{10}\left[\frac{K_2}{K_1}\right] \qquad \text{...(30)}$$

$$[B]_{\max} = [A]_0\left[\frac{K_1}{K_2}\right]^{\frac{K_2}{K_1 - K_2}} \qquad \text{...(31)}$$

Kinetic Studies of Reversible Elementary Reaction:

(a) Case I: First order – opposed by first order:

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$t = 0$	A_0	0
$t = t$	$A_0 - X$	X

$$t = \frac{2.303}{K_f + K_b}\log\frac{X_{eq.}}{X_{eq.} - X} \qquad \text{...(32)}$$

($X_{eq.}$ is the concentration of B at equilibrium)

(b) Case II: First order – opposed by first order:

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$t = 0$	A_0	B_0
$t = t$	$A_0 - X$	$B_0 + X$

$$t = \frac{2.303}{K_f + K_b}\log\frac{X_{eq.}}{X_{eq.} - X} \qquad \text{...(33)}$$

($X_{eq.}$ is the concentration of product formed at equilibrium)

The Basic Problems with Solution

➤ Problem 1. Which of the following will react fastest (produce more product in a given time) and which will react at the highest rate?

(a) 1 mole of *A* and 1 mole of *B* in 1 litre vessel.

(b) 2 mole of *A* and 2 mole of *B* in 2 litre vessel.

(c) 0.2 mole of *A* and 0.2 mole of *B* in 0.1 litre vessel.

➤ Problem 2. N_2O_5 decomposes according to equation; $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(a) What does $-\frac{d[N_2O_5]}{dt}$ denote?

(b) What does $\frac{d[O_2]}{dt}$ denote?

(c) What is the unit of rate of this reaction?

➤ Problem 3. Dinitrogen pentaoxide decomposes as follows :

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2. \quad \text{If, } -\frac{d[N_2O_5]}{dt} = K'[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = K''[N_2O_5]$$

$$\frac{d[O_2]}{dt} = K'''[N_2O_5]$$

Derive a relation in K', K'' and K'''.

➤ Problem 4. The reaction; $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism,

(i) $NO + Br_2 \overset{\text{fast}}{\rightleftharpoons} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$

Suggest the rate law expression.

➤ Problem 5. The thermal decomposition of N_2O_5 occurs in the following steps :

Step I $\quad N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$

Step II $\quad N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$

Overall reaction $\quad 2N_2O_5 \longrightarrow 4NO_2 + O_2$

Suggest the rate expression.

➤ Problem 6. It has been proposed that the conversion of ozone into O_2 proceeds in two steps :

$$O_{3(g)} \rightleftharpoons O_{2(g)} + O_{(g)}$$

$$O_{3(g)} + O_{(g)} \longrightarrow 2O_{2(g)}$$

(a) Write the equation for overall reaction.
(b) Identify the intermediate, if any.
(c) Derive molecularity for each step of mechanism.

➤ **Problem 7.** Derive the relationship between rate of reaction, rate of disappearance of X, Y and rate of formation of X_2Y_3 for the reaction :

$$2X + 3Y \longrightarrow X_2Y_3$$

➤ **Problem 8.** For the reaction; $4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$, the rate of reaction in terms of disappearance of NH_3 is $-\frac{d[NH_3]}{dt}$, then write the rate expression in terms of concentration of O_2, NO and H_2O.

➤ **Problem 9.** The decomposition of N_2O_5 in CCl_4 solution at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 M and after 184 minute, it is reduced to 2.08 M. The reaction takes place according to the equation :

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Calculate the average rate of this reaction in terms of hour, minute and second. What is the rate of production of NO_2 during this period?

➤ **Problem 10.** The reaction; $2N_2O_5 \longrightarrow 4NO_2 + O_2$, shows an increase in concentration of NO_2 by 20×10^{-3} mol litre^{-1} in 5 second. Calculate
(a) rate of appearance of NO_2,
(b) rate of reaction and
(c) rate of disappearance of N_2O_5.

➤ **Problem 11.** For the decomposition reaction: $N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$; the initial pressure of N_2O_4 falls from 0.46 atm to 0.28 atm in 30 minute. What is the rate of appearance of NO_2?

➤ **Problem 12.** The rate of change in concentration of C in the reaction; $2A + B \longrightarrow 2C + 3D$, was reported as 1.0 mol litre^{-1} sec^{-1}. Calculate the reaction rate as well as rate of change of concentration of A, B, and D.

➤ **Problem 13.** A chemical reaction $2A \longrightarrow 4B + C$; in gaseous phase shows an increase in concentration of B by 5×10^{-3} M in 10 second. Calculate:
(a) rate of appearance of B,
(b) rate of the reaction,
(c) rate of disappearance of A.

➤ **Problem 14.** From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.
(a) $3NO_{(g)} \longrightarrow N_2O_{(g)} + NO_{2(g)}$; Rate = $K[NO]^2$
(b) $H_2O_{2(aq)} + 3I^-_{(aq.)} + 2H^+ \longrightarrow 2H_2O_{(l)} + I_3^-$;
Rate = $K[H_2O_2][I^-]$

(c) $CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$; Rate = $K[CH_3CHO]^{3/2}$

(d) $CHCl_{3(g)} + Cl_{2(g)} \longrightarrow CCl_{4(g)} + HCl_{(g)}$;
Rate = $K[CHCl_3][Cl_2]^{1/2}$

(e) $C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$; Rate = $K[C_2H_5Cl]$

➤ **Problem 15.** The reaction; $2A + B + C \longrightarrow D + 2E$; is found to be I order in A, II order in B and zero order in C.

(a) Write the rate expression.

(b) What is the effect on rate on increasing the conc. of A, B and C two times?

➤ **Problem 16.** For ; $\underset{\text{(excess)}}{2A} + B + C \longrightarrow$ Products, calculate the;

(a) rate expression.

(b) units of rate and rate constant.

(c) effect on rate if concentration of A is doubled and of B is tripled.

➤ **Problem 17.** Find the order of reaction for the rate expression rate = $K[A]\,[B]^{2/3}$. Also suggest the units of rate and rate constant for this expression.

➤ **Problem 18.** For a reaction; $3A \longrightarrow$ Products, it is found that the rate of reaction becomes nine times if concentration of A is increased three times, calculate order of reaction.

➤ **Problem 19.** 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 if $K = 2.5 \times 10^{-4}$ mol litre^{-1} s^{-1}.

➤ **Problem 20.** At 25°C, the rate constant for the reaction $I^- + ClO^- \longrightarrow IO^- + Cl^-$ is 0.0606 litre mol^{-1} sec^{-1}. If a solution is initially 1.0 M in I^- and 5.0×10^{-4} M in ClO^-. Can you calculate the $[ClO^-]$ after 300 sec. If yes, then how much. If no, then why?

➤ **Problem 21.** In a reaction; $2A \longrightarrow$ Products, the concentration of A decreases from 0.5 mol litre^{-1} to 0.4 mol litre^{-1} in 10 minutes. Calculate rate during this interval.

➤ **Problem 22.** In a reaction; $n_1A + n_2B \longrightarrow m_1C + m_2D$, 5 mol litre^{-1} of A are allowed to react with 3 mol litre^{-1} of B. After 5 second, the concentration of A was found to be 4 M. Calculate rate of reaction in terms of A and D.

➤ **Problem 23.** For the reaction; $2A + B + C \longrightarrow A_2B + C$.
The rate = $K[A][B]^2$ with $K = 2.0 \times 10^{-6}$ M^{-2} s^{-1}. Calculate the initial rate of the reaction when $[A] = 0.1$ M, $[B] = 0.2$ M and $[C] = 0.8$ M. If the rate of reverse reaction is negligible then calculate the rate of reaction after $[A]$ is reduced to 0.06 M.

➤ **Problem 24.** A reaction is second order with respect to a reaction. How is the rate of reaction affected if the concentration of the reactant is :
(a) doubled, (b) reduced to 1/2?

➤ **Problem 25.** A reaction is first order in *A* and second order in *B* :

(i) Write differential rate equation.

(ii) How is the rate affected when the concentration of *B* is tripled?

(iii) How is the rate affected when the concentration of both *A* and *B* is doubled?

➤ **Problem 26.** The rates of most reactions double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.

➤ **Problem 27.** Calculate the rate constant and half life period for first order reaction having activation energy 39.3 kcal mol^{-1} at 300°C and the frequency constant 1.11×10^{11} sec^{-1}.

➤ **Problem 28.** The specific rate constant for the decomposition of formic acid is 5.5×10^{-4} sec^{-1} at 413 K. Calculate the specific rate constant at 458 K if the energy of activation is 2.37×10^4 cal mol^{-1}.

➤ **Problem 29.** The temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate the activation energy.

➤ **Problem 30.** The experimental data for the reaction, $2A + B_2 \longrightarrow 2AB$ are as follows. Write probable rate expression;

$[A]$ mol $litre^{-1}$	$[B_2]$ mol $litre^{-1}$	Rate $\times 10^4$ mol $litre^{-1}$ sec^{-1}
0.50	0.50	1.6
0.50	1.00	3.2
1.00	1.00	3.2

➤ **Problem 31.** In a reaction between *A* and *B*, the initial rate of reaction was measured for different initial concentrations of *A* and *B* as given below :

A/M	0.20	0.20	0.40
B/M	0.30	0.10	0.05
r_0/Ms^{-1}	5.07×10^{-5}	5.07×10^{-5}	7.6×10^{-5}

What is the order of reaction with respect to *A* and *B*?

➤ **Problem 32.** The reaction between *A* and *B* is first order with respect to *A* and zero order with respect to *B*. Fill in the blanks in the following table :

Experiment	$[A]/M$	$[B]/M$	Initial rate/M min
I	0.1	0.1	2.0×10^{-2}
II	....	0.2	4.0×10^{-2}
III	0.4	0.4	......
IV	....	0.2	2.0×10^{-2}

➤ **Problem 33.** The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

$[Cl_2]$	[NO]	Initial rate $\times 10^3$ (mol $litre^{-1}$ sec^{-1})
0.05	0.05	1
0.15	0.05	3
0.05	0.15	9

(a) What is the order with respect to NO and Cl_2 in the reaction?

(b) Write the rate expression.

(c) Calculate the rate constant.

(d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 *M* and 0.4 *M* respectively.

➤ **Problem 34.** The decomposition of N_2O_5 at an initial pressure of 380 mm and 50°C is 50% complete in 56 minutes and 71% complete in 100 minutes. What is the order of reaction? How much of N_2O_5 will decompose in 100 minutes at 50°C but at an initial pressure of 500 mm?

➤ **Problem 35.** The decomposition of N_2O_5 takes place according to I order as

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Calculate :

(a) The rate constant, if instantaneous rate is 1.4×10^{-6} mol litre^{-1} sec^{-1} when concentration of N_2O_5 is 0.04 *M*.

(b) The rate of reaction when concentration of N_2O_5 is 1.20 *M*.

(c) The concentration of N_2O_5 when the rate of reaction will be 2.45×10^{-5} mol litre^{-1} sec^{-1}.

➤ **Problem 36.** Calculate the rate of reaction for the change $2A \longrightarrow$ Products, when rate constant of the reaction is 2.1×10^{-5} time^{-1} and $[A]_0 = 0.2$ *M*.

➤ **Problem 37.** In a pseudo first order hydrolysis of ester in water the following results were obtained :

t/s	0	30	60	90
[Ester]/*M*	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

➤ **Problem 38.** Calculate the half life of a first order reaction from their rate constants given below :

(a) 200 s^{-1}; (b) 2 min^{-1}; (c) 4 year^{-1}.

➤ **Problem 39.** The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

➤ **Problem 40.** 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 year and 60 year if it is not lost metabolically.

➤ **Problem 41.** For the decomposition, $N_2O_{5(g)} \longrightarrow N_2O_{4(g)} + \frac{1}{2}O_{2(g)}$, the initial pressure of N_2O_5 is 114 mm and after 20 sec., the pressure of reaction mixture becomes 133 mm. Calculate the rate of reaction in terms of (a) change in pressure sec^{-1} and (b) change in molarity sec^{-1}. Given that reaction is carried out at 127°C.

➤ **Problem 42.** A substance reacts according to I order kinetics and rate constant for the reaction is 1×10^{-2} sec^{-1}. If its initial concentration is 1 *M*.

(a) What is initial rate?

(b) What is rate after 1 minute?

➤ **Problem 43.** A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion?

➤ **Problem 44.** Show that time required to complete 99.9% completion of a first order reaction is 1.5 times to 90% completion.

➤ **Problem 45.** Thermal decomposition of a compound is of first order. If 50% sample of the compound is decomposed in 120 minute, how long will it take for 90% of the compound to decompose?

➤ **Problem 46.** A first order gaseous reactions has $K = 1.5 \times 10^{-[illegible]}$ sec^{-1} at 200°C. If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction?

➤ **Problem 47.** The rate constant for a first order reaction was found to be 0.082 min^{-1}. If initial concentration of reactant is 0.15 *M*.how long would it take,

(a) to reduce the concentration of *A* to 0.03 *M*.

(b) to reduce the concentration of *A* by 0.03 *M*.

➤ **Problem 48.** The following data represent for the decomposition of NH_4NO_2 in aqueous solution.

Time in minutes	10	15	20	25	∞
Volume of N_2 (in mL)	6.25	9.0	11.40	13.65	33.05

(a) Show that reaction is of first order.

(b) Calculate velocity constant.

➤ **Problem 49.** Derive the order of reaction for decomposition of H_2O_2 from the following data.

Time in minutes	10	15	20	25	∞
Volume of O_2 given by H_2O_2	6.30	8.95	11.40	13.5	35.75

➤ **Problem 50.** Derive order of reaction for the decomposition of H_2O_2 from the following data.

Time in minutes	0	10	20	30
Volume of $KMnO_4$ needed for H_2O_2	25	16	10.5	7.09

➤ **Problem 51.** The pre exponential factor for free radical addition of chlorine is 2×10^{13} sec^{-1}. Find out the rate constant of this reaction at STP. Given $R = 8.314$ J/mol-K.

➤ **Problem 52.** The rate constant of a certain reaction is given by :

$$\log_{10} K = 5.4 - \frac{212}{T} + 2.17 \log_{10} T$$

Calculate the activation energy at 127°C.

Answers

1. See solution
2. See solution;
3. $2K' = K'' = 4K'''$
4. rate = $K^1[NO]^2[Br_2]$;
5. rate = $K[N_2O_5]$;
6. (a) See solution, (b) O (g), (c) First step is unimolecular and second is bimolecular.
7. See solution ;
8. See solution ;
9. 6.79×10^{-4} M min^{-1},
   1.13×10^{-5} M s^{-1},
   4.076×10^{-2} M hr^{-1},
   2.716×10^{-3} M min^{-1} ;
10. (a) 4×10^{-3} mol litre^{-1} sec^{-1},
    (b) 1×10^{-3} mol litre^{-1} sec^{-1},
    (c) 2×10^{-3} mol litre^{-1} sec^{-1};
11. 1.2×10^{-2} atm min^{-1};
12. 1.0 mol litre^{-1} sec^{-1}, 0.5 mol litre^{-1} sec^{-1},
    1.5 mol litre^{-1} sec^{-1}, 0.5 mol litre^{-1} sec^{-1};
13. (a) 5×10^{-4} mol litre^{-1} sec^{-1}, (b) 1.25×10^{-4} mol litre^{-1} sec^{-1},
    (c) 2.5×10^{-4} mol litre^{-1} sec^{-1};
14. See solution ;
15. (a) $K[A]^1[B]^2[C]^0$, (b) $r_2 = 8r_1$;
16. (a) $K[A]^0[B]^1[C]^1$, (b) Unit of rate = mol litre^{-1} time^{-1},
    Unit of rate constant = litre mol^{-1} time^{-1}, (c) $r_2 = 3r_1$;
17. 1.67, unit of rate = mol litre^{-1} time^{-1},
    unit of rate constant = mol$^{-2/3}$ litre$^{+2/3}$ time^{-1}
18. 2 ;
19. For $N_2 = 1.25 \times 10^{-4}$ mol litre^{-1} sec^{-1}, For $H_2 = 3.75 \times 10^{-4}$ mol litre^{-1} sec^{-1} ;
20. See solution;
21. 0.005 mol litre^{-1} minute^{-1};
22. For $A = 0.2\ Ms^{-1}$; For $D = \frac{m_2}{n_1} \times 0.2\ Ms^{-1}$;
23. 3.89×10^{-9} mol litre^{-1} time^{-1};
24. (a) $r_1 = 4r_0$, (b) $r_2 = \frac{1}{4} r_0$;
25. (i) $K[A]^1[B]^2$, (ii) $r_1 = 9r_0$, (iii) $r_2 = 8r_0$;

26. 52.903 kJ ; **27.** 1.14×10^{-4} sec^{-1}, 6078 sec;

28. 9.38×10^{-3} sec^{-1}; **29.** 10.207 kcal mol^{-1};

30. $r = K[B_2]^1$;

31. 0 for B; 0.58 for A;

32. (II) –0.2, (III) 8×10^{-2}, (IV) 0.1;

33. (a) NO = 2, Cl_2 = 1, (b) $K[Cl_2]^1[NO_2]^2$,
(c) 8 litre^2 mol^{-2} sec^{-1}, (d) 0.256 mol litre^{-1} sec^{-1};

34. I order, 71%;

35. (a) 3.5×10^{-5} sec^{-1}, (b) 4.2×10^{-5} mol litre^{-1} sec^{-1}, (c) 0.7 mol litre^{-1};

36. 4.2×10^{-6} mol litre^{-1} sec^{-1}; **37.** 1.96×10^{-2};

38. (a) 3.465×10^{-3} sec, (b) 3.465×10^{-1} min, (c) 1.733×10^{-1} yr;

39. 0.0462 sec^{-1};

40. 0.7814 µg, 0.227 µg;

41. 2.5×10^{-3} atm sec^{-1}, 7.61×10^{-5} Ms^{-1};

42. (a) 1×10^{-2} mol litre^{-1} sec^{-1}, (b) 5.49×10^{-3} mol litre^{-1} sec^{-1};

43. 160.97 minute; **44.** See solution;

45. 398.78 min ; **46.** 5.25%, 128.33 hr. ;

47. (a) 19.63 minutes, (b) 2.72 minutes;

48. I order; $K = 2.0 \times 10^{-2}$ min^{-1}; **49.** I order; $K = 1.92 \times 10^{-2}$ min^{-1};

50. I order; **51.** 2×10^{13} sec^{-1};

52. 2712 cal

Solution

Solution 1. (i) (b) will react fastest because of more reactant present, there will be more product produced per unit time.

(ii) (c) will react at highest rate because $[A]$ and $[B]$ are highest and thus rate will be more.

Solution 2. (a) Rate of decomposition of N_2O_5.

(b) Rate of formation of O_2.

(c) Unit of rate = mol litre^{-1} time^{-1}.

Solution 3. For the given change $-\dfrac{d[N_2O_5]}{dt} = +\dfrac{1}{2}\dfrac{d[NO_2]}{dt} = +2\dfrac{d[O_2]}{dt}$

On substituting values, $K'[N_2O_5] = \dfrac{1}{2}K''[N_2O_5] = 2K'''[N_2O_5]$

or $\mathbf{2K' = K'' = 4K'''}$

Solution 4. The rate expression is derived by step II of the mechanism, as it is the slower one

$$\text{rate} = K[NOBr_2][NO] \qquad ...(1)$$

However, $NOBr_2$ is an intermediate and thus its concentration should be replaced
from equation (1).

For step (I) Equilibrium constant $K_c = \dfrac{[NOBr_2]}{[NO][Br_2]}$

$$[NOBr_2] = K_c[NO][Br_2] \qquad ...(2)$$

Thus by eq. (1) and (2) $\quad \mathbf{Rate = K'[NO]^2[Br_2]}$

Solution 5. Rate = $K[N_2O_5]$. (from slow step).

Solution 6. **(a)** Addition of the two steps gives the overall reaction :

$$2O_{3(g)} \longrightarrow 3O_{2(g)}$$

(b) Intermediate is $O_{(g)}$.

(c) The first step is unimolecular. The second step is bimolecular.

Solution 7. Average rate of reaction $= -\dfrac{1}{2}\dfrac{\Delta[X]}{\Delta t} = -\dfrac{1}{3}\dfrac{\Delta[Y]}{\Delta t} = \dfrac{\Delta[X_2Y_3]}{\Delta t}$

Instantaneous rate of reaction $= -\dfrac{1}{2}\dfrac{d[X]}{dt} = -\dfrac{1}{3}\dfrac{d[Y]}{dt} = \dfrac{d[X_2Y_3]}{dt}$

Solution 8.
$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

or
$$NH_3 + \frac{5}{4}O_2 \longrightarrow NO + \frac{6}{4}H_2O$$

Then, rate of disappearance of $NH_3 = -\frac{d[NH_3]}{dt}$

Also, rate of reaction $= -\frac{d[NH_3]}{dt}$

$$= -\frac{4}{5}\frac{d[O_2]}{dt} = \frac{d[NO]}{dt} = \frac{4}{6}\frac{d[H_2O]}{dt}$$

Solution 9.
$$\text{Average Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{1}{2}\frac{[2.08 - 2.33]}{184}$$

$$= \mathbf{6.79 \times 10^{-4}\ M\ min^{-1}}$$

$$= 6.79 \times 10^{-4} \times \frac{1}{60}\ Ms^{-1}$$

$$= \mathbf{1.13 \times 10^{-5}\ Ms^{-1}}$$

$$= 6.79 \times 10^{-4} \times 60\ Mhr^{-1}$$

$$= \mathbf{4.076 \times 10^{-2}\ Mhr^{-1}}$$

Also
$$= \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

$$\frac{\Delta[NO_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} \times 4 = 6.79 \times 10^{-4} \times 4$$

$$= 6.79 \times 10^{-4} = \mathbf{2.716 \times 10^{-3}\ Mmin^{-1}}$$

Solution 10.
Increase in concentration of $NO_2 = 20 \times 10^{-3}$ mol litre^{-1}

time taken = 5 sec

(a) $\therefore$ Rate of appearance of $NO_2 = \frac{\Delta[NO_2]}{\Delta t} = \frac{20 \times 10^{-3}}{5}$

$$= \mathbf{4 \times 10^{-3}\ mol\ litre^{-1}\ sec^{-1}}$$

(b) Rate of reaction $= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$

$$= \frac{1}{4} \times 4 \times 10^{-3}$$

$$= \mathbf{1 \times 10^{-3}\ mol\ litre^{-1}\ sec^{-1}}$$

(c) Rate of disappearance of $N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}$

$$= \frac{1}{2} \times 4 \times 10^{-3}$$

$$= \mathbf{2 \times 10^{-3}\ mol\ litre^{-1}\ sec^{-1}}$$

Solution 11. Rate of reaction $= -\frac{d[N_2O_4]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

$$\therefore \quad \frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{(0.28-0.46)}{30}$$

$$\therefore \quad \frac{1}{2}\frac{d[NO_2]}{dt} = 6\times10^{-3}$$

$$\frac{d[NO_2]}{dt} = \mathbf{1.2\times10^{-2}\ atm\ min^{-1}}$$

Solution 12. We have, $-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt}$ = rate of reaction

$$\because \quad \frac{d[C]}{dt} = 1.0\ \text{mol litre}^{-1}\ \text{sec}^{-1}$$

$$\therefore \quad -\frac{d[A]}{dt} = \frac{d[C]}{dt} = \mathbf{1.0\ mol\ litre^{-1}\ sec^{-1}}$$

$$-\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \mathbf{0.5\ mol\ litre^{-1}\ sec^{-1}}$$

$$\frac{d[D]}{dt} = \frac{3}{2}\frac{d[C]}{dt} = \frac{3}{2}\times1 = \mathbf{1.5\ mol\ litre^{-1}\ sec^{-1}}$$

Also, Rate $= \frac{1}{2}\frac{d[C]}{dt}$

$$\therefore \quad \text{Rate} = \frac{1}{2}\times1 = \mathbf{0.5\ mol\ litre^{-1}\ sec^{-1}}$$

Solution 13. (a) Rate of appearance of $B = \frac{\text{increase in }[B]}{\text{time}} = \frac{5\times10^{-3}}{10}$

$$= \mathbf{5\times10^{-4}\ \mathit{M}\ s^{-1}}$$

(M is mol litre^{-1})

(b) Also, rate of reaction $= -\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

$$\therefore \quad -\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{4}\times5\times10^{-4}$$

$$\therefore \quad -\frac{1}{2}\frac{d[A]}{dt} = \mathbf{1.25\times10^{-4}\ \mathit{M}\ sec^{-1}}$$

(c) rate of disappearance of $A = 1.25\times2\times10^{-4}$

$$= \mathbf{2.5\times10^{-4}\ \mathit{M}\ sec^{-1}}$$

Solution 14. (a) Second order ; Litre mol^{-1} time^{-1}

(b) —do— ; —do—

(c) 3/2 order ; Litre$^{1/2}$ mol$^{-1/2}$ time^{-1}

(d) —do— ; —do—

(e) First order ; time^{-1}

Solution 15. **(a)** Rate = $K[A]^1 [B]^2 [C]^0$

(b) Let initial conc. of A, B and C be a, b, and c mol litre^{-1} respectively

Then, $$\text{Rate } r_1 = K a^1 b^2 c^0 \quad \text{...(1)}$$

Now if conc. of A, B and C are doubled, *i.e.* $2a$, $2b$ and $2c$ respectively, then,

$$r_2 = K(2a)^1 (2b)^2 (2c)^0 \quad \text{...(2)}$$

By eqs. (1) and (2), $\dfrac{r_1}{r_2} = \dfrac{1}{8}$ $\therefore$ $r_2 = 8r_1$

Solution 16. **(a)** Rate = $K[A]^0 [B]^1 [C]^1$

(b) Unit of rate = mol litre^{-1} time^{-1}

Unit of rate constant = litre mol^{-1} time^{-1}

(c) Let initial conc. of A, B and C be a, b and c, respectively.

$$\therefore \quad r_1 = K(a)^0 (b)^1 (c)^1 \quad \text{...(1)}$$

Now $$[A] = 2a; \ [B] = 3b$$

$$\therefore \quad r_2 = K(2a)^0 (3b)^1 (c)^1 \quad \text{...(2)}$$

By eqs. (1) and (2), $\dfrac{r_1}{r_2} = \dfrac{1}{3}$

$$\therefore \quad r_2 = 3r_1$$

Solution 17. $$\text{Rate} = K[A][B]^{2/3}$$

$$\therefore \quad \text{Order of reaction} = 1 + \frac{2}{3} = \frac{5}{3} = 1.67$$

Unit of rate $\left(\dfrac{dx}{dt}\right)$ is **mol litre^{-1} time^{-1}**

Unit of rate constant : rate constant $(K) = \dfrac{dx/dt}{[\text{reactant}]^{5/3}} = \dfrac{\text{mol litre}^{-1}\ \text{t}^{-1}}{\left(\frac{\text{mol}}{\text{litre}}\right)^{5/3}}$

$$= \textbf{mol}^{-2/3}\ \textbf{litre}^{+2/3}\ \textbf{time}^{-1}$$

Solution 18. $$\text{Rate} = K[\text{Reactant}]^n$$

if $[\text{Reactant}] = a$; rate $= r_1$

$$\therefore \quad r_1 = K[a]^n$$

if $[\text{Reactant}] = 3a$; rate $= 9r_1$

$$9r_1 = K[3a]^n$$

$$\therefore \quad \frac{1}{9} = \left[\frac{1}{3}\right]^n$$

$$\therefore \quad n = 2$$

Solution 19.

$$2NH_3 \longrightarrow N_2 + 3H_2.$$

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\text{Rate} = K[NH_3]^0$$

or

$$\frac{d[NH_3]}{dt} = 2.5 \times 10^{-4} \text{ mol litre}^{-1}\text{ s}^{-1}$$

$$\frac{d[N_2]}{dt} = \frac{1}{2} \times 2.5 \times 10^{-4} = \mathbf{1.25 \times 10^{-4}\text{ mol litre}^{-1}\text{ s}^{-1}}$$

$$\frac{d[H_2]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4} = \mathbf{3.75 \times 10^{-4}\text{ mol litre}^{-1}\text{ s}^{-1}}$$

Solution 20. No doubt the unit of rate constant shows that it is II order. But it is necessary to know the rate law expression, which from the statement of the problem, could be any of the following (given below) :
Rate = $K[I][ClO^-]$ or Rate = $K[I^-]^2$ or Rate = $K[ClO^-]^2$

Solution 21.

Rate of reaction = rate of disappearance of A

$$\frac{1}{2}\left(-\frac{d[A]}{dt}\right) = \frac{1}{2}\left[\frac{0.5-0.4}{10}\right]$$

$$= \mathbf{0.005\text{ mol litre}^{-1}\text{ minute}^{-1}}$$

Solution 22. Change in $[A]$ in 5 sec. = $5\,M - 4\,M = 1\,M$

$\therefore$ Rate of reaction in terms of $A = -\frac{d[A]}{dt} = \frac{1}{5} = \mathbf{0.2\,M\text{ sec}^{-1}}$

Also,

$$-\frac{1}{n_1}\frac{d[A]}{dt} = \frac{1}{m_2}\frac{d[D]}{dt}$$

$\therefore$ Rate of reaction in terms of $D = \frac{d[D]}{dt} = \frac{m_2}{n_1} \times \mathbf{0.2\,M\text{ sec}^{-1}}$

Solution 23.

$$\text{Rate} = K[A][B]^2$$

$$[A] = 0.1\,M,\ [B] = 0.2\,M,\ K = 2.0 \times 10^{-6}$$

$$\therefore \text{Initial rate} = 2.0 \times 10^{-6} \times 0.1 \times (0.2)^2$$

$$= 8 \times 10^{-9}\text{ mol litre}^{-1}\text{ time}^{-1}$$

New rate when A is reduced to 0.06 M and B is 0.18 M. See stoichiometry of reaction.

$$\text{Rate} = 2.0 \times 10^{-6} \times (0.06) \times (0.18)^2$$

$$= \mathbf{3.89 \times 10^{-9}\text{ mol litre}^{-1}\text{ time}^{-1}}$$

Solution 24. Given, rate $(r_0) = K[A]^2$

(a) If $[A]$ is doubled : $r_1 = K[2A]^2$ $\therefore$ $\boldsymbol{r_1 = 4r_0}$

(b) If $[A]$ is reduced to half : $r_2 = K\left[\frac{A}{2}\right]^2$ $\therefore$ $\boldsymbol{r_2 = \frac{1}{4}r_0}$

Solution 25. (i) $\text{Rate} = \frac{dx}{dt} = K[A]^1[B]^2$

(ii) $r_0 = K[A]^1[B]^2$

$r_1 = K[A]^1[3B]^2$

$\therefore$ $\boldsymbol{r_1 = 9 \times r_0}$

(iii) $r_0 = K[A^1][B]^2$

$r_2 = K[2A]^1[2B]^2$

$\therefore$ $\boldsymbol{r_2 = 8 \times r_0}$

Solution 26.

$$2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$\frac{K_2}{K_1} = 2;\ T_2 = 308\text{ K},\ T_1 = 298\text{ K}$

$$\therefore \quad 2.303 \log 2 = \frac{E_a}{8.314} \times \frac{10}{308 \times 298}$$

$E_a = 52.903 \times 10^3$ J or $\boldsymbol{E_a = 52.903\text{ kJ}}$

olution 27. Given : $A = 1.11 \times 10^{11}\ \text{sec}^{-1}$; $E_a = 39.3 \times 10^3\ \text{cal mol}^{-1}$;
$R = 1.987$ cal ; $T = 573$ K.

$$\because \quad K = Ae^{-E_a/RT}$$

$$\therefore \quad \ln K = \ln A - \frac{E_a}{RT}$$

$$\text{or} \quad \log_{10} K = \log_{10} A - \frac{E_a}{2.303\, RT}$$

$$\log_{10} K = \log_{10} 1.11 \times 10^{11} - \left\{\frac{39.3 \times 10^3}{2.303 \times 1.987 \times 573}\right\}$$

$$\therefore \quad \boldsymbol{K = 1.14 \times 10^{-4}\ \text{sec}^{-1}}$$

Also for first order, $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.14 \times 10^{-4}} = \boldsymbol{6078\ \text{sec}}$

Solution 28. Given :

$K_2 = ?,\ \ K_1 = 5.5 \times 10^{-4},\ \ R = 1.987\text{ cal},\ \ T_1 = 413\text{ K},\ \ T_2 = 458\text{ K}$

$E_a = 2.37 \times 10^4\ \text{cal mol}^{-1}$

$$\because \quad 2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

$$2.303 \log \frac{K_2}{5.5 \times 10^{-4}} = \frac{2.37 \times 10^4}{1.987}\left[\frac{458-413}{458 \times 413}\right]$$

$$\therefore \quad K_2 = \mathbf{9.38 \times 10^{-3}\ sec^{-1}}$$

Solution 29. Given : $\frac{K_2}{K_1} = 1.75$

$T_1 = 25°C = 25 + 273 = 298\ K, \quad T_2 = 35°C = 35 + 273 = 308\ K$

(Since temperature coefficient is ratio of rate constants at 35°C and 25°C respectively.)

$$\because \quad 2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \quad 2.303 \log 1.75 = \frac{E_a}{1.987}\left[\frac{308-298}{308 \times 298}\right]$$

$$\mathbf{E_a = 10.207\ kcal\ mol^{-1}}$$

Solution 30. Let rate expresion be: rate $= K[A]^m\ [B_2]^n$

Thus, $1.6 \times 10^{-4} = K(0.5)^m\ (0.5)^n$ ...(i)

$3.2 \times 10^{-4} = K(0.5)^m\ (1.0)^n$ ...(ii)

$3.2 \times 10^{-4} = K(1.0)^m\ (1.0)^n$ ...(iii)

By (i) and (ii) $n = 1$

By (ii) and (iii) $m = 0$

$$\therefore \quad \text{rate} = \frac{dx}{dt} = \mathbf{K\ [B_2]^1}$$

Solution 31. Let the rate expression be $r = K\ [A]^m[B]^n$

$\therefore \quad 5.07 \times 10^{-5} = K\ [0.20]^m[0.30]^n$ ...(1)

$5.07 \times 10^{-5} = K\ [0.20]^m[0.10]^n$ ...(2)

$7.6 \times 10^{-5} = K\ [0.40]^m[0.05]^n$ ...(3)

By eq. (1) and (2) $1 = [3]^n \quad \therefore \quad \mathbf{n = 0}$

By eq. (1) and (3) $\frac{5.07}{7.6} = \left[\frac{1}{2}\right]^m \times [6]^n$

$\because n = 0 \quad \therefore \quad \frac{5.07}{7.6} = \left[\frac{1}{2}\right]^m$

$$m = \mathbf{0.58}$$

Thus, reaction is 0.58 order in A and zero order in B.

Solution 32. (II)—is 0.2; (III)—is 8×10^{-2}; (IV)—is 0.1

Solution 33. For the reaction; $2NO + Cl_2 \longrightarrow 2NOCl$

$$\text{Rate} = K[Cl_2]^m [NO]^n \quad \text{...(1)}$$

Where, m and n are order of reaction w.r.t. Cl_2 and NO, respectively.

From the given data :

$$1 \times 10^{-3} = K[0.05]^m [0.05]^n \quad \text{...(2)}$$

$$3 \times 10^{-3} = K[0.15]^m [0.05]^n \quad \text{...(3)}$$

$$9 \times 10^{-3} = K[0.05]^m [0.15]^n \quad \text{...(4)}$$

By eqs. (2) and (3),

$$m = 1$$

By eqs. (2) and (4)

$$n = 2$$

(a) ∴ Order with respect to NO is **2** and w.r.t. to Cl_2 is **1**.

(b) Also, rate expression $r = K[Cl_2]^1 [NO_2]^2$

(c) And rate constant., $K = \dfrac{r}{[Cl_2]^1[NO]^2} = \dfrac{1 \times 10^{-3}}{[0.05]^1[0.05]^2}$

$$= \mathbf{8\ litre^2\ mol^{-2}\ sec^{-1}}$$

(d) Further, $r = K[Cl_2]^1 [NO]^2 = 8\,[0.2]^1\,[0.4]^2$

$$= \mathbf{0.256\ mol\ litre^{-1}\ sec^{-1}}$$

Solution 34. The first order rate equation is,

$$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

We have for 50% completion of decomposition in 56 min.

$$K = \frac{2.303}{56} \log \frac{100}{50} = \frac{2.303}{56} \times 0.3010 = 0.0124 \text{ min}^{-1}.$$

For 71% completion of decomposition in 100 min, we have

$$K = \frac{2.303}{100} \log \frac{100}{29} = \frac{2.303}{100} \times 0.5376 = 0.0124 \text{ min}^{-1}$$

A constant value of K indicates the order of reaction to be **one**.

Also for I order $t_{1/n} \propto (a)^0$. Thus **71%** of the reaction will be completed at initial pressure of 500 mm.

Solution 35. (a) Rate $= K[N_2O_5]$

$$\therefore \quad K = \frac{1.4 \times 10^{-6}}{0.04} = \mathbf{3.5 \times 10^{-5}\ sec^{-1}}$$

(b) Also rate $= K[N_2O_5]$

$$= 3.5 \times 10^{-5} \times 1.20 = \mathbf{4.2 \times 10^{-5}\ mol\ litre^{-1}\ sec^{-1}}$$

(c) Further rate $= K[N_2O_5]$

$$\therefore \quad [N_2O_5] = \frac{2.45 \times 10^{-5}}{3.5 \times 10^{-5}} = \mathbf{0.7\ mol\ litre^{-1}}$$

Solution 36. The unit of rate constant suggest it to be first order.

$$\text{Thus rate} = K\,[A]$$
$$= 2.1 \times 10^{-5} \times 0.2 = \mathbf{4.2 \times 10^{-6}\ mol\ litre^{-1}\ sec^{-1}}$$

Solution 37. (i) Average rate of reaction $= \dfrac{\Delta[\text{ester}]}{\Delta\text{time}}$

$$= \frac{0.17 - 0.31}{60 - 30} = -4.67 \times 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

(ii) $$K = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

Where a is initial conc. of ester ($t = 0$) and x is the concentration of ester at time t.

$$K_1 = \frac{2.303}{30}\log\frac{0.55}{0.31} = 1.91 \times 10^{-2}$$

$$K_2 = \frac{2.303}{60}\log\frac{0.55}{0.17} = 1.96 \times 10^{-2}$$

$$K_3 = \frac{2.303}{90}\log\frac{0.55}{0.085} = 2.01 \times 10^{-2}$$

Thus, $$K = \frac{K_1 + K_2 + K_3}{3} = \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2} + 2.01 \times 10^{-2}}{3}$$

$$= \mathbf{1.96 \times 10^{-2}}$$

Solution 38. (a) $$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{200} = \mathbf{3.465 \times 10^{-3}\ sec}$$

(b) $$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{2} = \mathbf{3.465 \times 10^{-1}\ min}$$

(c) $$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{4} = \mathbf{1.733 \times 10^{-1}\ yr}$$

Solution 39. $$t = \frac{2.303}{K}\log\frac{a}{(a-x)}$$

If $a = 1$ then $(a - x) = 1/16$

$$K = \frac{2.303}{60}\log\frac{1}{1/16} = \mathbf{0.0462\ sec^{-1}}$$

Solution 40. $t_{1/2}$ Sr^{90} = 28.1 yr. $\therefore$ $K = \dfrac{0.693}{28.1}\ \text{yr}^{-1}$

Now, $t = \dfrac{2.303}{K}\log\dfrac{a}{(a-x)}$ $a = 1\ \mu g$

at $t = 10$ yr $$10 = \frac{2.303 \times 28.1}{0.693} \log \frac{1}{(a-x)}$$

∴ amount of Sr left $= (a-x) = \mathbf{0.7814\ \mu g}$

at $t = 60$ yr $$60 = \frac{2.303 \times 28.1}{0.693} \log \frac{1}{(a-x)}$$

∴ $(a-x) = \mathbf{0.227\ \mu g.}$

Solution 41.

	$N_2O_{5(g)} \longrightarrow$	$N_2O_{4(g)}$ +	$\frac{1}{2}O_{2(g)}$,
Initial pressure	P	0	0
Pressure at $t = 20$	$(P - P')$	P'	$P'/2$

Given $P = 114$ mm; $P + \left(\frac{P'}{2}\right) = 133$ mm, $\therefore \left(\frac{P'}{2}\right) = 19$ mm, $\therefore P' = 38$ mm,

Thus rate of reaction in terms of change in pressure = 38/20

$= 1.9 \text{ mm sec}^{-1}$

$= \mathbf{2.5 \times 10^{-3}\ atm\ sec^{-1}}$

Also we have $$PV = nRT$$

or $$\frac{n}{V} = C = \frac{P}{RT}$$

∴ Change in concentration in 20 sec $= \dfrac{38}{760 \times 0.0821 \times 400}$

$= 1.52 \times 10^{-3}\ M$

∴ Rate of reaction in terms of change in conc. $= \dfrac{1.52 \times 10^{-3}}{20}$

$= \mathbf{7.61 \times 10^{-5}\ M\ sec^{-1}}$

Solution 42. (a) Initial rate $= K\,[\text{Reactant}]^1 = 1 \times 10^{-2} \times [1] = 1 \times 10^{-2}$

∴ Rate $= \mathbf{1 \times 10^{-2}\ mol\ litre^{-1}\ sec^{-1}}$

(b) Now, $$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$10^{-2} = \frac{2.303}{1 \times 60} \log \frac{1}{(1-x)} \quad (\because\ t = 1 \text{ minute} = 60 \text{ sec.})$$

$(1-x) = 0.549$

∴ Rate after 1 minute $= K\,[\text{Reactant}]$ after 1 minute

$= K\,[0.549] = 10^{-2}\,[0.549]$

Rate after 1 minute $= \mathbf{5.49 \times 10^{-3}\ mol\ litre^{-1}\ sec^{-1}}$

Solution 43. $$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} \text{ minute}^{-1} \qquad (\because\ t_{1/2} = 69.3 \text{ min.})$$

Now, $$K = \frac{2.303}{t} \log \frac{100}{20} \quad [\text{If } a = 100, x = 80 \text{ and } a - x = 20]$$

$$\therefore \quad \frac{0.693}{69.3} = \frac{2.303}{t} \log 5$$

$$\therefore \quad t = \mathbf{160.97\ minute}$$

Solution 44. For 99.9% completion $[A]_0 = 100 \quad [A] = 0.1$

$$t_{99.9\%} = \frac{2.303}{K} \log \frac{100}{0.1} = \frac{2.303}{K} \times 3$$

Similarly $$t_{99\%} = \frac{2.303}{K} \log \frac{100}{1} = \frac{2.303}{K} \times 2$$

$$\therefore \quad t_{99.9\%} = 1.5 \times t_{90\%}.$$

Solution 45. Given : $t_{50\%} = 120$ minute

$$\because \quad K = \frac{2.303}{t} \log \frac{N_0}{N}$$

for 50% decay $$K = \frac{2.303}{120} \log \frac{N_0}{N_0/2} \quad (N = N_0/2) \qquad \text{...(i)}$$

for 90% decay $$K = \frac{2.303}{t} \log \frac{N_0}{N_0/10} \quad (N = N_0/10) \qquad \text{...(ii)}$$

By (i) and (ii) $$t = \mathbf{398.78\ minute}$$

Solution 46. $$t = \frac{2.303}{K} \log \frac{N_0}{N}$$

Given : $K = 1.5 \times 10^{-6}\ \text{sec}^{-1}$ (thus reaction is I order), $t = 10$ hour

$$10 \times 60 \times 60 = \frac{2.303}{1.5 \times 10^{-6}} \log \frac{N_0}{N}$$

$$\therefore \quad \frac{N_0}{N} = 1.0555$$

$$\therefore \quad N = 0.9475 \times N_0$$

$$\therefore \quad \text{Product formed} = N_0 - 0.9475\ N_0$$

$$= 0.0525\ N_0 = \mathbf{5.25\%}$$

Also $$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1 \cdot 5 \times 10^{-6}}$$

$$= 462000 \text{ sec} = \mathbf{128.33\ hr.}$$

Solution 47. Case (a) : Given $K = 0.082\ \text{min}^{-1}$, $[A]_0 = 0.015\ M$, $[A]_t = 0.03\ M$.

$$t = \frac{2.303}{K} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{0.082} \log \frac{0.15}{0.03} = \mathbf{19.63\ min.}$$

Case (b) : Given $K = 0.082\ \text{min}^{-1}$, $[A]_0 = 0.15\ M$;

$$[A]_t = 0.15 - 0.03 = 0.12\ M$$

$$t = \frac{2.303}{0.082}\log\frac{0.15}{0.12} = \mathbf{2.72\ min.}$$

Solution 48.

$$NH_4NO_{2(s)} \longrightarrow N_{2(g)} + 2H_2O_{(l)}$$

Moles at $t = 0$ a 0 0

Moles at $t = t$ $(a - x)$ x $2x$

The volume of N_2 formed at any time is proportional to the amount of NH_4NO_2 decomposed in that time.

At $t = \infty$ $V_{N_2} = 33.05$ mL $\therefore$ $a \propto 33.05$

(I) At $t = 10$ $V_{N_2} = 6.25$ mL $\therefore$ $x \propto 6.25$

(II) At $t = 15$ $V_{N_2} = 9.0$ mL $\therefore$ $x \propto 9.0$

(III) At $t = 20$ $V_{N_2} = 11.40$ mL $\therefore$ $x \propto 11.40$

(IV) At $t = 25$ $V_{N_2} = 13.65$ mL $\therefore$ $x \propto 13.65$

Now use, $$K = \frac{2.303}{t}\log\frac{a}{(a - x)}$$

Case I : $$K = \frac{2.303}{10}\log\frac{33.05}{33.05 - 6.25}$$

$$K = \mathbf{2.0 \times 10^{-2}\ min^{-1}}$$

Similarly, calculate K for each case. The values of K come almost constant and thus, showing that reaction is I order. For K, take average of all value of K.

Solution 49. Volume of O_2 at any given time $\propto$ Moles of H_2O_2 decomposed

$$\therefore \quad a \propto 35.75$$

At $t = 10$, $x \propto 6.30$ $\therefore K = \frac{2.303}{10}\log\frac{35.75}{35.75 - 6.30} = 1.94 \times 10^{-2}$

At $t = 15$, $x \propto 8.95$ $\therefore K = \frac{2.303}{15}\log\frac{35.75}{35.75 - 8.95} = 1.92 \times 10^{-2}$

At $t = 20$, $x \propto 11.40$ $\therefore K = \frac{2.303}{20}\log\frac{35.75}{35.75 - 11.40} = 1.92 \times 10^{-2}$

At $t = 25$, $x \propto 13.50$ $\therefore K = \frac{2.303}{25}\log\frac{35.75}{35.75 - 13.50} = 1.90 \times 10^{-2}$

Since K values are constant using first order equation and thus, reaction obeys first order kinetics

$$\mathbf{K = 1.92 \times 10^{-2}\ min^{-1}}$$

Solution 50. The volume of $KMnO_4$ used at any time is proportional to conc. H_2O_2 at that time.

At $t = 0$ $V = 25$ $\therefore$ $a \propto 25$

(i) At $t = 10$ $V = 16$ $\therefore$ $(a - x) \propto 16$

(ii) At $t = 20$ $V = 10.5$ $\therefore$ $(a - x) \propto 10.5$

(iii) At $t = 30$ $V = 7.09$ $\therefore$ $(a - x) \propto 7.09$

Now use, $$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

For (i) $$K = \frac{2.303}{10} \log \frac{25}{16} = \mathbf{4.46 \times 10^{-2}\ min^{-1}}$$

For (ii) $$K = \frac{2.303}{20} \log \frac{25}{10.5} = \mathbf{4.34 \times 10^{-2}\ min^{-1}}$$

For (iii) $$K = \frac{2.303}{30} \log \frac{25}{7.09} = \mathbf{4.20 \times 10^{-2}\ min^{-1}}$$

The values of K come almost constant and thus confirming first order reaction. For velocity constant, take average of all values of K.

Solution 51. Free radical addition reactions have $E_a = 0$

Thus from $$K = Ae^{-E_a/RT} \qquad (\text{if } E_a = 0)$$
$$K = A = 2 \times 10^{13}\ \text{sec}^{-1}$$

Solution 52. $$\log_{10} K = 5.4 - \frac{212}{T} + 2.17 \log_{10} T$$

or $$\ln K = 5.4 \times 2.303 - \frac{212 \times 2.303}{T} + 2.17 \ln T$$

or $$\frac{d}{dt} \ln K = 0 + \frac{212 \times 2.303}{T^2} + \frac{2.17}{T}$$

$$\frac{d}{dt} \ln K = \frac{[488.236 + 2.17T]}{T^2}$$

$\because$ $$\frac{d}{dt} \ln K = \frac{E_a}{RT^2} \qquad \text{(Arrhenius equation)}$$

$\therefore$ $$\frac{E_a}{R} = 488.236 + 2.17T$$

if $T = 127°\text{C}$ $$E_a = 2 \times [488.236 + 2.17 \times 400]$$
$$= \mathbf{2712\ cal}$$

Selected Problems with Solutions

► **Problem 1.** For the reaction $2NO_2 + F_2 \rightarrow 2NO_2F$, the experimental rate law is $r = K[NO_2][F_2]$. Propose the mechanism of reaction.

► **Problem 2.** The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

► **Problem 3.** A given sample of milk turns sour at room temperature (20°C) in 64 hour. In a refrigerator at 3°C, milk can be stored three times as long before it sours. Estimate

(a) The activation energy for souring of milk,
(b) How long it take milk to sour at 40°C?

► **Problem 4.** Find out the percentage of the reactant molecules crossing over the energy barrier at 325 K, given that $\Delta H_{325} = 0.12$ kcal, $E_{a(b)} = +0.02$ kcal.

► **Problem 5.** The catalytic decomposition of formic acid may take place in two ways:

(i) $HCOOH \longrightarrow H_2O + CO$
(ii) $HCOOH \longrightarrow H_2 + CO_2$

The rate constant and activation energy for reaction (i) are 2.79×10^{-3} min^{-1} at 237°C and 12.0 kcal mol^{-1} respectively. These values for reaction (ii) are 1.52×10^{-4} min^{-1} at 237°C and 24.5 kcal mol^{-1} respectively. Find out the temperature at which equimolar quantities of H_2O, CO, CO_2 and H_2 are formed. ($R = 2$ cal)

► **Problem 6.** A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate:

(i) the concentration of oxygen atoms needed so that the reaction $O + O_3 \rightarrow 2O_2$ having rate constant equal to 1.5×10^7 litre mol^{-1} sec^{-1} can proceed with a rate of 0.15 mol $litre^{-1}$ sec^{-1}.
(ii) the rate of formation of oxygen under this condition.

► **Problem 7.** The rate law of a chemical reaction given below:

$$2NO + O_2 \longrightarrow 2NO_2$$

is given as rate $= K[NO]^2[O_2]$. How will the rate of reaction change if the volume of reaction vessel is reduced to 1/4th of its original value?

► **Problem 8.** For a gaseous reaction $2A + B_2 \longrightarrow 2AB$, the following rate data were obtained.

Rate of disappearance of B_2 × 10^3	mol litre^{-1} [A]	[B_2]
1.8	0.015	0.15
10.8	0.090	0.15
5.4	0.015	0.45

Calculate:

(a) the rate constant,

(b) rate of formation of AB when,

$$[A] = 0.02 \text{ and } [B_2] = 0.04$$

➤ **Problem 9.** The rate of a certain reaction depends on concentration according to the equation : $\frac{-dC}{dt} = \frac{K_1 C}{1 + K_2 C}$.

What will be the order of reaction, when concentration (C) is:

(a) very-very high,

(b) very-very low.

➤ **Problem 10.** Surface catalysed reactions that are inhibited by the products obey the rate equation (in same cases) $\frac{dx}{dt} = \frac{K(a-x)}{1+bx}$, where a is the initial concentration of the reactant and K and b are constants. Integrate this equation. Derive an expression for $t_{1/2}$. x is the concentration of products at any time t and the reaction is $A \longrightarrow B$.

➤ **Problem 11.** Show that the time $t_{1/2}/t_{3/4}$ for nth order reaction is a function of 'n' alone. $t_{3/4}$ is the time required for concentration to become 1/4 of original concentration.

➤ **Problem 12.** The inversion of cane sugar proceeds with constant half life of 500 minute at pH = 5 for any concentration of sugar. However, if pH = 6, the half life changes to 50 minute. Derive the rate law for inversion of cane sugar.

➤ **Problem 13.** The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to the equation,

$$[Co(NH_3)_5F]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + F^-$$

The rate of reaction = rate constant × $[\text{complex}]^n \times [H^+]^m$ $= K[\text{complex}]^n[H^+]^m$. The reaction is acid catalyzed, *i.e.*, $[H^+]$ does not change during the reaction. Thus,

$$\text{rate} = K'[\text{complex}]^n \text{ where } K' = K[H^+]^m$$

Calculate m and n if they are integers from the following data at 25°C.

[complex] M	**[H^+] M**	**$t_{1/2}$ (hour)**	**$t_{3/4}$ (hour)**
0.1	0.01	1	2
0.2	0.02	0.5	1

$t_{3/4}$ is the time required for three fourth completion of the reaction.

➤ **Problem 14.** The conversion of trypsinogen (A) into trypsin (B) is an autocatalytic reaction $A \longrightarrow B$ where B catalyses the reaction. The rate equation is

$\frac{-dx}{dt} = K\,x \cdot y$, Where x and y are concentration of tripsinogen at time t. Integrate this equation for initial concentration of x_0 and y_0 for A and B. Show that $Kt = \frac{2.303}{x_0 + y_0} \log \frac{y \cdot x_0}{x \cdot y_0}$.

► **Problem 15.** The oxidation of certain metal is found to obey the equation $A^2 = \alpha t + \beta$, where A is the thickness of the oxide film at time t, α and β are constants. What is the order of this reaction.

► **Problem 16.** If a reaction $A \longrightarrow$ Products, the concentrations of reactant A are $C_0, aC_0, a^2C_0, a^3C_0, \ldots$ after time interval $0, t, 2t, 3t, \ldots$ where a is constant. Given $0 < a < 1$. Show that the reaction is of I order. Also calculate the relation in K, a and t.

► **Problem 17.** For a homogeneous gaseous phase reaction $2A \longrightarrow 3B + C$, the initial pressure was P° while pressure at time 't' was P. Find the pressure after time $2t$. Assume first order reaction.

► **Problem 18.** Arsine decomposes on heating to give As and H_2. The decomposition studied at constant volume and temperature gives the following data.

T in hr.	0	5.5	6.5	8
P in atm.	0.9654	1.06	1.076	1.1

Calculate velocity constant, assuming first order reaction.

► **Problem 19.** Two I order reactions having same reactant concentration proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C.

► **Problem 20.** Two reactants A and B separately shows two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half lives compare their rates

(a) at the start of reaction,

(b) after the lapse of one half life.

► **Problem 21.** A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_{3(g)} \longrightarrow CH_{4(g)} + CO_{(g)} + H_{2\,(g)}$. The rate constant of decomposition is 4.78×10^{-3} min^{-1}. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and gas diffused to be same.

► **Problem 22.** Bi-cyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexane was measured as 1.26×10^{-4} s^{-1} and for the formation of methyl cyclopentene the rate constant was 3.8×10^{-5} s^{-1}. What was the % distribution of the rearrangement products.

➤ **Problem 23.** Ethylene is produced by

$$\underset{\text{Cyclobutane}}{C_4H_8} \xrightarrow{\Delta} 2C_2H_4$$

The rate constant is 2.48×10^{-4} sec^{-1}. In what time will the molar ratio of the ethylene to cyclobutane in reaction mixture attain the value (a) 1, (b) 100?

➤ **Problem 24.** Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 *M* $KMnO_4$ acidified solution. Calculate the rate constant for decomposition of H_2O_2.

➤ **Problem 25.** In a certain reaction B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing agent which reacts only with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of reagent consumed is 25 mL and at $t = 10$ min, the volume used is 32 mL. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

➤ **Problem 26.** For the reaction $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ under certain conditions of pressure and temperature of the reactants, the rate of formation of NH_3 is 0.001 kg h^{-1}. Calculate the rate of reaction for N_2 and H_2.

➤ **Problem 27.** For a reversible first order reaction,

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B \; ; \; K_f = 10^{-2}\ s^{-1}$$

and $\dfrac{B_{eq.}}{A_{eq.}} = 4$. If $A_0 = 0.01$ ML^{-1} and $B_0 = 0$, what will be concentration of *B* after 30 sec.

➤ **Problem 28.** For a reversible reaction $C \rightleftharpoons D$, heat of reaction at constant volume is -33.0 kJ mol^{-1}, calculate :

(i) the equilibrium constant at 300 K.

(ii) If E_f and E_b are energy of activation for forward and backward reactions respectively, calculate E_f and E_b at 300 K. Given that $E_f : E_b = 20 : 31$. Assume pre exponential factor same for forward and backward reaction.

➤ **Problem 29.** The rate expression for a reaction is $-\dfrac{dA}{dt} = \dfrac{\alpha A}{1 + \beta A}$, where α, β are constants and greater than zero. Calculate $t_{1/2}$ for this reaction if initial concentration is $[A]_0$.

Answers

1. See solution ;
2. 282 K ;
3. (a) 10.454 kcal, (b) 20.5 hr ;
4. 80.65% ;
5. $T = 394°C$;
6. (i) 2.45×10^{-4}, (ii) 0.30 mol L^{-1} t^{-1} ;
7. 64 ;
8. (i) 2 , (ii) 1.28×10^{-3} ;
9. (a) zero , (b) first ;
10. See solution ;
11. See solution ;
12. $K\,[\text{Sugar}]^1\,[H^+]^0$;
13. $m = 0,\ n = 2$;
14. See solution ;
15. = 1 ;
16. See solution ;
17. See solution ;
18. See solution ;
19. 7.5937 ;
20. (a) 0.693 , (b) 1.386 ;
21. 0.261 ;
22. 0.768 , 0.232 ;
23. (a) 27.25 minute, (b) 264.2 minute ;
24. 0.022 hr^{-1} ;
25. 2.07×10^{-2} min^{-1} ;
26. $N_2 = 8.12 \times 10^{-4}$ kg hr^{-1} , $H_2 = 1.76 \times 10^{-4}$ kg hr^{-1} ;
27. 2.50×10^{-3} ML^{-1};
28. 5.572×10^{5}, 60 kJ, 93 kJ
29. $t_{1/2} = \dfrac{0.693}{\alpha} + \dfrac{B[A]_0}{2\alpha}$

Problems for Self Assessment

1. The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/mol and 3.46×10^{-5} $\sec^{-1}$ respectively. Determine the temperature at which half life of reaction is 2 hour.

$$\underset{\text{(in CCl}_4)}{2N_2O_5} \longrightarrow \underset{\text{(in CCl}_4)}{2N_2O_4} + O_2$$

2. The activation energy of a certain uncatalysed reaction at 300 K is 76 kJ mol^{-1}. The activation energy is lowered by 19 kJ mol^{-1} by the use of catalyst. By what factor, the rate of catalysed reaction is increased?
3. On the top of a certain mountain, the atmospheric pressure is 0.7 atm and pure water boils at 363 K. A climber finds that it takes 300 minute to boil an egg as against 3 minute at 373 K. Calculate:
   (a) Ratio of rate constants at 373 K and 363 K,
   (b) Energy of activation for the reaction when egg boiled. Assume Arrhenius factor be same.
4. For the reactions of I, II and III orders, $K_1 = K_2 = K_3$ when concentrations are expressed in mol $litre^{-1}$. What will be the relation in K_1, K_2, K_3, if concentrations are expressed in mol/mL?
5. A first order gaseous reactions has $K = 1.5 \times 10^{-6}$ $\sec^{-1}$ at 200°C. If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction?
6. The half life period of a compound is 50 minute. If the initial concentration is halved, the half life period is reduced to 25 minute. What is O.R.?
7. Decomposition of the gaseous phase reaction $2A \longrightarrow B$, was mentioned by measuring total pressure as a function of time. The results are given below:

Time in minute	0	100	200	300	400
Pressure in torr	400	322	288	268	256

   Calculate rate constant and find O.R.

8. 10 g sugar in 100 mL water rotates the plane of polarized light by +13.10° and after complete hydrolysis it shows rotation –3.75°. What is % hydrolysis of sugar in a solution having a rotation by an angle of 5°?
9. At 300 K, the specific rate constant for hydrolysis of ethyl ester by alkali is 6.36 mol^{-1} litre min^{-1}. Starting with concentration of base and ester as 0.01 mol per litre, what proportion of the ester will be hydrolysed in 10 minute?
10. Following data were obtained for the chlorination of acetone as shown below:

$$CH_3COCH_3 + Cl_2 \xrightarrow{H^+} CH_3COCH_2Cl + H^+ + Cl^-$$

$[CH_3COCH_3]$	$[Cl_2]$	$[H^+]$	$-\frac{dCl_2}{dt} \times 10^5$
0.30	0.05	0.05	5.7
0.30	0.10	0.05	5.7
0.30	0.05	0.10	11.4
0.40	0.05	0.05	7.6

Establish the rate law. Also find the rate constant for the reaction.

11. Show that for a reaction following the rate law:

$$\frac{-d[A]}{dt} = K[A]^{\alpha},$$

the half life for the reaction can be given by:

$$t_{1/2} = \frac{2^{\alpha-1}-1}{K[A_0]^{\alpha-1}(\alpha-1)}, \text{ where } \alpha \text{ is an integer but greater than unity.}$$

12. The rate constant for the reaction: $H^+ + OH^- \longrightarrow H_2O$ is 1.3×10^{11} litre mol^{-1} s^{-1}. Calculate the half life for the neutralisation process if:

(a) $[H^+] = [OH^-] = 10^{-1}\,M$,

(b) $[H^+][OH^-] = 10^{-4}\,M$.

13. The dissociation constant of acetic acid, NH_4^+ are 1.75×10^{-5} and 5.71×10^{-10} respectively. The second order rate constant for the formation of acids from bases CH_3COO^- and NH_3 and proton to form acids are 4.5×10^{10} and 4.3×10^{10} litre mol^{-1} s^{-1} respectively. Calculate the rate constant for the dissociation of acetic acid and NH_4^+.

14. For a first order reversible reaction $A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$, the rate constants K_f and K_b are 1.2×10^{-3} sec^{-1} and 3.3×10^{-3} sec^{-1}. If $[A]_0 = 0.5$ mole litre^{-1} and $[B]_0 = 0$, calculate the equilibrium concentration of A. Also calculate the time taken for B to reach its half equilibrium concentration.

15. For a first order reversible reaction $A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$, the initial concentration of A and B are $[A]_0$ and zero respectively. If concentrations at equilibrium are $[A]_{eq.}$ and $[B]_{eq.}$, derive an expression for the time taken by B to attain concentration equal to $[B]_{eq/2}$.

16. For a consecutive first order reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, the values of K_1 and K_2 are 45 sec^{-1} and 15 sec^{-1} respectively. If the reaction is carried out with pure A at a concentration of 1.0 mol dm^{-3},

(a) How much time will be required for the concentration of B to reach a maximum.

(b) What will be the maximum concentration of B.

(c) What will be the composition of the reacting system after a time interval of 10 minute.

Answers

1. 306 K ;
2. 2033.8 ;
3. (a) 100, (b) −124.729 kcal ;
4. $K_1 = K_2 \times 10^{-3} = K_3 \times 10^{-6}$;
5. 5.25%, 128.33 hr ;
6. Zero ;
7. 1.6×10^{-5}, II ;
8. 48.07% ;
9. 38% ;
10. Rate $= K\,[CH_3COCH_3]\,[Cl_2]^0\,[H^+]^1$, $K = 3.8 \times 10^{-3}$ litre mol^{-1} $time^{-1}$;
11. — ;
12. (a) 77 ps, (b) 77 ns ;
13. K_1 for acetic acid $= 7.88 \times 10^{-5}\ s^{-1}$,
    K_1 for $NH_4^+ = 24.55\ s^{-1}$;
14. $[A]_{eq} = 0.367\ M$, $t = 1.54 \times 10^{-4}$ sec ;
15. $t = \dfrac{0.693}{K_f + K_b}$;
16. (a) 132 sec , (b) 0.58 mol dm^{-3},
    (c) $[A] = 0$, $[B] = 0.12$ mol dm^{-3}, $[C] = 0.88$ mol dm^{-3}.

10

Chemical Equilibrium

Chapter at a Glance

Equilibrium constant

$$n_1A + n_2B + \ldots\ldots \rightleftharpoons m_1Z + m_2Y + \ldots\ldots$$

$$\text{Reaction Quotient } Q = \frac{[Z]_0^{m_1}\,[Y]_0^{m_2}}{[A]_0^{n_1}\,[B]_0^{n_2}}$$

$$K_C = \frac{[Z]^{m_1}\,[Y]^{m_2}\ldots\ldots}{[A]^{n_1}\,[B]^{n_2}\ldots\ldots} \qquad \ldots(1)$$

K_C is equilibrium constant in terms of concentration.

$$K_p = \frac{(P'_Z)^{m_1}\,(P'_Y)^{m_2}\ldots\ldots}{(P'_A)^{n_1}\,(P'_B)^{n_2}\ldots\ldots} \qquad \ldots(2)$$

or

$$K_p = \frac{(n_Z)^{m_1}(n_Y)^{m_2}\ldots\ldots}{(n_A)^{n_1}(n_B)^{n_2}\ldots\ldots} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n} \text{ (If gaseous phase reaction)} \qquad \ldots(3)$$

$$K_p = K_c \times (RT)^{\Delta n} \qquad \ldots(4)$$

K_p is equilibrium constant in terms of pressure, T is temperature in K.

Δn = [moles of product − moles of reactants] (only for gaseous phase moles) . . .(5)
as represented by stoichiometry of change.

$$\text{Degree of dissociation} = \frac{\text{Moles dissociated}}{\text{Total moles present initially}} \qquad \ldots(6)$$

Unit of Equilibrium constant: K_p : (unit of pressure)$^{\Delta n}$

K_C : (unit of concentration)$^{\Delta n}$

Van't Hoff Equation

$$2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\,\frac{[T_2 - T_1]}{T_1T_2} \qquad \ldots(7)$$

Standard free energy change

$\Delta G = \Delta G^\circ + RT \ln Q$ where Q is reaction Quotient . . . (8)

∵ $\Delta G = 0$ at equilibrium

and $Q = K_C$ or K_p

$$\therefore \quad \Delta G^\circ = -RT \ln K \qquad \ldots(9)$$

$$\Delta G^\circ = -2.303\, RT \log_{10} K \qquad \ldots(10)$$

$$\Delta G^\circ = \Sigma G^\circ_{\text{product}} - \Sigma G^\circ_{\text{reactant}} \qquad \ldots(11)$$

Henry's law

$$a \propto P \qquad \ldots(12)$$

a is amount of gas dissolved per unit volume of solvent at pressure P

$$V \propto (P)^\circ \qquad \ldots(13)$$

V is volume of gas dissolved per unit volume of solvent at pressure P

The Basic Problems with Solutions

➤ Problem 1. State which one is homogeneous or heterogeneous?

(a) $C_{Diamond} \rightleftharpoons C_{graphite}$

(b) $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$

(c) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(d) $MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$

(e) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

➤ Problem 2. Write euilibrium constant for the each :

(a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

(b) $KClO_{3(s)} \rightleftharpoons KCl_{(s)} + (3/2)O_{2(g)}$

(c) $CaC_{2(s)} + 5O_{2(g)} \rightleftharpoons 2CaCO_{3(s)} + 2CO_{2(g)}$

(d) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(e) $Fe^{3+}_{(aq)} + SCN^{-}_{(aq.)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$

(f) $CuSO_4.5H_2O_{(s)} \rightleftharpoons CuSO_{4(s)} + 5H_2O_{(v)}$

➤ Problem 3. The equilibrium constant expression for a gas reaction is :

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

➤ Problem 4. The equilibrium constant of the reaction; $SO_{3(g)} \rightleftharpoons SO_{2(g)} + ½O_{2(g)}$; is 0.20 mole^{½} litre$^{-½}$ at 1000 K. Calculate equilibrium constant for

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}.$$

➤ Problem 5. Calculate the equilibrium constant for the reaction ;

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

at 1395 K, if the equilibrium constants at 1395 K for the following are

$$2H_2O_{(g)} \rightleftharpoons 2H_2 + O_{2(g)} \quad K_1 = 2.1 \times 10^{-13}$$

$$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \quad K_2 = 1.4 \times 10^{-12}$$

➤ Problem 6. For the reaction; $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$.

At 400 K, $K_p = 41\ atm^{-2}$. Find the value of K_p for each of the following reactions at the same temperature:

(i) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$;

(ii) $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$;

(iii) $2N_{2(g)} + 6H_{2(g)} \rightleftharpoons 4NH_{3(g)}$.

➤ Problem 7. Find out the value of K_c for each of the following equilibria from the value of K_p :

(a) $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$; $K_p = 1.8 \times 10^{-2}$ atm at 500 K

(b) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$; $K_p = 167$ atm at 1073 K

➤ Problem 8. The rate of reversible reaction (change in concentration per second) : $PtCl_4^{2-} + H_2O \rightleftharpoons Pt(H_2O)Cl_3^- + Cl^-$; was observed at 0.3 ionic strength at 25°C and noticed that

$$\frac{\Delta[PtCl_4^{2-}]}{\Delta t} = 3.9 \times 10^{-5}\,[PtCl_4^{2-}] - 2.1 \times 10^{-3}\,[Pt(H_2O)Cl_3^-][Cl^-]$$

Calculate :

(a) Rate constant for forward and backward reaction.

(b) The equilibrium constant for the complexation of fourth Cl^- at 0.3 ionic strength.

➤ Problem 9. Write a stoichiometric equation for the reaction between A_2 and C whose mechanism is given below. Determine the value of equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial reactants.

(i) $A_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2A \qquad K_1 = 10^{10}\,s^{-1}$ and $K_2 = 10^{10}\,M^{-1}s^{-1}$

(ii) $A + C \longrightarrow AC \qquad K = 10^{-4}\,M^{-1}s^{-1}$

➤ Problem 10. Equilibrium constant, K_c for the reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; at 500 K is 0.061 litre^2 mole^{-2}. At a particular time, the analysis shows that composition of the reaction mixture is 3.00 mol litre^{-1}. N_2, 2.00 mol litre^{-1} H_2, and 0.500 mol litre^{-1} NH_3. Is the reaction at equilibrium? If not, in which direction does the reaction tend to proceed to reach equilibrium?

➤ Problem 11. Which of the following reactions will get affected by increase of pressure? Also mention, whether change will cause the reaction to go into the right or left direction?

(i) $CH_{4(g)} + 2S_{2(g)} \rightleftharpoons CS_{2(g)} + 2H_2S_{(g)}$

(ii) $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$

(iii) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

(iv) $C_2H_{4(g)} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}$

➤ Problem 12. In which case does the reaction go farthest to completion : $K = 1$; $K = 10^{10}$; $K = 10^{-10}$ and why?

➤ Problem 13. The equilibrium constant K_c for $A_{(g)} \rightleftharpoons B_{(g)}$ is 1.1. Which gas has a molar concentration greater than 1?

➤ Problem 14. Nitric oxide reacts with bromine and gives nitrosyl-bromide as per reaction given below:

$$2NO_{(g)} + Br_{2(g)} \rightleftharpoons 2NOBr_{(g)}$$

When 0.087 mole of NO and 0.0437 mole of Br_2 are mixed is a closed container at constant temperature, 0.0518 mole of NOBr is obtained at equilibrium. Calculate equilibrium amount of nitric oxide and bromine.

➤ **Problem 15.** At 700 K equilibrium constant for the reaction;

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

is 54.8. If 0.5 mol litre^{-1} of $HI_{(g)}$ is present at equilibrium at 700 K, what are the concentrations of $H_{2(g)}$ and $I_{2(g)}$ assuming that we initially started with $HI_{(g)}$ and allowed it to reach equilibrium at 700 K.

➤ **Problem 16.** Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium.

$$2BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.30×10^{-3} mol litre^{-1}; what is its molar concentration in the mixture at equilibrium?

➤ **Problem 17.** 60 mL of H_2 and 42 mL of I_2 are heated in a closed vessel. At equilibrium the vessel contains 28 mL of HI. Calculate degree of dissociation of HI.

➤ **Problem 18.** The reaction $2HI \rightleftharpoons H_2 + I_2$, at equilibrium contained 7.8 g, 203.2 g and 1638.4 g of H_2, I_2 and HI, respectively. Calculate K_c.

➤ **Problem 19.** In the dissociation of HI, 20% of HI is dissociated at equilibrium. Calculate K_p for

$$HI_{(g)} \rightleftharpoons \tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}I_{2(g)}$$

➤ **Problem 20.** If a mixture of 3 moles of H_2 and one mole of N_2 is completely converted into NH_3. What would be the ratio of the initial and final volume at same temperature and pressure?

➤ **Problem 21.** At a certain temperature and a total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms; Calculate K_p for the equilibrium.

$$I_{2(g)} \rightleftharpoons 2I_{(g)}$$

➤ **Problem 22.** Reaction between nitrogen and oxygen takes place as following :

$$2N_{2(g)} + O_2 \rightleftharpoons 2N_2O_{(g)}$$

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 litre and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$ litre mole^{-1}. Determine the composition of equilibrium mixture.

➤ **Problem 23.** One mole of H_2O and one mole of CO are taken in a 10 litre vessel and heated to 725 K. At equilibrium 40 per cent of water (by mass) reacts with carbon monoxide according to the equation;

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

Calculate the equilibrium constant for the reaction.

➤ **Problem 24.** A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol litre^{-1}. If value of K_c is 8.3×10^{-3} mole litre^{-1} What are the concentrations of PCl_3 and Cl_2 at equilibrium?

➤ **Problem 25.** The equilibrium constant for the following reactions is 1.6×10^5 at 1024 K, $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

➤ **Problem 26.** At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass;

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$$

Calculate K_c for the reaction at the above temperature.

➤ **Problem 27.** The ester, ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as :

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

(a) Write the concentration ratio (reaction quotient), Q_c, for this reaction. Note that water is not in excess and is not a solvent in this reaction.

(b) At 293 K, if one starts with 1.00 mole of acetic acid and 0.180 of ethanol, there is 0.171 mole of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(c) Starting with 0.500 mole of ethanol and 1.000 mole of acetic acid and maintaining it at 293 K, 0.214 mole of ethyl acetate is found after some time. Has equilibrium been reached?

➤ **Problem 28.** K_c for $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ at 986°C is 0.63. A mixture of 1 mole $H_2O_{(g)}$ and 3 moles $CO_{(g)}$ is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

(a) How many moles of H_2 are present at equilibrium?

(b) Calculate partial pressure of each gas at equilibrium.

➤ **Problem 29.** When C_2H_5OH and CH_3COOH are mixed in equivalent proportion, equilibrium is reached when 2/3 of acid and alcohol are used. How much ester will be present when 2 g molecule of acid were to react with 2 g molecule of alcohol.

➤ **Problem 30.** When (α) *d*-glucose is dissolved in water, it undergoes a partial conversion to (β) *d*-glucose to exhibit mutarotation. This conversion stops when 63.6% of glucose is in β-form. Assuming that equilibrium has been attained, calculate K_c for mutarotation.

➤ **Problem 31.** Determine the concentration of CO_2 which will be in equilibrium with 2.5×10^{-2} mol litre^{-1} of CO at 100°C for the reaction;

$$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}\ ; \qquad K_c = 5.0$$

➤ **Problem 32.** For the gaseous reaction; $2NO_2 \rightleftharpoons N_2O_4$, calculate $\Delta G°$ and K_p for the reaction at 25°C. Given $G^{\circ}_{f\,N_2O_4}$ and $G^{\circ}_{f\,NO_2}$ are 97.82 and 51.30 kJ respectively. Also calculate $\Delta G°$ and K_p for reverse reaction.

➤ **Problem 33.** $\Delta G°$ for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ is -16.5 kJ mol^{-1} at 25°C. Find out K_p for the reaction. Also report K_p and $\Delta G°$ for :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \text{at } 25°C$$

➤ **Problem 34.** Calculate the values of ΔE° and ΔH° for the reaction : $2A_{(g)} + B_{(g)} \rightleftharpoons A_2B_{(g)}$ for which $K_p = 1.0 \times 10^{-10}$ atm^{-2} and $\Delta S = 5$ JK^{-1} and $T = 300$ K.

➤ **Problem 35.** Derive the best conditions for dissociation of NH_3 ; Given,

$$2NH_3 \rightleftharpoons N_2 + 3H_2; \quad \Delta H = +91.94 \text{ kJ}$$

➤ **Problem 36.** Derive the best condition for the formation of NH_3; Given,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 ; \quad \Delta H = -91.94 \text{ kJ}$$

➤ **Problem 37.** K_c for the reaction; $A + B \rightleftharpoons P + Q$, is 2.0×10^{-2} at 25°C and it is 2.0×10^{-1} at 50°C. Predict whether the forward reaction is exothermic or endothermic.

➤ **Problem 38.** In a gaseous reaction, $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$. Predict the effect of addition of inert gas if addition is made at (a) constant volume, (b) constant pressure.

➤ **Problem 39.** In a gaseous reaction; $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$, the increase in temperature causes the change in the concentrations of A, B, C and D. The concentrations of C and D also change on addition of some amount of A. Does the value of K change in either of the two situations?

➤ **Problem 40.** 100 g of NaCl is stirred in 100 mL of water at 20°C till the equilibrium is attained :

(a) How much NaCl goes into the solution and how much of it is left undissolved at equilibrium? The solubility of NaCl at 20°C is 6.15 mol/litre.

(b) What will be the amount of NaCl left undissolved if the solution is diluted to 200 mL?

➤ **Problem 41.** Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 4.0 atm over the liquid at 25°C. The Henry's law constant for CO_2 in water is 3.1×10^{-2} mol/litre-atm at this temperature.

➤ **Problem 42.** Calculate the concentration of CO_2 in a soft drink bottle after the bottle is opened and sits at 25°C under a CO_2 partial pressure of 3.0×10^{-4} atm. Henry's law constant for CO_2 in water is 3.1×10^{-2} mol/litre–atm at this temperature.

Answers

1. (c) and (e) homogeneous, (a), (b) and (d) heterogeneous ;
2. See solution ;
3. $4NO + 6H_2O \rightleftharpoons 4NH_3 + 5O_2$;
4. 25 mol^{-1} $litre^{+1}$;
5. 2.58 ;
6. (i) 0.024, (ii) 6.4, (iii) 1.681×10^3;
7. (a) 4.38×10^{-4}, (b) 1.90;
8. 53.85;
9. $K[C][A_2]^{1/2}$;
10. See solution ;
11. (i) No change, (ii) left direction, (iii) left direction, (iv) right direction ;
12. See solution ;
13. See solution ;
14. NO = 0.0352 mole, Br_2 = 0.0178 mole;
15. 0.068 mol $litre^{-1}$;
16. 3×10^{-4} mol $litre^{-1}$;
17. 71.9%;
18. 0.019;
19. 0.125;
20. 2;
21. 2.67×10^4 Pa;
22. N_2 = 0.0482 mol $litre^{-1}$, O_2 = 0.0933 mol $litre^{-1}$,
$N_2O = 6.6 \times 10^{-21}$ mol $litre^{-1}$;
23. 0.44;
24. $[PCl_3] = [Cl_2] = 2.037 \times 10^{-2}$;
25. $H_2 = Br_2$ = 0.025 bar, HBr = 9.95 bar;
26. 0.156 mol $litre^{-1}$;
27. (a) See solution, (b) 3.92, (c) No;
28. (a) 0.681, (b) $CO_2 = H_2$ = 0.34 atm, CO = 1.16 atm, H_2O = 0.16 atm;
29. 1.33;
30. 1.747;
31. 12.5×10^{-2} mol $litre^{-1}$;
32. –4.78 kJ, $K_p = 6.88$, +4.78 kJ, $K_p = 0.145$;
33. 779.41 atm^{-1}, 6.07×10^5 atm^{-2}, –32.998 kJ mol^{-1};
34. 63.93 kJ;
35. See solution;
36. See solution;
37. Endothermic;
38. (a) no change, (b) backward direction;
39. See solution;
40. (a) 36 g, 64 g, (b) 28 g;
41. 0.12 mol $litre^{-1}$;
42. 9.3×10^{-6} mol $litre^{-1}$.

Solutions

Solution 1. Homogeneous systems have phase (P) = 1

A system with P > 2 is called heterogeneous.

Phases in a system can be determined by following the rules given below.

System	Phase (P)	Explanation
S + S	2	No. of solid in mixture give number of phase = 2 *i.e.* P = 2
S + L	1	Soluble systems lead to P = 1
S + L	2	Insoluble systems lead to P = 2
L + L	2	Immiscible liquids lead to P = 2
L + L	1	Miscible liquids lead to P = 1
G + G	1	All gases in a mixture give P = 1

Thus given systems	a	b	c	d	e
Number of phase	2	2	1	3	1

∴ (c) and (e) are Homogeneous systems.

(a), (b) and (d) are Heterogeneous systems.

Solution 2. (a) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$, (b) $K_p = [Po_2]^{3/2}$

(c) $K_p = \frac{[P_{CO_2}]^2}{[P_{O_2}]^5}$, (d) $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(e) $K_c = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$, (f) $K_p = [P_{H_2O}]^5$

Solution 3. $4NO + 6H_2O \rightleftharpoons 4NH_3 + 5O_2$

Solution 4. For $SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$

$$K_{c_1} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 0.20 \quad ...(1)$$

For $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad ...(2)$$

By reversing Eq. (1),

$$\frac{1}{K_{c_1}} = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

Squaring both sides

$$\left(\frac{1}{K_{c_1}}\right)^2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_c \qquad \text{by Eq. (2)}$$

$$\therefore \quad K_c = \left[\frac{1}{0.20}\right]^2 = \mathbf{25\ mol^{-1}\ litre^{+1}}$$

Solution 5. For $2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)} \quad K_1 = \frac{[H_2]^2[O_2]}{[H_2O]^2}$ ...(1)

For $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \quad K_2 = \frac{[CO]^2[O_2]}{[CO_2]^2}$ ...(2)

For $CO_{2(g)} + H_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \quad K = \frac{[H_2O][CO]}{[CO_2][H_2]}$ ...(3)

By dividing eq. (2) by eq. (1) :

$$\frac{K_2}{K_1} = \frac{[CO]^2[O_2]}{[CO_2]^2} \times \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

$$\frac{K_2}{K_1} = \frac{[CO]^2[H_2O]^2}{[CO_2]^2[H_2]^2} = K^2 \qquad \text{by Eq. (3)}$$

or $$K = \sqrt{\left(\frac{K_2}{K_1}\right)} = \sqrt{\left(\frac{1.4\times10^{-12}}{2.1\times10^{-13}}\right)} = \mathbf{2.58}$$

Solution 6. (i) $$K_p = \frac{[H_2]^3[N_2]}{[NH_3]^2} = \left[\frac{[NH_3]^2}{[N_2][H_2]^3}\right]^{-1} = (41)^{-1} = \frac{1}{41} = \mathbf{0.024\ atm^2}$$

$$\left(\because \frac{[NH_3]^2}{[N_2][H_2]^3} = 41\right)$$

(ii) $$K_p = \frac{[NH_3]}{[H_2]^{3/2}[N_2]^{1/2}} = \left[\frac{[NH_3]^2}{[H_2]^3[N_2]}\right]^{1/2} = (41)^{1/2} = \mathbf{6.4\ atm^{-1}}$$

(iii) $$K_p = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} = \left[\frac{[NH_3]^2}{[N_2][H_2]^3}\right]^2 = (41)^2 = \mathbf{1.681 \times 10^3\ atm^{-4}}$$

Solution 7. (a) $\Delta n = 1$, $T = 500$ K; $K_p = K_c\,(RT)^{\Delta n}$ $\therefore$ $K_c = \frac{K_p}{(RT)^{\Delta n}}$,

$R = 0.0821$ litre atm K^{-1} mol^{-1}

$$K_c = \frac{1.8 \times 10^{-2}}{[(0.0821)(500)]^1} = \mathbf{4.38 \times 10^{-4}}$$

(b) $$K_c = \frac{167}{[(0.0821)(1073)]^1} = \mathbf{1.90} \quad [\because \Delta n = 1,\ T = 1073\ \text{K}]$$

Solution 8. (a) Rate constant for forward reaction $K_f = 3.9 \times 10^{-5}$ sec^{-1}

Rate constant for backward reaction $K_b = 2.1 \times 10^{-3}$ litre mol^{-1} sec^{-1}

(b) Equilibrium constant for the complexation of fourth Cl^- is equilibrium

Constant for backward reaction *i.e.*, $K_c = \frac{K_b}{K_f} = \frac{2.1 \times 10^{-3}}{3.9 \times 10^{-5}}$

$= \mathbf{53.85\ litre\ mole^{-1}}$

Solution 9. It is aparent from both the steps that step (ii) is slowest and thus

$$\text{rate} = K_2\,[A]\,[C] \quad \ldots(1)$$

However overall rate constant K can be obtained in terms of A_2 as follows,

(i) + 2 × (ii) $A_2 + 2C \longrightarrow 2AC$

Also for step (i) $K_c = \frac{K_1}{K_2} = \frac{[A]^2}{[A_2]} = \frac{10^{10}}{10^{10}} = 1$

or $[A_2] = [A]^2$ or $[A] = [A_2]^{1/2}$

Thus by eq. (i) rate $= K_2[C][A_2]^{1/2} = \mathbf{K_2[C]\,[A_2]^{1/2}}$

Solution 10. $$Q = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.5)^2}{(2.0)^3 \times (3.0)} = \frac{0.25}{24} = 0.0104 \neq K_c.$$

∴ The reaction is not in equilibrium.

∴ Reaction proceeds from left to right. ∵ $Q < K_c$.

Solution 11. (i) No change.

(ii) Reaction goes into the **left direction.**

(iii) Reaction goes into the **left direction.**

(iv) Reaction goes into the **right direction.**

Solution 12. The ratio $\frac{[\text{product}]}{[\text{reactant}]}$ is maximum when $K = 10^{10}$ and thus, reaction goes farthest to completion when $K = 10^{10}$.

Solution 13. For $A_{(g)} \rightleftharpoons B_{(g)}$; $K_c = \frac{[B]}{[A]} = 1.1 \Rightarrow [B] > [A]$

If $[B] = 1$; $[A] = 0.91$

Case I : $0.91 < [A] < 1$ Only $[B] > 1$

Case II : $[A] > 1$ Both $[A]$ and $[B] > 1$

Solution 14.

	$2NO_{(g)}$	+ $Br_{2(g)}$	$\rightleftharpoons$ $2NOBr_{(g)}$
Initial mole	0.087	0.0437	—
Equilibrium	$(0.087 - 2a)$	$(0.0437 - a)$	$2a$

Given : $2a = 0.0518$

$\therefore$ $a = 0.0259$

At equilibrium, $NO = 0.0870 - 0.0518 = \mathbf{0.0352\ mole}$

$\therefore$ $Br_2 = 0.0437 - 0.0259 = \mathbf{0.0178\ mole.}$

Solution 15.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 54.8$$

$\because$ $[HI] = 0.5\ \text{mol litre}^{-1}$;

$\therefore$ $$[H_2][I_2] = \frac{[0.5]^2}{54.8} = 4.56 \times 10^{-3}$$

Since at equilibrium equal conc. of H_2 and I_2 will exist if dissociation of HI is carried out. Thus,

$[H_2] = [I_2]$ $\therefore$ $[H_2]^2 = 4.56 \times 10^{-3}$

or $\mathbf{[H_2] = 0.068\ mol\ litre^{-1} = [I_2]}$

Solution 16.

	$2BrCl_{(g)}$	$\rightleftharpoons$ $Br_{2(g)}$	+ $Cl_{2(g)}$
Initial conc.	0.0033	0	0
Conc. at equilibrium	$(0.0033 - a)$	$a/2$	$a/2$

$$K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2} = 32$$

$\therefore$ $$\frac{\frac{a}{2} \times \frac{a}{2}}{(0.0033 - a)^2} = 32$$

or $$\frac{a}{2 \times (0.0033 - a)} = 5.66$$

$\therefore$ $a = 3 \times 10^{-3}$

$\therefore$ $[BrCl] = 3.3 \times 10^{-3} - 3 \times 10^{-3} = \mathbf{3 \times 10^{-4}\ mol\ litre^{-1}}$

Solution 17.

	H_2	+ I_2	$\rightleftharpoons$ 2HI	Given,
Volume at $t = 0$	60	42	0	$\because 2x = 28$
Volume at equilibrium	$(60 - x)$	$(42 - x)$	$2x$	$\therefore x = 14$
	$(60 - 14)$	$(42 - 14)$	28	

Since at constant P and T, moles $\propto$ volume of gas (by $PV = nRT$). Thus, volume of gases given can be directly used as concentration. This can be done only for reactions having $\Delta n = 0$.

$\therefore$ $$K_c = \frac{28 \times 28}{46 \times 28} = \frac{28}{46}$$

Now for dissociation of HI;	$2HI \rightleftharpoons$	H_2	+	I_2
Moles at $t = 0$	1	0		0
Moles at equilibrium	$(1-\alpha)$	$\alpha/2$		$\alpha/2$

where α is the degree of dissociation

$$K_{c_1} = \frac{\alpha^2}{4(1-\alpha)^2} = \frac{1}{K_c}$$

$$\therefore \quad \frac{\alpha}{2(1-\alpha)} = \sqrt{\left(\frac{46}{28}\right)}$$

$$\therefore \quad \alpha = \mathbf{0.719} \text{ or } \mathbf{71.9\%}$$

Solution 18.

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Moles at equilibrium	$\frac{1638.4}{128}$ $= 12.8$		$\frac{7.8}{2}$ 3.9		$\frac{203.2}{254}$ 0.8

Let volume of container by V litre

$$[H_2] = \frac{3.9}{V}; \quad [HI] = \frac{12.8}{V}; \quad [I_2] = \frac{0.8}{V}$$

$$\therefore \quad K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{3.9 \times 0.8}{V \times V \times \left(\frac{12.8}{V}\right)^2} = 0.019$$

$$\therefore \quad K_c = \mathbf{0.019}$$

Solution 19.

	HI	$\rightleftharpoons$	$\frac{1}{2}H_2$	+	$\frac{1}{2}I_2$
Initial moles	1		0		0
Moles at equilibrium	$(1-\alpha)$		$\alpha/2$		$\alpha/2$

where α is the degree of dissociation and volume of container is V litre.

$$K_p = K_c = \frac{\left(\frac{\alpha}{2V}\right)^{1/2}\left(\frac{\alpha}{2V}\right)^{1/2}}{\frac{(1-\alpha)}{V}} \qquad (\because \Delta n = 0)$$

$$K_p = K_c = \frac{\alpha}{2(1-\alpha)} \qquad (\alpha = 0.2)$$

$$K_p = K_c = \frac{0.2}{2(1-0.2)}$$

$$K_p = K_c = \mathbf{0.125}$$

Solution 20.

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$	
Initial moles	1		3		0	
Final moles	0		0		2	($\because$ complete conversion)

$$\text{Ratio of initial and final volumes} = \frac{\text{initial moles}}{\text{final moles}}$$

$$(\because\ V \propto n \text{ if } P \text{ and } T \text{ are constant}) \qquad = \frac{4}{2} = \mathbf{2}$$

Solution 21.

$$I \rightleftharpoons 2I_{(g)}$$

	I	$2I_{(g)}$
Initially moles :	a	0
Moles at equilibrium	$(a-x)$	$2x$

Total moles at equilibrium $= a - x + 2x = a + x$

Given $\quad \frac{2x}{a+x} = \frac{40}{100}$; $\quad \therefore \quad = \frac{a}{4}$

($\because$ Mole ratio = Volume ratio if P and T are constant)

This, $\quad n_{I_2} = a - \frac{a}{4} = \frac{3a}{4}$; $\quad 2$, $\quad \Delta n = 2 - 1 = 1$

$$K_p = \frac{[n_I]^2}{[n_{I_2}]} \times \left[\frac{P}{\Sigma n}\right]^{\Delta n}$$

$$\frac{(a^2/4)}{(3a/4)}\left[\frac{10}{[a+(a/4)]}\right] = \mathbf{2.67 \times 10^4\ Pa}$$

Solution 22.

$$[N_2] = \frac{n}{V} = \frac{0.482}{10} = \mathbf{0.0482\ mol\ litre^{-1}}$$

$$\frac{n}{} \quad \frac{0.933}{10} = \mathbf{0.0933\ mol\ litre^{-1}}$$

	$2N_2$ +	O_2 ⇌	$2N_2O$
Initial conc.	0.0482	0.0933	0
At equilibrium conc.	$(0.0482 - 2x)$	$(0.0933 - x)$	$2x$

$$K_c = \frac{[N_2O]^2}{[N_2]^2[O_2]} = 2 \times 10^{-37}$$

$$2 \times 10^{-37} = \frac{[N_2O]^2}{(0.0482 - 2x)^2(0.0933 - x)}$$

x is very small $\therefore$

$$[N_2O]^2 = (2 \times 10^{-37})(0.0482)^2(0.0933) = 4.34 \times 10^{-41}$$

$$[N_2O] = \mathbf{6.6 \times 10^{-21}\ mol\ litre^{-1}}$$

Solution 23.

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

	$H_2O_{(g)}$ +	$CO_{(g)}$ ⇌	$H_{2(g)}$ +	$CO_{2(g)}$
Initial mole	1	1	0	0
Mole at eq.	(1 − 0.4)	(1 − 0.4)	0.4	0.4

(40% of H_2O reacts at eq.)

$$K_c = \frac{[CO_2][H_2]}{[H_2O][CO]} = \frac{0.4 \times 0.4}{0.6 \times 0.6} = \mathbf{0.44}$$

Solution 24. The reaction is; $PCl_5 \rightleftharpoons PCl_3 + Cl_2;$

$$\therefore \quad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 8.3 \times 10^{-3}$$

$$\Rightarrow \quad [PCl_3][Cl_2] = (8.3 \times 10^{-3})(0.5 \times 10^{-1})$$

$[PCl_3] = [Cl_2] = x$ (say) at equilibrium

$$\therefore \quad x^2 = 4.15 \times 10^{-4}$$

$$\Rightarrow \quad x = \mathbf{2.037 \times 10^{-2} = [PCl_3] = [Cl_2]}$$

Solution 25. $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr$; $K_c = \frac{[HBr]^2}{[H_2][Br_2]} = 1.6 \times 10^5$

Given : $P_{HBr} = 10.0$ bar initially

$$\begin{array}{lccc} & 2HBr_{(g)} & \rightleftharpoons H_{2(g)} & + \; Br_{2(g)} \\ \text{Initial } P & 10 & 0 & 0 \\ \text{Equilibrium pressure} & (10-P) & P/2 & P/2 \end{array}$$

$$\therefore \quad K_p = \frac{P_{H_2} \times P_{Br_2}}{[P_{HBr}]^2} = \frac{(P/2) \times (P/2)}{(10-P)^2} = \frac{1}{1.6 \times 10^{+5}}$$

$$\text{or} \quad \frac{P}{2(10-P)} = \sqrt{\frac{1}{1.6 \times 10^{+5}}}$$

$$\therefore \quad P = 0.050 \text{ bar}$$

$$P_{H_2} = \frac{0.05}{2} = \mathbf{0.025\ bar} = P_{Br_2}\ ; \quad P_{HBr} = 10 - 0.05 = \mathbf{9.95\ bar}$$

Solution 26.

$$\begin{array}{lccc} & C_{(s)} + & CO_{2(g)} & \rightleftharpoons 2CO_{(g)} \\ \text{At equilibrium} & & 9.45 \text{ g} & 90.55 \text{ g} \\ & & = \frac{9.45}{44} \text{ mole} & = \frac{90.55}{28} \text{ mole} \\ & & = 0.21 \text{ mole} & = 3.23 \text{ mole} \end{array}$$

$$K_p = \frac{(n_{CO})^2}{n_{CO_2}} \times \left[\frac{P}{\Sigma n}\right]^1 = \frac{3.23 \times 3.23}{0.21} \times \frac{1}{3.44} = \mathbf{14.44\ atm}$$

$$\text{Now,} \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{14.44}{[0.0821 \times 1127]^1} = \mathbf{0.156\ mol\ litre^{-1}}$$

Solution 27. (a) $Q_c = \dfrac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$ [∵ Water is not a solvent here.]

(b) $K_c = \dfrac{(0.171)\times(0.171)}{(1-0.171)\times(0.180-0.171)} = \mathbf{3.92}$

(c) $Q_c = \dfrac{(0.214)\times(0.214)}{(0.786)\times(0.286)} = \mathbf{0.204 \neq K_c}$

∴ Equilibrium has not been reached.

Solution 28.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

	$CO_{(g)}$	$H_2O_{(g)}$	$CO_{2(g)}$	$H_{2(g)}$
Initial moles	3	1	0	0
Moles at equilibrium	$(3-x)$	$(1-x)$	x	x

Total moles at equilibrium $= (3-x) + (1-x) + (x) + (x) = 4$

Now $K_c = \dfrac{x^2}{(3-x)(1-x)}$

∴ $\dfrac{x^2}{3+x^2-4x} = 0.63$ (∵ $K_c = 0.63$)

Solving this quadratic equation by the formula : $x = \dfrac{-b \pm \sqrt{b^2-4ac}}{2a}$

∴ $x = 0.681$

∴ Moles of H_2 formed $= \mathbf{0.681}$

Total pressure at equilibrium = 2 atm

Total moles at equilibrium = 4

$P_g = P_M \times$ mole fraction of that gas

∴ $P_{CO_2} = P_{H_2} = \dfrac{x.P}{4} = \dfrac{0.681\times 2}{4} = \mathbf{0.34\ atm}$

$P_{CO} = \dfrac{(3-x).P}{4} = \mathbf{1.16\ atm}$

$P_{H_2O} = \dfrac{(1-x).P}{4} = \mathbf{0.16\ atm}$

Solution 29. **Case I :**

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	H_2O
Moles before reaction	1	1	0	0
Moles at equilibrium	$1-x$	$1-x$	x	x
∵	$x = 2/3$			
Moles at equilibrium ∴	$(1-2/3)$	$(1-2/3)$	2/3	2/3

$$\therefore \qquad K_c = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4$$

Note : Volume terms are eliminated.

Case II : $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	H_2O
Moles before reaction	2	2	0	0
Moles at equilibrium	$(2-x)$	$(2-x)$	x	x

$$\therefore \qquad K_c = 4 = \frac{x^2}{(2-x)^2} \quad \text{or} \quad \therefore \frac{x}{(2-x)} = 2$$

or $\qquad x = 1.33$

Solution 30. (α) *d*-glucose $\rightleftharpoons$ (β) *d*-glucose

At equilibrium 36.4 63.6

$$\therefore \qquad K_c = \frac{63.6}{36.4} = 1.747$$

Solution 31.

$$K_c = \frac{[CO_2]}{[CO]}$$

$$\therefore \qquad 5 = \frac{[CO_2]}{2.5 \times 10^{-2}}$$

$\therefore \quad [CO_2]$ at equilibrium $= 2.5 \times 10^{-2} \times 5 = \mathbf{12.5 \times 10^{-2}}$ **mol litre^{-1}**

Solution 32. For reaction, $\Delta G^\circ = G^\circ_{f\,N_2O_4} - 2 \times G^\circ_{f\,NO_2}$

$$= 97.82 - 2 \times 51.30 = -4.78\text{kJ}$$

$$\because \qquad -\Delta G^\circ = 2.303\, RT \log K_p$$

$$\therefore \qquad 4.78 \times 10^3 = 2.303 \times 8.314 \times 298 \log K_p$$

$$\therefore \qquad K_p = \mathbf{6.88}$$

For reverse reaction: $\Delta G^\circ = +4.78$ kJ

$$-4.78 \times 10^3 = 2.303 \times 8.314 \times 298 \log K_p$$

$$K_p = \mathbf{0.145}$$

Solution 33.

$$-\Delta G^\circ = 2.303\, RT \log K_p$$

$$-(-16.5 \times 10^3) = 2.303 \times 8.314 \times 298 \log K_p$$

$$\log K_p = \frac{16500}{2.303 \times 8.314 \times 298}$$

$$\therefore \qquad K_p = \mathbf{779.41\ atm^{-1}}$$

Also, K_{p_1} for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_{p_1} = (K_p)^2 = (779.41)^2$$

$$K_{p_1} = \mathbf{6.07 \times 10^5\ atm^{-2}}$$

Also, $-\Delta G_1° = 2.303 \times 8.314 \times 298 \log (6.07 \times 10^5)\ J$

$$= 32.998\ kJ$$

$\therefore$ $\Delta G_1° = \mathbf{-32.998\ kJ\ mol^{-1}}$

Solution 34. $\Delta G° = -2.303\ RT \log K_p = -2.303 \times 8.314 \times 300 \log 10^{-10}\ J$

$$= 57.441\ kJ$$

Now $\Delta H° = \Delta G° + T\Delta S° = 57.441 + 300 \times 5.0 \times 10^{-3} = 58.941\ kJ$

Also we have

$\Delta H° = \Delta E° + \Delta nRT$ $(\because \Delta n = -2$ for reaction)

$$58.941 = \Delta E° + (-2) \times 8.314 \times 300 \times 10^{-3}$$

$$\Delta E° = \mathbf{63.93\ kJ}$$

Solution 35. Low pressure favours reaction showing increase in moles *i.e.*, forward reaction.

High temperature favours reaction showing an endothermic nature *i.e.*, forward reaction.

Removal of NH_3 also favours forward reaction.

Solution 36. High pressure favours reactions showing decrease in moles *i.e.*, forward reaction.

Low temperature favours reaction showing exothermic nature *i.e.*, forward reaction.

More concentration of N_2 and H_2 also favours forward reaction.

Solution 37. Since, $2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

K increases with temperature and thus ΔH should be positive and thus the reaction is **endothermic.**

Solution 38. (a) No change, (b) In backward direction.

Solution 39. K change in the first case only but it remains same in II case.

Solution 40. Solubility of NaCl $= 6.15$ mol/litre

$$= 6.15 \times 58.5 \text{ g/litre}$$

$$= \frac{6.15 \times 58.5}{10} \text{ g/100 mL} = 36 \text{ g/100 mL}$$

(a) Thus amount of NaCl in 100 mL at 20°C get dissolved = 36 g and amount of NaCl in 100 mL at 20°C remained undissolved

= 100 – 36 = 64 g

(b) If volume of solution is diluted to 200 mL, 36 g more of NaCl will be dissolved leaving only 28 g NaCl dissolved in 200 mL.

Solution 41.

$$a_{(g)} = K.P._{(g)} = 3.1 \times 10^{-2} \times 4.0$$
$$= 0.12 \text{ mol litre}^{-1}$$

Solution 42.

$$a_{(g)} = K.P._{(g)} = 3.1 \times 10^{-2} \times 3.0 \times 10^{-4}$$
$$= 9.3 \times 10^{-6} \text{ mol litre}^{-1}$$

Selected Problems with Solutions

➤ **Problem 1.** Calculate the equilibrium constant for the reaction $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$ at 1395 K, if the equilibrium constants at 1395 K for following are:

$$2H_2O_{(g)} \rightleftharpoons 2H_2 + O_{2(g)} \qquad K_1 = 2.1 \times 10^{-13}$$

$$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \quad K_2 = 1.4 \times 10^{-12}$$

➤ **Problem 2.** The equilibrium constant K_C for $A_{(g)} \rightleftharpoons B_{(g)}$ is 1.1. Which gas has a molar concentration greater than 1?

➤ **Problem 3.** For the reaction $A + B \rightleftharpoons 3C$ at 25°C, a 3 litre vessel contains 1, 2, 4 mole of A, B and C respectively. Predict the direction of reaction if:

(a) K_C for the reaction is 10.

(b) K_C for the reaction is 15.

(c) K_C for the reaction is 10.66.

➤ **Problem 4.** The activation energy of $H_2 + I_2 \rightleftharpoons 2HI$ in equilibrium for the forward reaction is 167 kJ mol^{-1} whereas for the reverse reaction is 180 kJ mol^{-1}. The presence of catalyst lowers the activation energy by 80 kJ mol^{-1}. Assuming that the reactions are made at 27°C and the frequency factor for forward and backward reactions are 4×10^{-4} and 2×10^{-3} respectively, calculate K_C.

➤ **Problem 5.** For a gaseous phase reaction, $A + 2B \rightleftharpoons AB_2$ $K_C = 0.3475$ litre^2 mol^{-2} at 200°C. When 2 mole of B are mixed with one mole of A. What total pressure is required to convert 60% of A in AB_2?

➤ **Problem 6.** 0.96 g of HI were heated to attain equilibrium $2HI \rightleftharpoons H_2 + I_2$. The reaction mixture on titration requires 15.7 mL of $N/10$ hypo solution. Calculate degree of dissociation of HI.

➤ **Problem 7.** The degree of dissociation of HI at a particular temperature is 0.8. Calculate the volume of 2 M $Na_2S_2O_3$ solution required to neutralise the iodine present in a equilibrium mixture of a reaction when 2 mole each of H_2 and I_2 are heated in a closed vessel of 2 litre capacity.

➤ **Problem 8.** At 340 K and one atmospheric pressure, N_2O_4 is 66% dissociated into NO_2. What volume of 10 g N_2O_4 occupy under these conditions?

➤ **Problem 9.** N_2O_4 dissociates as $N_2O_4 \rightleftharpoons 2NO_2$. At 55°C and one atmosphere, % decomposition of N_2O_4 is 50.3%. At what P and same temperature, the equilibrium mixture will have the ratio of $N_2O_4 : NO_2$ as 1 : 8?

► **Problem 10.** At 273 K and one atm, '*a*' litre of N_2O_4 decomposes to NO_2 according to equation $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$. To what extent has the decomposition proceeded when the original volume is 25% less than that of existing volume?

► **Problem 11.** A mixture of one mole of CO_2 and one mole of H_2 attains equilibrium at a temperature of 250°C and a total pressure of 0.1 atm for the change $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$. Calculate K_p if the analysis of final reaction mixture shows 0.16 volume per cent of CO.

► **Problem 12.** For the equilibrium:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

the standard enthalpy and entropy changes at 300 K and 1200 K for the forward reaction are as follows:

$$\Delta H^\circ_{300\,K} = -41.16 \text{ kJ mol}^{-1} \qquad \Delta S^\circ_{300\,K} = -0.0424 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{1200\,K} = -32.93 \text{ kJ mol}^{-1} \qquad \Delta S^\circ_{1200\,K} = -0.0296 \text{ kJ mol}^{-1}$$

In which direction will the reaction be spontaneous

(a) At 300 K,

(b) At 1200 K,

Also calculate K_p for the reaction at each temperature.

► **Problem 13.** The equilibrium mixture for

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

present in 1 litre vessel at 600°C contains 0.50, 0.12 and 5.0 mole of SO_2, O_2 and SO_3 respectively.

(a) Calculate K_C for the given change at 600°C.

(b) Also calculate K_p.

(c) How many mole of O_2 must be forced into the equilibrium vessel at 600°C in order to increase the concentration of SO_3 to 5.2 mole?

► **Problem 14.** At 627°C and one atmosphere pressure SO_3 is partially dissociated into SO_2 and O_2 by $SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$. The density of the equilibrium mixture is 0.925 g/litre. What is the degree of dissociation?

► **Problem 15.** N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure, Calculate :

(a) K_p for $N_2O_4 \rightleftharpoons 2NO_2$

(b) % dissociation at 37°C and 0.1 atm.

► **Problem 16.** In a mixture of N_2 and H_2 in the ratio 1 : 3 at 30 atm and 300°C, the % of NH_3 at equilibrium is 17.8. Calculate K_p for $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

► **Problem 17.** The equilibrium concentration of the reactants and products for the given equilibrium in a two litre container are shown below:

$$\underset{2\,M}{PCl_{3(g)}} + \underset{1\,M}{Cl_{2(g)}} \rightleftharpoons \underset{4\,M}{PCl_{5(g)}}$$

(i) If 2 mole of Cl_2 are added in the container, find the new equilibrium concentration of each.

(ii) If the equilibrium mixture reported initially is transferred into 4 litre vessel, what would be the new concentrations at equilibrium?

➤ Problem 18. One mole of N_2 and 3 mole of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate degree of dissociation of PCl_5 and K_p of the reaction:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

➤ Problem 19. A mixture of 2 moles of CH_4 and 34 g of H_2S was placed in an evacuated chamber, which was then heated to and maintained at 727°C. When equilibrium was established in the gaseous phase reaction: $CH_4 + 2H_2S \rightleftharpoons CS_2 + 4H_2$, the total pressure in the container was 0.92 atm and the partial pressure of hydrogen was 0.2 atm. Calculate the volume of container.

➤ Problem 20. A graph plotted between $\log_{10} K_C$ and $1/T$ is straight line with intercept 10 and slope equal to 0.5. Calculate:

(i) pre-exponential factor A.

(ii) heat of reaction at 298 K.

(iii) equilibrium constant at 298 K.

(iv) equilibrium constant at 800 K assuming ΔH remains constant in between 298 K and 800 K.

➤ Problem 21. K_p for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.6×10^{-4} atm^{-2} at 400°C. What will be K_p at 500°C? Heat of reaction in this temperature range is − 25.14 kcal.

➤ Problem 22. $\Delta G°$ for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ is -16.5 kJ mol^{-1}. Find out K_p for the reaction. Also report K_p and $\Delta G°$ for:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \text{ at } 25°C.$$

➤ Problem 23. For gaseous reaction $A + B \rightleftharpoons C$, the equilibrium concentration of A and B at a temperature are 15 mol litre^{-1}. When volume is doubled the reaction has equilibrium concentration of A as 10 mol litre^{-1}. Calculate:

(i) K_C

(ii) Concentration of C in original equilibrium.

➤ Problem 24. K_p for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 1.64×10^{-4}. Find K_C. Also find $\Delta G°$ using K_p and K_C values and interpret the difference.

➤ Problem 25. Equilibrium constant K_p for $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is 0.0118 atm at 1065°C and heat of dissociation is 42.4 kcal. Find equilibrium constant at 1132°C.

➤ Problem 26. H_2 and I_2 are mixed at 400°C in a 2.0 litre container and when equilibrium was established, $[HI] = 0.49\ M$, $[H_2] = 0.08\ M$ and

$[I_2] = 0.06$ *M*. If now an additional 0.4 mole of HI are added, calculate the new equilibrium concentrations.

▶ **Problem 27.** 0.0755 g of selenium vapours occupying a volume of 114.2 mL at 700°C and 185 mm of Hg. The vapours are in equilibrium as:

$$Se_{6(g)} \rightleftharpoons 3Se_{2(g)}$$

Calculate:

(i) Degree of dissociation of Se,

(ii) K_p,

(iii) K_C.

Atomic weight of Se is 79.

▶ **Problem 28.** $COF_{2(g)}$ in presence of catalyst at 1000°C shows the equilibrium:

$$2COF_{2(g)} \rightleftharpoons CO_{2(g)} + CF_{4(g)}$$

At equilibrium 500 mL of the equilibrium mixture at STP contains 300 mL of (COF_2 and CO_2) at STP. If total pressure is 10 atm, calculate K_p.

▶ **Problem 29.** For $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$, the observed pressure for reaction mixture in equilibrium is 1.12 atm at 106°C. What is the value of K_p for the reaction?

▶ **Problem 30.** When 20 g of $CaCO_3$ were put into 10 litre flask and heated to 800°C, 35% of $CaCO_3$ remained unreacted at equilibrium. Calculate K_p for decomposition of $CaCO_3$.

▶ **Problem 31.** Some solid NH_4HS is placed in flask containing 0.5 atm of NH_3. What would be pressures of NH_3 and H_2S when equilibrium is reached?

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}; \quad K_p = 0.11$$

▶ **Problem 32.** At a certain temperature, K_p for dissociation of solid $CaCO_3$ is 4×10^{-2} atm and for the reaction, $C_{(s)} + CO_2 \rightleftharpoons 2CO$ is 2.0 atm respectively. Calculate the pressure of CO at this temperature when solid C, CaO, $CaCO_3$ are mixed and allowed to attain equilibrium.

▶ **Problem 33.** Ammonium carbamate dissociates as: $NH_2COONH_{4(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$. In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original pressure.

▶ **Problem 34.** In the preparation of quick lime from limestone, the reaction is,

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Experiments carried out between 850°C and 950°C led to set of K_p values fitting in empirical equation $\ln K_p = 7.282 - \frac{8500}{T}$ where *T* is absolute temperature. If the reaction is carried out in quiet air, what minimum temperature would be predicted from this equation for almost complete decomposition of lime?

➤ **Problem 35.** A vessel of 2.50 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at 440°C as:

$$Sb_2S_{3(s)} + 3H_{2(g)} \rightleftharpoons 2Sb_{(s)} + 3H_2S_{(g)}$$

After equilibrium the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 1.029 g of PbS as precipitate. What is value of K_C of the reaction at 440°C? (At. weight of Pb = 206)

➤ **Problem 36.** Sulphide ions in alkaline solution react with solid sulphur to form polyvalent sulphide ions. The equilibrium constant for the formation of S_2^{2-} and S_3^{2-} from S and S^{2-} ions are 1.7 and 5.3 respectively. Calculate equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S.

➤ **Problem 37.** Calculate K_C for the reaction, $KI + I_2 \rightleftharpoons KI_3$. Given that initial weight of KI is 1.326 g. Weight of KI_3 is 0.105 g and no. of mole of free I_2 is 0.0025 at equilibrium and the volume of solution is one litre.

➤ **Problem 38.** To 500 mL of 0.150 *M* $AgNO_3$ solution were added 500 mL of 1.09 *M* Fe^{2+} solution and the reaction is allowed to reach an equilibrium at 25°C.

$$Ag^+_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$$

For 25 mL of the solution, 30 mL of 0.0832 *M* $KMnO_4$ were required for oxidation. Calculate equilibrium constant for the reaction at 25°C.

➤ **Problem 39.** For the equilibrium:

$$LiCl{\cdot}3NH_{3(s)} \rightleftharpoons LiCl{\cdot}NH_{3(s)} + 2NH_3, \quad K_p = 9\ atm^2$$

at 40°C. A 5 litre vessel contains 0.1 mole of $LiCl{\cdot}NH_3$. How many mole of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion?

➤ **Problem 40.** Would 1% CO_2 in air be sufficient to prevent any loss in weight when M_2CO_3 is heated at 120°C?

$$M_2CO_{3(s)} \rightleftharpoons M_2O_{(s)} + CO_{2(s)}$$

$K_p = 0.0095$ atm at 120°C. How long would the partial pressure of CO_2 have to be to promote this reaction at 120°C?

➤ **Problem 41.** Under what pressure conditions $CuSO_4{\cdot}5H_2O$ be efflorescent at 25°C? How good a drying agent is $CuSO_4{\cdot}3H_2O$ at the same temperature? Given,

$$CuSO_4{\cdot}5H_2O_{(s)} \rightleftharpoons CuSO_4{\cdot}3H_2O_{(s)} + 2H_2O_{(v)}$$

$K_p = 1.086 \times 10^{-4}$ atm^2 at 25°C. Vapour pressure of water at 25°C is 23.8 mm of Hg.

➤ **Problem 42.** For the reaction,

$$2Fe^{3+}_{(aq)} + Hg_2^{2+}{}_{(aq)} \rightleftharpoons 2Fe^{2+}_{(aq)} + 2Hg^{2+}{}_{aq)}$$

$K_C = 9.14 \times 10^{-6}$ at 25°C. If the initial concentration of the ions are $Fe^{3+} = 0.5\ M$, $(Hg_2)^{2+} = 0.5\ M$, $Fe^{2+} = 0.03\ M$ and $Hg^{2+} = 0.03\ M$. What will be the concentrations of ions at equilibrium?

► **Problem 43.** When NO and NO_2 are mixed, the following equilibria are readily obtained;

$$2NO_2 \rightleftharpoons N_2O_4 \qquad K_p = 6.8\ \text{atm}^{-1}$$

and

$$NO + NO_2 \rightleftharpoons N_2O_3$$

In an experiment when NO and NO_2 are mixed in the ratio of 1 : 2, the final total pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate:

(a) the equilibrium partial pressure of NO.

(b) K_p for $NO + NO_2 \rightleftharpoons N_2O_3$.

► **Problem 44.** Two solid compounds *A* and *B* dissociate into gaseous products at 20°C as

(1) $A_{(s)} \rightleftharpoons A'_{(g)} + H_2S_{(g)}$ (2) $B_{(s)} \rightleftharpoons B'_{(g)} + H_2S_{(g)}$

At 20°C pressure over excess solid *A* is 50 mm and that over excess solid *B* is 68 mm. Find;

(i) the dissociation constant of *A* and *B*.

(ii) relative number of mole of *A'* and *B'* in the vapour phase over a mixture of the solids *A* and *B*.

(iii) Show that the total pressure of gas over the solid mixture would be 84.4 mm.

► **Problem 45.** Solid NH_4I on rapid heating in a closed vessel at 357°C develops a constant pressure of 275 mm Hg owing to partial decomposition of NH_4I into NH_3 and HI but the pressure gradually increases further (when the excess solid residue remains in the vessel) owing to the dissociation of HI. Calculate the final pressure developed at equilibrium. K_p for HI dissociation is 0.015 at 357°C.

► **Problem 46.** In a reaction at equilibrium, '*x*' mole of the reactant *A* decompose to give 1 mole each of *C* and *D*. It has been found that the fraction of *A* decomposed at equilibrium is independent of initial concentration of *A*. Calculate *x*.

► **Problem 47.** The heat of reaction for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300 K. Calculate the ratio of equilibrium constants K_p and K_C.

► **Problem 48.** N_2 and O_2 combine at a given temperature to produce NO. At equilibrium the yield of NO is '*x*' per cent by volume. If $x = \sqrt{K \cdot a \cdot b} - \dfrac{K(a+b)}{4}$ where *K* is the equilibrium constant of the given reaction at the given temperature and *a* and *b* are the volume percentage of N_2 and O_2 respectively in the initial pure mixture, what should be the initial composition of the reacting mixture in order that maximum yield of NO is ensured? Also report the maximum value of *K* at which '*x*' is maximum.

➤ **Problem 49.** The moisture content of a gas is often expressed in terms of the dew point. The dew point is the temperature to which the gas must be cooled before the gas becomes saturated with water vapour. At this temperature, water or ice (depending on the temperature) will be deposited on a solid surface. Dew point of H_2O is −43°C at which vapour pressure of ice formed is 0.07 mm. Assuming that the $CaCl_2$ owes its desiccating properties to the formation of $CaCl_2{\cdot}2H_2O$, calculate:

(i) K_p at that temperature of the reaction,

(ii) $\Delta G°$

$$CaCl_{2(s)} + 2H_2O_{(g)} \rightleftharpoons CaCl_2{\cdot}2H_2O_{(s)}$$

➤ **Problem 50.** Consider the equilibrium: $P_{(g)} + 2Q_{(g)} \rightleftharpoons R_{(g)}$. When the reaction is carried out at a certain temperature, the equilibrium concentration of P and Q are $3M$ and $4M$ respectively. When the volume of the vessel is doubled and the equilibrium is allowed to be reestablished, the concentration of Q is found to be $3M$. Find:

(a) K_C,

(b) Concentration of R at two equilibrium stages.

➤ **Problem 51.** (i) The equilibrium $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$ is established in an evacuated vessel at 723 K starting with 0.1 mole of H_2 and 0.2 mole of CO_2. If the equilibrium mixture contains 10 mole per cent of water vapour, calculate K_p, given that the equilibrium pressure is 0.5 atm. Calculate the partial pressures of the component species and the volume of the container.

(ii) If now, into the flask, solid CoO and solid Co are introduced two new equilibria are established.

$$CoO_{(s)} + H_{2(g)} \rightleftharpoons Co_{(s)} + H_2O_{(g)} \;;$$
$$CoO_{(s)} + CO_{(g)} \rightleftharpoons Co_{(s)} + CO_{2(g)}$$

The new equilibrium mixture contains 30 mole per cent of water vapour. Calculate the equilibrium constants for the new equilibria.

➤ **Problem 52.** The equilibrium *p*-xyloquinone + methylene white = *p*-xylohy- droquinone + methylene blue, may be studied convinently by observing the difference in colour methylene white and methylene blue. One milli mole of methylene blue was added to 1 litre of solution that was 0.24 M in *p*-xylohydroquinone and 0.012 M in *p*-xyloquinone. It was then found that 4% of the added methylene blue was reduced to methylene white. What is the equilibrium constant of the above reaction? The equation is balanced with one mole each of 4 substances.

➤ **Problem 53.** A certain gas A polymerizes to a small extent at a given temperature and pressure, $nA \rightleftharpoons A_n$. Show that the gas obeys the approx. equation $\frac{PV}{RT} = \left[1 - \frac{(n-1)\,K_C}{V^{n-1}}\right]$ where $K_C = \frac{[A_n]}{[A]^n}$ and V is the volume of the container. Assume that initially one mole of A was taken in the container.

► **Problem 54.** A 100 dm^3 flask contains 10 mole each of N_2 and H_2 at 777 K. After equilibrium was reached, partial pressure of H_2 was 1 atm. At this point 5 litre of $H_2O_{(l)}$ was injected and gas mixture was cooled to 298 K. Find out the pressure of gaseous mixture left.

► **Problem 55.** Calculate ΔG for the reaction at 25°C when partial pressure of reactants H_2, CO_2, H_2O, and CO are 10, 20, 0.02 and 0.01 atm respectively.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

Given G°_f for $H_{2(g)}$, $CO_{2(g)}$, $H_2O_{(g)}$ and $CO_{(g)}$ are 0, –394.37, –228.58, –137.15 kJ respectively.

Answers

1. 2.58 ; **2.** See solution ;
3. See solution ; **4.** 36.8 ;
5. 181.5 atm ; **6.** 20.9% ;
7. 1.6 litre ; **8.** 5.02 litre ;
9. 0.19 atm ; **10.** 33% ;
11. 1.03×10^{-5} ;
12. See solution , $K_p = 8.91 \times 10^4$ at 300 K, $K_p = 0.773$ at 1200 K ;
13. (a) $K_C = 833.33$ mol^{-1} $litre^{-1}$, (b) $K_p = 11.62$ $(atm)^{-1}$, (c) 0.34 mole ;
14. 34.08% ; **15.** (a) 0.267 atm ; (b) 63.26%
16. $K_p = 7.29 \times 10^{-4}$ atm^{-2} ;
17. (i) $PCl_3 = 1.5\,M$, $Cl_2 = 1.5\,M$, $PCl_5 = 4.5\,M$,
(ii) $PCl_3 = 1.225\,M$, $Cl_2 = 0.725\,M$, $PCl_5 = 1.775\,M$;
18. 33.13%, $K_p = 0.20$; **19.** 300.38 litre ;
20. (i) 10^{10}, (ii) –2.303 cal mol^{-1}, (iii) 1.004×10^{10}, (iv) 1.001×10^{10} ;
21. 1.462×10^{-5} atm^{-2} ;
22. 779.41 atm^{-1}, 6.07×10^5 atm^{-2} ; 32.998 kJ ;
23. $K_C = 0.2$ mol^{-1} $litre^{-1}$, 45 M ;
24. $K_C = 0.5006$ mol^2 $litre^{-2}$, +11.733 kcal, +931 cal ;
25. 0.025 atm ;
26. $H_2 = 0.1516\,M$, $I_2 = 0.1316\,M$, $HI = 0.5468\,M$;

27. (i) 59% , (ii) 0.168 atm, (iii) 2.633×10^{-5} mol^2 litre^{-2} ;
28. 4 ;
29. 0.3136 atm^2 ;
30. 1.145 atm ;
31. NH_3 = 0.6653 atm, H_2S = 0.1653 atm ;
32. 0.28 ;
33. $\frac{31}{27}$;
34. 894.26°C ;
35. 4.3×10^{-1} ;
36. 3.11 ;
37. 0.032 ;
38. 3.1420 ;
39. 0.7837 mole ;
40. See solution ;
41. See solution ;
42. $[Fe^{3+}] = 0.4973\ M$, $[Hg_2^{2+}] = 0.4987\ M$, $[Fe^{2+}] = 0.0327\ M$, $[Hg^{2+}] = 0.0327\ M$;
43. (a) 1.05 atm, (b) 3.43 atm^{-1} ;
44. (i) $A = 625\ (\text{mm})^2$, $B = 1156\ (\text{mm})^2$, (ii) 0.5407, (iii) 84.38 mm ;
45. 307.46 mm ;
46. $x = 2$;
47. 1.648×10^{-3} ;
48. See solution ;
49. (i) 1.178×10^8 atm, (ii) –35.544 kJ ;
50. (a) $K_c = \frac{1}{12}$ litre^2 mol^{-2}, (b) 4 M, 1.5 M ;
51. (i) $K_p = 7.56 \times 10^{-2}$, $P'_{H_2O} = 0.05$ atm , $P'_{H_2} = 0.1166$ atm,
$P'_{CO_2} = 0.2833$ atm, $V = 35.6$ litre, (ii) $K_{C_1} = 9.04$, $K_{C_2} = 110.1$;
52. 478 ;
53. See solution ;
54. 2.25 atm ;
55. –5.61 kJ

Problems for Self Assessment

1. What is equilibrium constant for the reaction:

   $3Ag_2S_{(s)} + Ba_3(AsO_4)_{2(s)} + 3H^+ \rightleftharpoons 2Ag_3AsO_{4(s)} + 3HS^- + 3Ba^{2+}$

   Given K_{a_2} for H_2S is 1.10×10^{-15} and K_{SP} for $Ba_3(AsO_4)_2$, Ag_2S and Ag_3AsO_4 are 7.70×10^{-51}, 2.0×10^{-49} and 1.0×10^{-22} respectively.

2. The value of K_C for $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ is 1.0×10^{-13} at a particular temperature. At a certain time, the concentration of HF, H_2 and F_2 were found to be 0.5, 1×10^{-3} and 4×10^{-3} mol $litre^{-1}$ respectively. Predict whether the reaction is in equilibrium? If not, what is the direction of reaction to attain equilibrium?

3. Show that for the reaction $AB_{(g)} \rightleftharpoons A_{(g)} + B_{(g)}$, the total pressure at which AB is 50% dissociated is numerically equal to three times of K_p.

4. When 1 mole $H_2O_{(g)}$ and 1 mole $CO_{(g)}$ are heated at 1000°C in a closed vessel of 5 litre, it was found that 40% of H_2O react at equilibrium according to $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$. Find K_C of the reaction.

5. 0.96 g of hydrogen iodide was heated to 450°C till the equilibrium was reached. It was then quickly cooled and the amount of iodine formed required 15.7 mL of $N/10$ $Na_2S_2O_3$. Calculate degree of dissociation of HI at 450°C.

6. N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate:
   (a) K_p for $N_2O_4 \rightleftharpoons 2NO_2$
   (b) % dissociation at 37°C and 0.1 atm.

7. A mixture of SO_2 and O_2 under atmospheric pressure in the ratio of 2 : 1 is passed over a catalyst at 1170°C. After equilibrium has reached, the gas coming out has been found to contain 87% SO_3 by volume. Calculate K_p for $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$.

8. n mole each of H_2O, H_2 and O_2 are mixed at a suitable high temperature to attain the equilibrium $2H_2O \rightleftharpoons 2H_2 + O_2$. If y mole of H_2O are dissociated and the total pressure maintained is P, calculate the K_p.

9. Pure PCl_5 is introduced into an evacuated chamber and comes to equilibrium at 250°C and 2 atmosphere. The equilibrium mixture contains 40.7% Cl_2 by volume.
   (a) What are the partial pressures of each constituent at equilibrium?
   (b) What are K_p and K_C?
   (c) If the gas mixture is expanded to 0.200 atm at 250°C, calculate
      (i) The % of PCl_5 dissociated at this equilibrium.
      (ii) The partial pressure of each at equilibrium.

10. 4.5 g of PCl_5 were completely vaporised at 250°C and the vapours occupied 1.7 litre at one atmospheric pressure. Calculate the degree of dissociation, K_C and K_p for the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

11. 5 mole of PCl_5 and 4 mole of neon are introduced in a vessel of 110 litre and allowed to attain equilibrium at 250°C. At equilibrium, the total pressure of reaction mixture was 4.678 atm. Calculate degree of dissociation of PCl_5 and equilibrium constant for the reaction.

12. In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 18 kcal mol^{-1}, it is decreased to 6 kcal mol^{-1} when the decomposition was carried out in presence of catalyst at 300 K. How many times is the catalytic reaction faster than the uncatalysed one?

13. A mixture of N_2 and H_2 in the molar ratio 1 : 3 at 50 atm and 650°C is allowed to react till equilibrium is obtained. The NH_3 present at equilibrium is 25% by weight, calculate K_p for

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

14. For a reaction $A + 3B \rightleftharpoons 2C$, the reaction was carried out at a temperature of 400°C and pressure 1 atm in closed container with the molar ratio of $A : B$ as 1 : 3. At equilibrium, (C) was found to be 20% of the mixture. What are K_p and K_C?

15. A two litre vessel contains 0.48 mole of CO_2, 0.48 mole of H_2, 0.96 mole of H_2O and 0.96 mole of CO at equilibrium.

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

(a) How many mole and how many g of H_2 must be added to bring the concentration of CO to 0.6 *M*?

(b) How many mole and how many g of CO_2 must be added to bring the concentration of CO to 0.6 *M*?

(c) How many mole of H_2O must be removed to bring the concentration of CO to 0.6 *M*?

16. For the gaseous reaction;

$$C_2H_2 + D_2O \rightleftharpoons C_2D_2 + H_2O;$$

ΔH is 530 cal. At 25°C $K_p = 0.82$. Calculate how much C_2D_2 will be formed if 1 mole of C_2H_2 and 2 mole or D_2O are put together at a total pressure of 1 atm at 100°C?

17. The rate of disappearance of A at two temperature for the equilibrium $A \rightleftharpoons B$ is given by:

$$-\frac{d[A]}{dt} = 2 \times 10^{-2}\,[A] - 4 \times 10^{-3}\,[B] \text{ at } 300\text{ K}$$

$$-\frac{d[A]}{dt} = 4 \times 10^{-2}\,[A] - 16 \times 10^{-4}\,[B] \text{ at } 400\text{ K}$$

Calculate:

(i) equilibrium constants at 300 K and 400 K and

(ii) heat of reaction.

18. Carbon was heated with 1.0 g hydrogen in a 5.0 litre flask at 1000°C. At equilibrium 0.22 g of CH_4 was found in tank. Calculate the equilibrium constant for the equilibrium $C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$. Assume that no other reaction takes place.

19. For the dissociation of phosgene gas, the value of K_p at 100°C is 6.7×10^{-9} atm. Find the fraction of phosgene dissociated at this temperature when 1 mole of phosgene is placed in 100 litre vessel containing nitrogen at partial pressure of 1 atm.

20. 0.1 mole of ethanol and 0.1 mole of benzoic acid are allowed to react. At equilibrium, the mixture is treated with 0.85 *M* NaOH solution and the titre value was 100 mL. Assuming that ester is not hydrolysed by the base. Calculate K_C for the reaction,

$$C_2H_5OH + C_3H_7COOH \longrightarrow C_3H_7COOC_2H_5 + H_2O$$

21. The equilibrium constant for the reaction:

$$F_3O_{4(s)} + CO \rightleftharpoons 3FeO_{(s)} + CO_2$$

at 600°C is 1.15. If a mixture containing initially 1 mole of Fe_3O_4, 2 mole of CO, 0.5 mole of FeO and 0.3 moles of CO_2 were heated to 600°C at constant pressure of 5.0 atm, calculate the amount of each substance at equilibrium.

22. K_p for $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$ is 0.0529 at 26°C. 0.092 mole of solid NH_4HS are introduced into 2.46 litre evacuated vessel at 26°C.

(i) Calculate the % of solid NH_4HS decomposed.

(ii) Calculate the number of moles of NH_3 to be added to reduce the decomposition to 1% of the solid at the same temperature.

23. If for the reaction $NiO + H_{2(g)} \rightleftharpoons Ni + H_2O_{(g)}$; $\Delta G^\circ = -9000$ cal at 500°C. What ratio of pressures of H_2 and H_2O vapour will be in equilibrium with nickel and nickel oxide at 500°C.

24. Anhydrous calcium chloride is often used as a dessicant. In the presence of excess of $CaCl_2$, the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85}$ for the following reaction at room temperature. $CaCl_{2(s)} + 6H_2O_{(v)} \longrightarrow CaCl_2 \cdot 6H_2O_{(s)}$. What is the equilibrium partial pressure of water in a closed vessel that contains $CaCl_{2(s)}$?

25. A sample of $CaCO_{3(s)}$ is introduced into a sealed container of volume 0.821 litre and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ is 4×10^{-2} atm at this temperature. Calculate mass of CaO present at equilibrium.

26. The dissociation pressure of solid ammonium hydro-sulphide at 27°C is 60 cm. What will be the total pressure when it dissociates at the same temperature in presence of NH_3 at a pressure of 45 cm? Assume NH_4HS dissociates completely into NH_3 and H_2S.

27. The reaction : $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$ attains the equilibrium and the equilibrium mixture of steam and hydrogen has partial pressures of 50 mm and 940 mm respectively at 250°C. Calculate the partial pressure of steam at equilibrium when the partial pressure of hydrogen at equilibrium is 1800 mm.

28. A saturated solution of I_2 in water contains 0.33 g litre^{-1} of I_2 more than this can be dissolved in a KI solution because of the following equilibrium:

$I_2 + I^- \rightleftharpoons I_3^-$. A 0.1 *M* KI solution (0.1 *M* I^-) actually dissolves 12.5 g/litre I_2, most of which is converted to I_3^-. Assuming that the concentration of I_2 in all saturated solution is the same, calculate the equilibrium constant (K_C) for the above reaction. What is the effect of adding water to clear saturated solution of I_2 in KI solution.

29. In the reaction $CuSO_4 \cdot 3H_2O_{(s)} \rightleftharpoons CuSO_4 \cdot H_2O_{(s)} + 2H_2O_{(v)}$, the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H^\circ = 2700$ cal. What will be the dissociation pressure at 127°C?

30. In a closed container nitrogen and hydrogen mixture initially in a mole ratio of 1 : 4 reached equilibrium. It is found that the half hydrogen is converted to ammonia. If the original pressure was 180 atm, what will be the partial pressure of ammonia and total pressure at equilibrium. (There is no change in temperature)

31. Calculate the enthalpy and equilibrium constant K_p of reaction ;

$N_2O_4 \rightleftharpoons 2NO_2$ at 348 K. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/litre at 288 K and 1.84 g/litre at 348 K. Also report the change in entropy during the reaction at 348 K. Also predict the colour change when temperature increases from 288 K to 348 K.

32. A gaseous mixture containing 50% CO_2, 45% CO and rest N_2 was passed at 1400 K over ZnO granules to produce Zn vapours following the reaction :

$ZnO_{(s)} + CO \rightleftharpoons Zn_{(g)} + CO_2$. At equilibrium, the rate of input of gas flow at STP is 224 mL/min. The rate of loss of mass of ZnO is 5×10^{-14} mol/min. Calculate K_c for the reaction at 1400 K, assuming ideal gas behaviour.

Answers

1. 4.63×10^{-108} ; **2.** Backward reaction will follow ;

3. —do— ; **4.** 0.444 ;

5. 20.9% ; **6.** (a) 0.267 atm, (b) 63.26% ;

7. $48.22 \text{ atm}^{-1/2}$; **8.** $\dfrac{P(n+y/2)(n+y)^2}{(3n+y/2)(n-y)^2}$;

9. (a) $P_{Cl_2} = P_{Cl_3} = 0.814$ atm, $P_{Cl_5} = 0.372$ atm,

(b) 1.78 atm, 0.04 mol litre^{-1},

(c) (i) 94.8%, (ii) 0.0053, 0.097 atm ;

10. 83.5%, 5.09×10^{-2} mol litre^{-1}, 2.302 atm ;

11. 0.6, 1.75 atm ; **12.** 4.8×10^8 times ;

13. $1.434 \times 10^{-4} \text{ atm}^{-2}$;

14. $K_p = 1.33 \text{ atm}^{-2}$, $K_C = 4.07 \times 10^3 M^{-2}$;

15. (a) 1.26 mole, 2.52 g, (b) 1.26 mole, 55.44 g, (c) 1.008 mole ;

16. 0.64 mole of C_2D_2 ;

17. (i) 5 at 300 K, 25 at 400 K, (ii) 3.863 kcal ;

18. $K_C = 0.308$ litre mol^{-1} ; **19.** 1.48×10^{-4} ;

20. 0.0311 ;

21. $CO_2 = 1.23$ mole, $CO = 1.07$ mole, $Fe_3O_4 = 0.07$ mole, $FeO = 3.29$ mole ;

22. (i) 25% , (ii) 0.578 mole of NH_3 ;

23. 2.97×10^{-3} ; **24.** $P_{H_2O} = 5 \times 10^{-15}$ atm ;

25. 22.4 mg ; **26.** 75 cm ;

27. 95.76 mm ; **28.** 707, Reverse reaction is favoured ;

29. 12.46×10^{-3} atm ;

30. $P'_{NH_3} = 48$ atm, $P_T = 132$ atm.

31. $K_p = 0.0228$ atm at 288 K, $K_p = 5.283$ atm at 348 K, $\Delta H = 18.196$ kcal,

$\Delta S = 55.62$ cal, the brown colour will deepen.

32. $K_c = 5.776 \times 10^{-3}$ mol litre^{-1}.

11

Ionic Equilibrium

Chapter at a Glance

For weak mono-basic acid or for weak mono-acidic base dissociation

$$K_a = \frac{C\alpha^2}{(1-\alpha)} \qquad \ldots(1)$$

K_a is dissociation constant of acid, α is degree of dissociation at concentration C

If α is small

$$K_a = C\alpha^2 \qquad \ldots(2)$$

or

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{(K_a \cdot V)} \qquad \ldots(3)$$

Similarly $K_b = C\alpha^2$ ...(4)

K_b is dissociation constant of base

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{(K_b \cdot V)} \qquad \ldots(5)$$

Relative Strength

For weak acids: Relative strength $= \sqrt{\frac{K_{a_1}}{K_{a_2}}}$ ...(6)

For strong acid: Relative strength $= \frac{K_1}{K_2}$ ...(7)

where K_1, K_2 are rate constant of hydrolysis of esters in presence of acids.

Ionic Product of water and pH:

$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25°C \qquad \ldots(8)$$

K_w is ionic product of water

$$\text{pH} = -\log[H^+] \qquad \ldots(9)$$

Henderson Equation or pH of buffer solutions

For acidic buffer mixtures:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad \ldots(10)$$

For basic buffer mixtures:

$$\mathrm{pOH} = \mathrm{p}K_b + \log \frac{[\mathrm{Salt}]}{[\mathrm{Base}]} \qquad \ldots(11)$$

$$\text{Buffer capacity} = \frac{n}{\Delta \mathrm{pH}} \qquad \ldots(12)$$

Solubility Product:

For solute $AxBy \rightleftharpoons xA^{y+} + yB^{x-}$

$$K_{SP} = [A^{y+}]^x \, [B^{x-}]^y \qquad \ldots(13)$$

$$= X^x . Y^y \, (S)^{x+y} \qquad \ldots(14)$$

where S is solubility of salt in mol litre^{-1}

Salt Hydrolysis

Hydrolysis constant (K_H):

For weak base + strong acid salt $K_H = \frac{K_w}{K_b}$ . . .(15)

For weak acid + strong base salt $K_H = \frac{K_w}{K_a}$ . . .(16)

For weak acid + weak base salt $K_H = \frac{K_w}{K_a \times K_b}$ . . .(17)

Degree of hydrolysis and pH of salt in solution

For weak base + strong acid salt : $h = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{K_w}{K_b . C}}$ . . .(18)

$$\mathrm{pH} = \frac{1}{2}[\mathrm{p}K_w - \log C - \mathrm{p}K_b] \qquad \ldots(19)$$

For weak acid + strong base salts : $h = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{K_w}{K_a . C}}$ . . .(20)

$$\mathrm{pOH} = \frac{1}{2}[\mathrm{p}K_w - \log C - \mathrm{p}K_a] \qquad \ldots(21)$$

$$\mathrm{pH} = \frac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a + \log C] \qquad \ldots(22)$$

For weak acid + weak base salts : $h = \sqrt{K_H} = \sqrt{\frac{K_w}{K_a \times K_b}}$ . . .(23)

$$\mathrm{pH} = \frac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a - \mathrm{p}K_b] \qquad \ldots(24)$$

The Basic Problems with Solution

➤ **Problem 1.** (a) Suggest a solvent in which aniline acts as strong base.

(b) Write equation for the auto ionisation of (i) HCOOH, (ii) NH_3.

(c) $[Al(H_2O)_6]^{3+}$ is acid or base and write its conjugate partner and reaction.

(d) Write the order of acidic nature of HCl, HCOOH and CH_3COOH in (i) H_2O, (ii) liq. NH_3.

➤ **Problem 2.** The ionization constant of propionic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05 *M* solution and also its pH. What will be its degree of ionization in the solution of 0.01 *N* HCl?

➤ **Problem 3.** The ionization constant of dimethyl amine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 *M* solution. What percentage of dimethyl amine is ionized if the solution is also 0.1 *M* in NaOH.

➤ **Problem 4.** The pH of 0.1 *M* solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

➤ **Problem 5.** Calculate the degree of ionization of 0.05 *M* acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution is also (a) 0.01 *M* and (b) 0.1 *M* in hydrochloric acid?

➤ **Problem 6.** The pH of a 0.005 *M* codeine ($C_{18}H_{21}NO_2$) solution is 9.95. Calculate its ionisation constant.

➤ **Problem 7.** Determine degree of dissociation of 0.05 *M* NH_3 at 25°C in a solution of pH = 11.

➤ **Problem 8.** K_1 and K_2 for dissociation of H_2A are 4×10^{-3} and 1×10^{-5}. Calculate concentration of A^{2-} ion in 0.1 *M* H_2A solution. Also report $[H^+]$ and pH.

➤ **Problem 9.** The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 *M* solution and how will this concentration be effected if the solution is 0.1 *M* in HCl also. If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

➤ **Problem 10.** The ionization constants of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

➤ **Problem 11.** Calculate pH of :

(a) 10^{-3} *N* HNO_3, (b) 10^{-3} *M* H_2SO_4, (c) 10^{-3} *N* H_2SO_4,

(d) 0.01 *N* HCl, (e) 10^{-8} *N* HCl, (f) 10^2 *M* HCl.

➤ **Problem 12.** Calculate pH for :

(a) 0.001 *N* NaOH, (b) 0.01 *N* $Ca(OH)_2$, (c) 0.01 *M* $Ca(OH)_2$,

(d) 10^{-8} *M* NaOH, (e) 10^2 *M* NaOH, (f) 0.0008 *M* $Mg(OH)_2$
Assume complete ionisation of each.

➤ **Problem 13.** The pH of 0.05 *M* aqueous solution of diethyl amine is 12.0. Calculate K_b.

➤ **Problem 14.** Calculate the pH of the following solutions :
(a) 2 g of TlOH dissolved in water to give 2 litre of solution.
(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.
(c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.
(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

➤ **Problem 15.** Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below :
(a) Human muscle-fluid 6.83 (b) Human stomach fluid 1.2
(c) Human blood 7.38 (d) Human saliva 6.4

➤ **Problem 16.** If 0.561 g KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

➤ **Problem 17.** The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

➤ **Problem 18.** How many mole of $Ca(OH)_2$ must be dissolved to produce 250 mL of an aqueous solution of pH 10.65, assuming complete dissociation?

➤ **Problem 19.** The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g $litre^{-1}$. Calculate the pH of its saturated solution. Assume 100% ionisation.

➤ **Problem 20.** Calculate the pH of a solution made by mixing 50 mL of 0.01 *M* $Ba(OH)_2$ with 50 mL water. Assume complete ionisation.

➤ **Problem 21.** A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be the pH of resulting solution?

➤ **Problem 22.** A solution of 0.01 *M* concentration of NH_4OH is 2.6% dissociated. Calculate $[H^+]$, $[OH^-]$, $[NH_4^+]$, $[NH_4OH]$ and pH of solution.

➤ **Problem 23.** Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

➤ **Problem 24,** The K_w for $2H_2O \rightleftharpoons H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. What is pH of water at 60°C? What happens to its neutrality?

➤ **Problem 25.** Calculate the pH of a solution of given mixtures;
(a) (4g CH_3COOH + 6g CH_3COONa) in 100 mL of mixture;
K_a for $CH_3COOH = 1.8 \times 10^{-5}$
(b) 5 mL of 0.1 *M* *M*OH + 250 mL of 0.1 *M* *M*Cl;
K_a for $MOH = 1.8 \times 10^{-5}$
(c) (0.25 mole of CH_3COOH + 0.35 mole of CH_3COONa) in 500 mL mixture;
K_a for $CH_3COOH = 3.6 \times 10^{-4}$

Problem 26. How many mole of NH_4Cl must be added to one litre of 1.0 M NH_4OH to have a buffer of pH = 9. $K_{NH_4OH} = 1.8 \times 10^{-5}$?

Problem 27. The ionization constant of formic acid is 1.8×10^{-4}. Around what pH will its mixture with sodium formate give buffer solution of higher capacity. Calculate the ratio of sodium formate and formic acid in a buffer of pH 4.25.

Problem 28. How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solutions of pH 8.65 and 10. Given pK_b of $NH_4OH = 4.75$.

Problem 29. How much volume of 0.1 M HAc should be added to 50 mL of 0.2 M NaAc solution if we want to prepare a buffer solution of pH 4.91. Given pK_a of $CH_3COOH = 4.76$.

Problem 30. The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenate?

Problem 31. The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be pH of 0.1 M acid and its 0.1 M sodium salt solution?

Problem 32. Calculate the pH of the mixture formed by the addition of 5, 9, 9.5, 9.9, 9.95, 10, 10.05 and 10.1 mL of 0.5 M KOH solution to 100 mL of 0.05 HBr solution. What will be the most suitable indicator for this titration?

Problem 33. Calculate the pH of the resultant mixtures :

(a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl,
(b) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$,
(c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH.

Problem 34. Benzoic acid is monobasic and when 1.22 g of its pure sample after dissolution in distilled water is titrated against a base it uses 50 mL of 0.2 M NaOH. Calculate the molar mass of benzoic acid.

Problem 35. Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants given below. Determine also the molarities of individual ions.

$K_{SP(Ag_2CrO_4)} = 1.1 \times 10^{-12}$; $K_{SP(BaCrO_4)} = 1.2 \times 10^{-10}$;
$K_{SP[Fe(OH)_3]} = 1.0 \times 10^{-38}$, $K_{SP(PbCl_2)} = 1.6 \times 10^{-5}$;
$K_{SP(Hg_2I_2)} = 4.5 \times 10^{-29}$.

Problem 36. K_{SP} of $BaSO_4$ is 1.5×10^{-9}. Calculate its solubility in :

(i) pure water ; (ii) 0.10 M $BaCl_2$.

Problem 37. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide. For iron sulphide $K_{SP} = 6.3 \times 10^{-18}$.

➤ **Problem 38.** Equal volumes of 0.002 *M* solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? For copper iodate $K_{SP} = 7.4 \times 10^{-8}$.

➤ **Problem 39.** What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K. For calcium sulphate, K_{SP} is 9.1×10^{-6}.

➤ **Problem 40.** 50 mL of a sample of clear saturated solution of Ag_2CrO_4 requires 20 mL of a *X M* $Pb(NO_3)_2$ for its titration. What is the value of *X*. K_{SP} for Ag_2CrO_4 is 1.6×10^{-12}.

➤ **Problem 41.** Calculate pH of a saturated solution of $Mg(OH)_2$. K_{sp} for $Mg(OH)_2$ is 8.9×10^{-12}.

➤ **Problem 42.** The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Calculate the hydrolysis constant of ammonium chloride and pH of 0.04 *M* ammonium chloride solution.

➤ **Problem 43.** Calculate the pH of 0.05 *M* sodium acetate solution if the pK_a of acetic acid is 4.74.

➤ **Problem 44.** The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.70 and 4.75 respectively. Calculate the hydrolysis constant of ammonium acetate at 298 K and also the degree of hydrolysis and pH of its (a) 0.01 *M* and (b) 0.04 *M* solutions.

➤ **Problem 45.** The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 *M* sodium nitrite solution and also its degree of hydrolysis.

➤ **Problem 46.** A 0.02 *M* solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

Answers

1. (a) liquid acetic acid, (b) see solution, (c) see solution, (d) see solution ;
2. 1.63×10^{-2}, 3.09, 1.32×10^{-3} ;
3. 0.0054 ;
4. 4.57×10^{-2}, 2.09×10^{-4} ;
5. 0.0018, 0.00018 ;
6. 5.78 ;
7. 2% ;
8. $[H^+] = 0.018\ M$, pH = 1.7447, $[HA^-] = 0.018\ M$, $[H_2A] = 0.082\ M$;
   $[A^{-2}] = 10^{-5}\ M$
9. **I** $[HS^-] = 9.54 \times 10^{-5}\ M$; **II** $[HS^-] = 9.1 \times 10^{-8}$; $[S^{2-}]$ in I $= 1.2 \times 10^{-13}\ M$,
   $[S^{2-}]$ in II $= 1.092 \times 10^{-19}\ M$;
10. $F^- = 1.47 \times 10^{-11}$, $HCOO^- = 5.6 \times 10^{-11}$, $CN^- = 2.08 \times 10^{-7}$;
11. (a) 3, (b) 2.6989, (c) 3, (d) 2, (e) 6.9586, (f) See solution ;
12. (a) 11, (b) 12, (c) 12.3010, (d) See solution, (e) See solution, (f) 11.2041;
13. 2.5×10^{-3} ;
14. (a) 11.6548, (b) 12.21, (c) 12.574, (d) 1.8665 ;
15. (a) $1.479 \times 10^{-7}\ M$, (b) $6.31 \times 10^{-2}\ M$, (c) $4.17 \times 10^{-8}\ M$, (d) $3.98 \times 10^{-7}\ M$;
16. 12.6998, $[H^+] = 1.996 \times 10^{-13}$, $[K^+] = 5.01 \times 10^{-2}$;
17. $OH^- = 0.316\ M$, $Sr^{2+} = 0.158\ M$, pH = 13.4997 ;
18. 5.58×10^{-5} mole;
19. 10.52 ;
20. 12 ;
21. 6.9788 ;
22. 10.415;
23. 6.785 ;
24. 6.51 ;
25. (a) 4.7851, (b) 7.5563, (c) 3.5898;
26. 1.8 ;
27. 3.24 ;
28. 109.9 mL ;
29. 70.80 mL ;
30. 4.47×10^{-5}, $2.2 \times 10^{-6}\ M$, 1.0×10^{-8} ;
31. 1.94, 7.94 ;
32. (i) 1.62, (ii) 2.34, (iii) 2.64, (iv) 3.34, (v) 7.0, (vi) 10.35, (vii) 10.66;
33. (a) 12.6125, (b) 7, (c) 1.3010 ;
34. 122 ;
35. $Ag^+ = 1.30 \times 10^{-4}\ M$, $CrO_4^- = 6.5 \times 10^{-5}\ M$, $Ba^{2+} = CrO_4^{2-} = 1.1 \times 10^{-5}\ M$,
   $Fe^{3+} = 1.39 \times 10^{-10}\ M$, $OH^- = 4.17 \times 10^{-10}\ M$, $Pb^{2+} = 1.59 \times 10^{-2}\ M$,
   $Cl^- = 3.18 \times 10^{-2}\ M$, $Hg_2^{2+} = 2.24 \times 10^{-10}\ M$, $I^- = 4.48 \times 10^{-10}\ M$;
36. $3.87 \times 10^{-5}\ M$, $1.5 \times 10^{-8}\ M$;
37. $5.02 \times 10^{-9}\ M$;
38. 10^{-9} ;
39. 2.43 litre water ;
40. $1.84 \times 10^{-4}\ M$;
41. 10.4168 ;
42. 5.32 ;
43. 8.7195 ;
44. 3.23×10^{-5}, 5.68×10^{-3}, 7.005 ;
45. $h = 2.36 \times 10^{-5}$, 7.975 ;
46. 1.52×10^{-9}

Solution

Solution 1. (a) Aniline (a weak base) acts as strong base in liquid acetic acid.

(b) (i) $2HCOOH \rightleftharpoons HCOO^- + HCOOH_2^+$

(ii) $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(c) $[Al(H_2O)_6]^{3+}$ is acid ;

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons \underset{\text{Conjugate base}}{[Al(H_2O)_5OH]^{2+}} + H_3O^+$$

(d) **(i) In H_2O :** $HCl > HCOOH > CH_3COOH$

(ii) In liq. NH_3 : All are strong acids.

Solution 2.
$$\underset{c(1-\alpha)}{CH_3CH_2COOH} \rightleftharpoons \underset{c\alpha}{CH_3CH_2COO^-} + \underset{c\alpha}{H^+}$$

$$K_a = 1.32 \times 10^{-5} = \frac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]} = \frac{c\alpha.c\alpha}{c(1-\alpha)} = c\alpha^2 \quad (\because\ 1-\alpha \approx 1)$$

$$\therefore \quad 0.05 \times \alpha^2 = 1.32 \times 10^{-5};$$

$$\alpha = \mathbf{1.63 \times 10^{-2}}$$

$$pH = -\log[H^+] = -\log(c\alpha)$$

$$= -\log(0.05 \times 1.63 \times 10^{-2}) = \mathbf{3.09}$$

In 0.01 *N* HCl : $[H^+] = 0.01$ and thus

$$1.32 \times 10^{-5} = \frac{c\alpha \times 0.01}{c(1-\alpha)}$$

$$= \alpha \times 0.01 \qquad (1-\alpha \approx 1)$$

$$\therefore \quad \alpha = \mathbf{1.32 \times 10^{-3}}$$

Solution 3.
$$\underset{\text{base}}{(CH_3)_2NH_2} + H_2O \rightleftharpoons \underset{\text{acid}}{(CH_3)_2NH_3^+} + OH^-$$

$$K_b = \frac{[(CH_3)_2NH_3^+][OH^-]}{[(CH_3)_2NH_2]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

$$5.4 \times 10^{-4} = 0.02 \times \alpha^2$$

$$\alpha = \mathbf{0.164}$$

Since $\alpha > 0.05$, we will use $K_b = \dfrac{c\alpha^2}{(1-\alpha)}$

or $$5.4 \times 10^{-4} = \frac{0.02 \times \alpha^2}{(1-\alpha)}$$

Now $\alpha = \mathbf{0.151}$

In presence of NaOH, the dissociation of diethyl amine will decrease due to common ion effect. Thus $0.1 + c\alpha \approx 0.1$ and $1 - \alpha \approx 1$

Thus $$K_b = 5.4 \times 10^{-4} = \frac{c\alpha \times (0.1 + c\alpha)}{c(1-\alpha)} = \alpha \times 0.1$$

or $$\alpha = 5.4 \times 10^{-3} = \mathbf{0.0054}$$

Solution 4. $$\underset{c(1-\alpha)}{HCNO} \rightleftharpoons \underset{c\alpha}{H^+} + \underset{c\alpha}{CNO^-}$$

$$pH = 2.34 \qquad -\log[H^+] = 2.34$$

or $$[H^+] = 4.57 \times 10^{-3}$$

or $$c\alpha = 4.57 \times 10^{-3}$$

$$\therefore \quad 0.1 \times \alpha = 4.57 \times 10^{-3} \qquad \text{or} \qquad \alpha = \mathbf{4.57 \times 10^{-2}}$$

$$\therefore \quad K_a = c\alpha^2 = (4.57 \times 10^{-2})^2 \times 0.1 = \mathbf{2.09 \times 10^{-4}}$$

Solution 5. $$\begin{matrix} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ 1 & & 0 & & 0 \\ 1-\alpha & & \alpha & & \alpha \end{matrix}$$

$$(pK_a = -\log K_a = 4.74, \quad \therefore \quad K_a = 1.82 \times 10^{-5})$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = c\alpha^2 \qquad (1 - \alpha \approx 1)$$

$$\therefore \quad \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = \mathbf{0.019} \quad \text{or} \quad \mathbf{1.9\%}$$

Always calculate α first by $K_b = c\alpha^2$, if α > 5% then use again

$$K = \frac{c\alpha^2}{(1-\alpha)}$$

(a) If H^+ are already present (due to HCl)

$$\begin{matrix} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ 1 & & 0 & & 0.01 \\ c(1-\alpha) & & c\alpha & & [0.01 + c\alpha] \end{matrix}$$

$$K_b = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \times (0.01 + c\alpha)}{c(1-\alpha)}$$

Since presence of H^+ will favour the severse reaction or α will decrease

i.e., $0.01 + c\alpha = 0.01$ and $1 - \alpha = 1$ (due to common ion effect)

$$\therefore \quad 1.82 \times 10^{-5} = \frac{0.05 \times \alpha \times 0.01}{0.05}$$

$$\therefore \quad \alpha = 1.82 \times 10^{-3} = \mathbf{0.0018}$$

(b) Similarly solve for 0.1 *M* HCl

$$\alpha = \mathbf{0.00018}$$

Solution 6. pH = 9.95, Thus codeine is a base.

$$\begin{matrix} C_{18}H_{21}NO_2 + H_2O & \longrightarrow & Codeine^+ & + & OH^- \\ 1 & & 0 & & 0 \\ (1-\alpha) & & \alpha & & \alpha \end{matrix}$$

$$\therefore \qquad [OH^-] = c\alpha$$

or $$\frac{10^{-14}}{[H^+]} = c\alpha \qquad \left[\because [H^+][OH^-] = 10^{-14}\right]$$

Also $\quad pH = 9.95 \;\therefore\; -\log H^+ = 9.95 \quad$ or $\quad [H^+] = 1.12 \times 10^{-10}$

$$\therefore \qquad \frac{10^{-14}}{1.12 \times 10^{-10}} = 0.005 \times \alpha$$

$$\therefore \qquad \alpha = 0.0179 \quad \text{or} \quad 1.79\%$$

Now $$K_b = \frac{[\text{Codeine}]^+[OH^-]}{[\text{Codeine}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

$$K_b = \frac{0.005 \times (0.0179)^2}{(1-0.0179)} = \mathbf{1.63 \times 10^{-5}}$$

Also $\quad pK_b = \mathbf{5.78}$

Solution 7.

$$\begin{array}{ccc} NH_4OH & \rightleftharpoons & NH_4^+ + OH^- \\ 1 & & 0 \qquad 0 \\ c(1-\alpha) & & c\alpha \qquad c\alpha \end{array}$$

Given, $\quad pH = 11$

$$\therefore \qquad [H^+] = 10^{-11} \qquad \left[\because [H^+][OH^-] = 10^{-14}\right]$$

$$\therefore \qquad [OH^-] = 10^{-3} = c\alpha$$

Since, $\quad c = 0.05$

$$\therefore \qquad \alpha = \frac{10^{-3}}{c} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2} \quad \text{or} \quad \mathbf{2\%}$$

Solution 8.

$$H_2A \rightleftharpoons H^+ + HA^-$$

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} = 4 \times 10^{-3}$$

$$\because \quad [H^+] = c\alpha, \quad [HA^-] = c\alpha; \quad [H_2A] = c(1-\alpha)$$

or $$4 \times 10^{-3} = \frac{c\alpha . c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad (c = 0.1\,M)$$

or $$4 \times 10^{-3} = \frac{0.1 \times \alpha^2}{(1-\alpha)} \qquad (1-\alpha \text{ should not be neglected})$$

$$\therefore \qquad \alpha = 0.18$$

$$\therefore \qquad [H^+] = c\alpha = 0.1 \times 0.18 = \mathbf{0.018\ M}$$

$$\therefore \qquad \mathbf{pH = 1.7447}$$

$$\therefore \qquad [HA^-] = c\alpha = 0.1 \times 0.18 = \mathbf{0.018\ M}$$

$$[H_2A] = c(1-\alpha) = 0.1(1-0.18) = \mathbf{0.082\ M}$$

Now HA^- further dissociates to H^+ and A^{-2} ; $c_1 = [HA^-] = 0.018\ M$

$$\begin{array}{ccccc} HA^- & \rightleftharpoons & H^+ & + & A^{-2} \\ 1 & & 0 & & 0 \\ (1-\alpha_1) & & \alpha_1 & & \alpha_1 \end{array}$$

$$\therefore \quad K_{a_2} = 1 \times 10^{-5} = \frac{[H^+][A^{-2}]}{[HA^-]}$$

$\because$ $[H^+]$ already in solution = 0.018 and thus, dissociation of HA^- further suppresses due to common ion effect and $1-\alpha \approx 1$

$$\therefore \quad 1 \times 10^{-5} = \frac{0.018 \times c_1\alpha_1}{c_1(1-\alpha_1)} = 0.018 \times \alpha_1$$

$$\therefore \quad \alpha_1 = \frac{1 \times 10^{-5}}{0.018} = 5.55 \times 10^{-4}$$

$$\therefore \quad [A^{-2}] = c_1\alpha_1 = 0.018 \times 5.55 \times 10^{-4} = \mathbf{10^{-5}\ M}$$

$$\therefore \quad [HA^-] = c_1\,(1-\alpha_1) \approx c_1 = \mathbf{0.018\ M}$$

Solution 9.

$$\begin{array}{ccccc} H_2S & \rightleftharpoons & H^+ & + & HS^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

I

$$K_{a_1} = 9.1 \times 10^{-8} = \frac{[H^+][HS^-]}{[H_2S]} \qquad (\text{Given } [H_2S] = 0.1 = c)$$

$$9.1 \times 10^{-8} = \frac{c^2\alpha^2}{c(1-\alpha)} = c\alpha^2 \qquad (\because 1-\alpha \approx 1)$$

$$9.1 \times 10^{-8} = 0.1 \times \alpha^2$$

$$\therefore \quad \alpha = 9.54 \times 10^{-4}$$

$$\therefore \quad [HS^-] = c\alpha = 0.1 \times 9.54 \times 10^{-4} = \mathbf{9.54 \times 10^{-5}\ M}$$

II If $[H^+] = 0.1$ then

$$K_{a_1} = 9.1 \times 10^{-3} - \frac{[H^+][HS^-]}{[H_2S]} = \frac{0.1 \times c\alpha}{c} = 0.1 \times \alpha$$

$$\alpha = \mathbf{9.1 \times 10^{-7}}$$

$$[HS^-] = c\alpha = 0.1 \times 9.1 \times 10^{-7} = \mathbf{9.1 \times 10^{-8}\ M}$$

$[S^{2-}]$ in I Case :

$$\begin{array}{ccccc} HS^- & \rightleftharpoons & H^+ & + & S^{2-} \\ (9.54 \times 10^{-5} - x) & & (9.54 \times 10^{-5} + x) & & x \end{array}$$

$$K_{a_2} = 1.2 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(9.54 \times 10^{-5} + x).x}{(9.54 \times 10^{-5} - x)}$$

or $\quad x = K_{a_2}$

(x is very very small due to common ion effect)

or $\quad [S^{2-}] = \mathbf{1.2 \times 10^{-13}\ M}$

$[S^{2-}]$ in II Case : $H_2S \rightleftharpoons 2H^+ + S^{2-}$

	H_2S	$2H^+$	S^{2-}
	$c(1-\alpha)$	0.1	$c\alpha$

$$K_{a_1} \times K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{(0.1)^2 \times c\alpha}{c(1-\alpha)}$$

$$\therefore \quad \alpha = \frac{9.1 \times 10^{-8} \times 1.2 \times 10^{-13}}{10^{-2}} = 10.92 \times 10^{-19}$$

$$\therefore \quad [S^{2-}] = c\alpha - 0.1 \times 10.92 \times 10^{-19}$$
$$= 1.092 \times 10^{-19} = \mathbf{1.092 \times 10^{-19}\ M}$$

Solution 10. For conjugate acid-base pair : $K_a \times K_b = K_w$

$$K_b \text{ of } F^- = \frac{10^{-14}}{6.8 \times 10^{-4}} = \mathbf{1.47 \times 10^{-11}}$$

$$K_b \text{ of } HCOO^- = \frac{10^{-14}}{1.8 \times 10^{-4}} = \mathbf{5.6 \times 10^{-11}}$$

$$K_b \text{ of } CN^- = \frac{10^{-14}}{4.8 \times 10^{-8}} = \mathbf{2.08 \times 10^{-7}}$$

Solution 11. Strong acids ionise completely at normal dilutions.

(a) 10^{-3} N HNO_3 :

	$HNO_3 \longrightarrow$	H^+ +	NO_3^-
Conc. before ionisation	10^{-3} N	0	0
Conc. after ionisation	0	10^{-3}	10^{-3}

$\therefore$ $[H^+] = 10^{-3}$ mol/litre or eq./litre (H$^+$ is monovalent)

$\therefore$ pH = – log $[H^+]$ = – log 10^{-3}

$\therefore$ **pH = 3**

(b) 10^{-3} M H_2SO_4 :

	$H_2SO_4 \longrightarrow$	$2H^+$ +	SO_4^{2-}
Conc. before ionisation	10^{-3} M	0	0
Conc. after ionisation	0	2×10^{-3}	10^{-3}

Mole ratio of $H_2SO_4 : H^+ : SO_4^{2-}$ :: 1 : 2 : 1

$[H^+] = 2 \times 10^{-3}$ M

$\therefore$ pH = –log $[H^+]$ = –log 2×10^{-3}

pH = 2.6989

(c) 10^{-3} N H_2SO_4 :

	$H_2SO_4 \longrightarrow$	$2H^+$ +	SO_4^{2-}
Conc. before ionisation	10^{-3} N	0	0
Conc. after ionisation	0	10^{-3}	10^{-3}

$\because$ Equal equivalent of a substance gives equal equivalent of its components.

$\therefore$ $[H^+] = 10^{-3}$ M

pH = –log $[H^+]$

$\therefore$ **pH = 3**

(d) 0.01 *N* HCl : $HCl \longrightarrow H^+ + Cl^-$

	HCl	H^+	Cl^-
Conc. before ionisation	10^{-2} *N*	0	0
Conc. after ionisation	0	10^{-2}	10^{-2}

$$[H^+] = 10^{-2}\ M$$

$\because$ $pH = -\log [H^+]$

$\therefore$ **pH = 2**

(e) 10^{-8} *N* HCl :

Solution I : $HCl \longrightarrow H^+ + Cl^-$

	HCl	H^+	Cl^-
Conc. before ionisation	10^{-8} *N*	0	0
Conc. after ionisation	0	10^{-8}	10^{-8}

$\therefore$ $[H^+] = 10^{-8}\ M$ but pH = 8 is not possible because it is acid. Now $[H^+] = 10^{-7}\ M$ are already present in solution and since $10^{-8} < 10^{-7}$ and thus, it should not be neglected.

$\because$ $[H^+] = 10^{-8} + 10^{-7} = 1.1 \times 10^{-7}\ M$

$pH = 1.1 \times 10^{-7}\ M$

$\therefore$ **pH = 6.9586**

Solution II.

The above solution lacks with discrepancy that dissociation of H_2O, a weak electrolyte is also suppresed in presence of HCl due to common ion effect and thus, $[H^+]_{H_2O}$ but will be lesser than 10^{-7}.

Therefore, dissociation of H_2O in presence of 10^{-8} H_2^+.

$$H_2O \rightleftharpoons \underset{(10^{-8}+a)}{H^+} + \underset{a}{OH^-}$$

$\therefore$ $K_w = (10^{-8} + a)^{-}a$

$a = 0.95 \times 10^{-7}$

$\therefore$ $[H^+] = 10^{-8} + 0.95 \times 10^{-7}$

$= 1.05 \times 10^{-7}$

$\therefore$ **pH = 6.9788**

(f) 10^2 *M* HCl : $HCl \longrightarrow H^+ + Cl^-$

	HCl	H^+	Cl^-
Conc. before dissociation	10^2 *M*	0	0
Conc. after dissociation	0	10^2	10^2

$\therefore$ $[H^+] = 10^2\ M$

pH = –2

But this is not true. This may be explained as follows :

Sorenson's originally intended pH to be related to $[H^+]$, but his fundamental method of measurement—the hydrogen electrode—is now known to depend on thermodynamics activities rather than $[H^+]$, *i.e.*, on log a_{H^+} and $a_{H^+} = [H^+] f_{H^+}$. In dilute solutions f_{H^+} is near enough to unity and thus, $a_{H^+} = [H^+]$. Thus, pH defined by $-\log [H^+]$ is not only of little theoretical significance, but in fact cannot be measured directly. It has therefore, came to be accepted that $pH = -\log_{10H^+}$, *i.e.* pH of 10^2 *M* HCl cannot be calculated and it practically lies near to zero.

Solution 12. **(a) 0.001 *N* NaOH :**

$$\begin{array}{cccc} NaOH & \longrightarrow & Na^+ & + \quad OH^- \\ 10^{-3}\,N & & 0 & 0 \\ 0 & & 10^{-3} & 10^{-3} \end{array}$$

$\therefore$ $[OH^-] = 10^{-3}\,M$

$\therefore$ $pOH = -\log [OH^-] = -\log 10^{-3} = 3$

$\therefore$ $pH = 14 - pOH = 14 - 3 = 11$

$\therefore$ $\mathbf{pH = 11}$

(b) 0.01 *N* Ca(OH)$_2$:

$$\begin{array}{cccc} Ca(OH)_2 & \longrightarrow & Ca^{2+} & + \quad 2OH^- \\ 10^{-2}\,N & & 0 & 0 \\ 0 & & 10^{-2} & 10^{-2} \end{array}$$

$\therefore$ $[OH^-] = 10^{-2}\,M$

$\therefore$ $pOH = 2$ $\qquad \therefore$ $\mathbf{pH = 12}$

(c) 0.01 *M* Ca(OH)$_2$:

$$\begin{array}{cccc} Ca(OH)_2 & \longrightarrow & Ca^{2+} & + \quad 2OH^- \\ 10^{-2}\,M & & 0 & 0 \\ 0 & & 10^{-2} & 2 \times 10^{-2} \end{array}$$

$[OH^-] = 2 \times 10^{-2}\,M$

$\therefore$ $pOH = 1.6989$

$\therefore$ $pH = 14 - 1.6989 = \mathbf{12.3010}$

(d) 10^{-8} *M* NaOH :

$$\begin{array}{cccc} NaOH & \longrightarrow & Na^+ & + \quad OH^- \\ 10^{-8}\,M & & 0 & 0 \\ 0 & & 10^{-8} & 10^{-8} \end{array}$$

$\therefore$ $[OH^-] = 10^{-8}\,M$

Now proceed for OH$^-$ as in Problem 11 part (e).

(e) 10^2 *M* NaOH :

$$\begin{array}{cccc} NaOH & \longrightarrow & Na^+ & + \quad OH^- \\ 10^{2}\,M & & 0 & 0 \\ 0 & & 10^{2} & 10^{2} \end{array}$$

$[OH^-] = 10^2\,M$

Now proceed as in Problem 11 part (f).

(f) 0.0008 *M* Mg(OH)$_2$:

$$\begin{array}{cccc} Mg(OH)_2 & \longrightarrow & Mg^{2+} & + \quad 2OH^- \\ 8 \times 10^{-4}\,M & & 0 & 0 \\ 0 & & 8 \times 10^{-4} & 2 \times 8 \times 10^{-4} \end{array}$$

$\therefore$ $[OH^-] = 16 \times 10^{-4}\,M$

$\therefore$ $pOH = 2.7958$

$\therefore$ $pH = \mathbf{11.2041}$

Solution 13. Diethyl amine is base and gives OH^- as,

$$(C_2H_5)_2NH + H_2O \longrightarrow (C_2H_5)_2NH_2^+ + OH^-$$

Initial conc. $\quad 1 \quad 0 \quad 0$

Equilibrium conc. $\quad (1-\alpha) \quad \alpha \quad \alpha$

$\therefore \quad [OH^-] = C\alpha$

where C is conc. of base and $C = 0.05\,M$.

$\because \quad pH = 12 \quad \therefore \quad pOH = 2$

or $\quad [OH^-] = 10^{-2}\,M$

$\therefore \quad C\alpha = 10^{-2}$

or $\quad 0.05 \times \alpha = 10^{-2} \quad (\because C = 0.05)$

$\therefore \quad \alpha = 0.2$

$$\text{Now for a base, } K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.05 \times (0.2)^2}{(1-0.2)}$$

$$= \frac{0.05 \times 0.04}{0.8} = \mathbf{2.5 \times 10^{-3}}$$

Note : Do not use $K_b = C\alpha^2$ since $\alpha = 0.2$ and $1-\alpha = 0.8$.

Solution 14. **(a)** $[TlOH] = \dfrac{2}{221.37 \times 2} = 4.517 \times 10^{-3}$ (mol.wt. TlOH = 221.37)

$\therefore \quad pOH = \log [OH^-] = -\log 4.517 \times 10^{-3} = 2.3452;$

$\therefore \quad$ **pH = 11.6548**

(b) $[Ca(OH)_2] = \dfrac{0.3 \times 1000}{74 \times 500} = 8.108 \times 10^{-3}\,M$

$\therefore \quad [OH^-] = 2 \times 8.108 \times 10^{-3}\,M$

$\therefore \quad pOH = -\log [OH^-] = -\log 16.216 \times 10^{-3} = 1.7900;$

$\therefore \quad$ **pH = 12.21**

(c) $[NaOH] = \dfrac{0.3 \times 1000}{40 \times 200} = 3.75 \times 10^{-2}\,M$

$[OH^-] = 3.75 \times 10^{-2}\,M;\ pOH = -\log 3.75 \times 10^{-2} = 1.426;$

pH = 12.574

(d) $[HCl]$ formed $= \dfrac{1 \times 13.6}{1000} = 13.6 \times 10^{-3}\,M \qquad (M_1V_1 = M_2V_2)$

$\therefore \quad [H^+] = 13.6 \times 10^{-3};\ pH = -\log 13.6 \times 10^{-3}$

pH = 1.8665

Solution 15. (a) $pH = 6.83$ or $-\log [H^+] = 6.83 \quad \therefore \quad [H^+] = \mathbf{1.479 \times 10^{-7}}\,M$

(b) $pH = 1.2$ or $-\log [H^+] = 1.2 \quad \therefore \quad [H^+] = \mathbf{6.31 \times 10^{-2}}\,M$

(c) $pH = 7.38$ or $-\log [H^+] = 7.38 \quad \therefore \quad [H^+] = \mathbf{4.17 \times 10^{-8}}\,M$

(d) $pH = 6.4$ or $-\log [H^+] = 6.4 \quad \therefore \quad [H^+] = \mathbf{3.98 \times 10^{-7}}\,M$

Solution 16.

$$KOH \longrightarrow K^+ + OH^-$$

$$[KOH] = \frac{0.561 \times 1000}{56 \times 200} = 5.01 \times 10^{-2}\ M$$

$\therefore$ $[OH^-] = 5.01 \times 10^{-2}\ M$

or $pOH = -\log [OH^-] = -\log 5.01 \times 10^{-2}$

$= \mathbf{1.3002}$ $\therefore$ $pH = \mathbf{12.6998}$

$[H^+] = \mathbf{1.996 \times 10^{-13}}$; $[K^+] = \mathbf{5.01 \times 10^{-2}}$

Solution 17.

$$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$$

$$[Sr(OH)_2] = \frac{19.23}{121.62 \times 1} = 0.158\ M$$

$\therefore$ $[OH^-] = 2 \times 0.158\ M = \mathbf{0.316\ M}$

or $pOH = 0.5003$ $\therefore$ $pH = \mathbf{13.4997}$

$[Sr^{2+}] = \mathbf{0.158\ M}$

Solution 18. Let a mole of $Ca(OH)_2$ be dissolved in 250 mL solution to have $pH = 10.65$

$$[Ca(OH)_2] = \frac{a \times 1000}{250} = 4a\ M$$

$$\begin{array}{lcccccl} & Ca(OH)_2 & \longrightarrow & Ca^{2+} & + & 2OH^- & \text{Complete ionization} \\ \text{Initial moles} & 4a & & 0 & & 0 & \\ \text{Final moles} & 0 & & 4a & & 2 \times 4a\ M & \end{array}$$

$\therefore$ $[OH^-] = 8a\ M$

$$[H^+] = \frac{10^{-14}}{8a}$$

$\because$ $pH = -\log [H^+]$

$\therefore$ $10.65 = -\log \dfrac{10^{-14}}{8a}$

$$\frac{10^{-14}}{8a} = 2.238 \times 10^{-11}$$

$\therefore$ $\mathbf{a = 5.58 \times 10^{-5}\ mole}$

Solution 19. Solubility of $Mg(OH)_2$ in pure water $= 9.57 \times 10^{-3}$ g/litre

$$= \frac{9.57 \times 10^{-3}}{58}\ \text{mole/litre}$$

$$= 1.65 \times 10^{-4}\ M$$

$$\begin{array}{ccccc} Mg(OH)_2 & \longrightarrow & Mg^{2+} & + & 2OH^- \\ & & S & & 2S \end{array}$$

$$\therefore \quad [OH^-] = 2 \times [Mg(OH)_2]$$
$$= 2 \times 1.65 \times 10^{-4}$$
$$= 3.3 \times 10^{-4}$$
$$\therefore \quad pOH = -\log [OH^-] = 3.48$$
$$\therefore \quad pH = 14 - 3.48 = \mathbf{10.52}$$

Solution 20. Milli mole of $Ba(OH)_2$ = 50 × 0.01 = 0.5

The solution is diluted with 50 mL H_2O and thus volume becomes 100 mL.

Thus $$[Ba(OH)_2] = \frac{0.5}{100} = 0.005\,M$$

	$Ba(OH) \longrightarrow$	Ba^{2+} +	$2OH^-$
Initial conc.	0.005	0	0
Final conc.	0	0.005	2 × 0.005 = 0.01

$$[OH^-] = 0.01 = 1 \times 10^{-2}$$
$$\therefore \quad pOH = 2$$
$$\therefore \quad pH = 14 - 2 = 12$$

Solution 21. $HCl_I = 10^{-5}\,M$ since pH = 5

Meq. of HCl_I in 1 mL = $10^{-5} \times 1$

Meq. of HCl_{II} in 1000 mL = $N \times 1000$

Since II is prepared by diluting I and Meq. does not change on dilution.

i.e. Meq. of HCl (conc.) = Meq. of HCl (dil.)

$$\therefore \quad 10^{-5} \times 1 = N \times 1000$$
$$\therefore \quad N_{HCl_{II}} = 10^{-8}$$

Now proceed as Problem 8 part (e).

$$\therefore \quad \mathbf{pH = 6.9788}$$

Solution 22.

	$NH_4OH \rightleftharpoons$	NH_4^+ +	OH^-
Before dissociation	1	0	0
After dissociation	$1 - \alpha$	α	α

$$[OH^-] = C.\alpha = C\sqrt{(K_b/C)} = \sqrt{(K_b.C)}$$

Also $$K_b = C\alpha^2 = 0.01 \times (0.026)^2 = 6.76 \times 10^{-6}$$

$$\therefore \quad [OH^-] = \sqrt{[6.76 \times 10^{-6} \times 0.01]} = 2.6 \times 10^{-4}\,M$$
$$\therefore \quad [H^+] = 10^{-14}/2.6 \times 10^{-4}$$
$$= 3.846 \times 10^{-11}\,M$$
$$\therefore \quad pH = -\log [H^+] = -\log 3.846 \times 10^{-11}$$
$$\therefore \quad = \mathbf{10.415}$$

Solution 23. $H_2O \rightleftharpoons H^+ + OH^-$

$\because$ $[H^+][OH^-] = K_w$ or $[H^+]^2 = K_w$ $\therefore$ $[H^+] = [OH^-]$

$\therefore$ $[H^+] = \sqrt{(2.7 \times 10^{-14})} = 1.64 \times 10^{-7}$ $\therefore$ pH = **6.785**

Solution 24. K_w for H_2O at 25°C $= 10^{-14}$

$\therefore$ $[H^+]\,[OH^-] = 10^{-14}$ $(\because K_w = [H^+]\,[OH^-])$

$\therefore$ $[H^+] = 10^{-7}\ M$ $\therefore$ pH = 7

Now K_w for H_2O at 60°C $= 9.62 \times 10^{-14}$

$\therefore$ $[H^+]\,[OH^-] = 9.62 \times 10^{-14}$

For pure water $[H^+] = [OH^-]$

$\therefore$ $[H^+]^2 = 9.62 \times 10^{-14}$

$\therefore$ $[H^+] = \sqrt{(9.62 \times 10^{-14})} = 3.10 \times 10^{-7}\ M$

$\therefore$ pH $= -\log H^+ = -\log 3.10 \times 10^{-7}$

$\therefore$ **pH = 6.51**

Thus, pH of water becomes 6.51 at 60°C but the nature is neutral since calculation for pure water has been made, *i.e.*, **pH scale at 60°C becomes in between 0 to 13.02.**

Solution 25. (a) We have $\text{pH} = -\log K_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

$\because$ $[\text{salt}] = \dfrac{6 \times 1000}{82 \times 100}\ M$ and $[\text{acid}] = \dfrac{4 \times 1000}{60 \times 100}\ M$

$\therefore$ $\text{pH} = -\log 1.8 \times 10^{-5} + \log \dfrac{6 \times 1000/82 \times 100}{4 \times 1000/60 \times 100}$

$\therefore$ pH = **4.7851**

(b) $\text{pOH} = -\log K_b + \log \dfrac{[\text{salt}]}{[\text{base}]}$

$\because$ Total volume after mixing = 250 + 5 = 255 mL

Meq. of salt = 250 × 0.1 = 25

Meq. of base = 5 × 0.1 = 0.5

$\therefore$ $[\text{salt}] = \dfrac{25}{255}$ and $[\text{base}] = \dfrac{0.5}{255}$

$\therefore$ $\text{pOH} = -\log 1.8 \times 10^{-5} + \log \dfrac{25/255}{0.5/255}$

pOH = 6.4437

$\therefore$ pOH = 14 – pOH = **7.5563**

(c) $\text{pH} = -\log K_b + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

$= -\log 3.6 \times 10^{-4} + \log \dfrac{0.35/500}{0.25/500}$

pH = **3.5898**

Solution 26. For Basic buffer solutions

$$pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Let a mole of NH_4Cl are added to (1.0×1) mole of NH_4OH in 1 litre

Given $\quad pH = 9 \quad \therefore \quad pOH = 5$

$$\therefore \quad 5 = -\log 1.8 \times 10^{-5} + \log \frac{a}{1.0 \times 1}$$

or $\quad a = \mathbf{1.8}$

Solution 27. For acidic buffer mixtures.

$$pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

The buffer capacity is $\dfrac{dpH}{dn_{\text{acid or base}}}$

Thus highest buffer capacity of this is $\dfrac{dpH}{dn_{\text{acid}}}$. This will be maximum when pH is near to pK_a. Also the best results are obtained by buffer when $\dfrac{[\text{Salt}]}{[\text{Acid}]} = 10$ or $\dfrac{1}{10}$ *i.e.*, within the range $pK_a \pm 1$

Also $\quad pH = -\log K_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$4.25 = -1.8 \times 10^{-4} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

or $\quad 4.25 = 3.74 + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \mathbf{3.24}$$

Solution 28. Let V mL of NH_4OH be mixed with NH_4Cl to have a buffer of pH 8.65. The total volume after mixing becomes $(V + 30)$ mL.

m mole of $NH_4OH = 0.3 \times V \quad \therefore \quad [NH_4OH] = \dfrac{0.3 \times V}{(V + 30)}$

m mole of $NH_4Cl = 0.2 \times 30 \quad \therefore \quad [NH_4Cl] = \dfrac{0.2 \times 30}{(V + 30)}$

Also pOH of buffer mixture is given by :

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

or $$14 - 8.65 = 4.74 + \log \frac{(0.2 \times 30)/(V+30)}{(0.3 \times V)/(V+30)} \quad (\text{pOH} = 14 - \text{pH})$$

$$0.61 = \log \frac{6}{0.3 \times V}$$

$\therefore$ $V = \mathbf{4.91\ mL}$

Similarly calculate $\left(14 - 10 = 4.74 + \log \frac{0.2 \times 30/(V_1 + 30)}{0.3 \times V_1/(V_1 + 30)}\right)$ for pH = 10;

$V = \mathbf{109.9\ mL}$

Solution 29. Let V mL of HAc on mixing with NaAc gives a pH of 4.91. Thus total volume after mixing becomes $(V + 50)$ mL.

m mole of [HAc] $= 0.1 \times V$ $\quad\therefore\quad$ $[\text{HAc}] = \frac{0.1 \times V}{(V+50)}$

m mole of NaAc $= 50 \times 0.2$ $\quad\therefore\quad$ $[\text{NaAc}] = \frac{10}{(V+50)}$

Also pH of acidic buffer mixture is given by :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$\therefore$ $$4.91 = 4.76 + \log \frac{10/(V+50)}{(0.1 \times V)/(V+50)}$$

$$\log \frac{10}{(0.1 \times V)} = 0.15$$

$\therefore$ $V = \mathbf{70.80\ mL}$

Solution 30.

$$\underset{c(1-\alpha)}{C_6H_5OH} \rightleftharpoons \underset{c\alpha}{C_6H_5O^-} + \underset{c\alpha}{H^+} \qquad K_a = 1.0 \times 10^{-10}$$

$$K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]} \quad \text{or} \quad 1.0 \times 10^{-10} = \frac{c\alpha . c\alpha}{c(1-\alpha)}$$

$(\because 1 - \alpha \approx 1)$ $\quad\therefore\quad$ $c\alpha^2 = 1.0 \times 10^{-10}$

$\therefore$ $$\alpha^2 = \frac{1.0 \times 10^{-10}}{0.05} \quad (\because c = 0.05\ M)$$

$\therefore$ $\alpha = \mathbf{4.47 \times 10^{-5}}$

$\therefore$ $[C_6H_5O^-] = c.\alpha = 0.05 \times 4.47 \times 10^{-5} = \mathbf{2.2 \times 10^{-6}}\ M$

If $[C_6H_5O^-] = 0.01\ M$; $[H^+] = 0.05 \times \alpha$;

$$[C_6H_5OH] = 0.05\,(1-\alpha) = 0.05$$

($\therefore$ α is small due to common ion effect)

$$\therefore \quad 1.0 \times 10^{-10} = \frac{0.05 \times \alpha \times 0.01}{0.05}$$

$$\therefore \quad \alpha = \mathbf{1.0 \times 10^{-8}}$$

Solution 31.

$$\underset{c(1-\alpha)}{CH_2ClCOOH} \rightleftharpoons \underset{c\alpha}{CH_2ClCOO^-} + \underset{c\alpha}{H^+}$$

$$[H^+] = c\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c} = \sqrt{(1.35 \times 10^{-3} \times 0.1)} = 1.16 \times 10^{-2}$$

$$\therefore \quad pH = -\log [H^+] = \mathbf{1.94}$$

For sod. salt $\underset{c(1-h)}{CH_2ClCOO^-} + H_2O \rightleftharpoons \underset{ch}{CH_2ClCOOH} + \underset{ch}{OH^-}$

$$\therefore \quad [OH^-] = ch = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \times c}{K_a}} = \sqrt{\frac{10^{-14} \times 0.1}{1.35 \times 10^{-3}}}$$

$$= 0.86 \times 10^{-6}$$

$$\therefore \quad pOH = -\log [OH^-] = -\log 8.6 \times 10^{-7} = 6.06$$

$$\therefore \quad pH = 14 - 6.06 = \mathbf{7.94}$$

Solution 32. (i) Meq. of KOH in mixture = 5 × 0.5 = 2.5

Meq. of HBr in mixture = 100 × 0.05 = 5

$\therefore$ Meq. of HBr left in mixture = 5 – 2.5 = 2.5

$$\therefore \quad M_{HBr} \text{ of } N_{HBr} = \frac{2.5}{105} = 0.0238 \quad (\text{Total volume} = 5 + 100 = 105)$$

$$\therefore \quad [H^+] = 0.0238$$

$$\therefore \quad pH = -\log [H^+] = -\log 2.38 \times 10^{-2} = \mathbf{1.62}$$

Proceed similarly for other cases :

(ii) pH = 2.34, (iii) pH = 2.64, (iv) 3.34,

(v) 7.0, (vi) 10.35, (vii) 10.66.

Indicator used is phenolphthalein.

Solution 33. (a) Meq. of $Ca(OH)_2 = 10 \times 0.2 \times 2 = 4$ $\left[\begin{aligned} \text{Meq.} &= N \times V_{mL} \\ &= M \times \text{Valance factor} \times V_{mL} \end{aligned}\right]$

$\therefore$ Meq. of HCl = 25 × 0.1 × 1 = 2.5

Meq. of $Ca(OH)_2$ left = 4 – 2.5 = 1.5

$$\therefore \quad NCa(OH)_2 = \frac{1.5}{10+25} = 4.29 \times 10^{-2}$$

$$\therefore \quad [OH^-] = 4.29 \times 10^{-2}, \qquad \therefore\ pOH = 1.3675,$$

$$\therefore \quad pH = \mathbf{12.6325}$$

(b) Meq. of $H_2SO_4 = 10 \times 0.01 \times 2 = 0.2$

$\therefore$ Meq. of $Ca(OH)_2 = 10 \times 0.01 \times 2 = 0.2$

Solution is neutral and pH = **7**

(c) Meq. of $H_2SO_4 = 10 \times 0.1 \times 2 = 2$

Meq. of KOH = $10 \times 0.1 \times 1 = 1$

$\therefore$ Meq. of H_2SO_4 left = 1

$\therefore$ $NH_2SO_4 = 1/20 = 5 \times 10^{-2}$

$\therefore$ $[H^+] = 5 \times 10^{-2}$ and pH = **1.3010**

Solution 34. Meq. of benzoic acid = $\frac{w}{E} \times 1000 = \frac{1.22}{M/1} \times 1000 = \frac{1220}{M}$

$\therefore$ Meq. of NaOH = $50 \times 0.2 = 10$

At equivalence point, Meq. of Benzoic acid = Meq. of NaOH

$$\therefore \quad \frac{1220}{M} = 10 \qquad \therefore \quad M = \mathbf{122}$$

Solution 35. **For Ag_2CrO_4 :** $K_{SP} = 4s^3$

$$Ag_2CrO_4 \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$$

$$S = \sqrt[3]{\frac{K_{SP}}{4}} = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = \mathbf{6.5 \times 10^{-5}}\ \boldsymbol{M}$$

$$[Ag^+] = 2 \times 6.5 \times 10^{-5} = \mathbf{1.30 \times 10^{-4}}\ \boldsymbol{M}$$

$$[CrO_4^-] = \mathbf{6.5 \times 10^{-5}}\ \boldsymbol{M}$$

For $BaCrO_4$: $BaCrO_4 \rightleftharpoons \underset{S}{Ba^{2+}} + \underset{S}{CrO_4^{2-}}$

$$K_{SP} = S^2$$

$$\therefore \quad S = \sqrt{K_{SP}} = \sqrt{1.2 \times 10^{-10}} = \mathbf{1.1 \times 10^{-5}}\ \boldsymbol{M}$$

$$[Ba^{2+}] = \mathbf{1.1 \times 10^{-5}}\ \boldsymbol{M} = [CrO_4^{2-}]$$

For $Fe(OH)_3$: $Fe(OH)_3 \rightleftharpoons \underset{S}{Fe^{3+}} + \underset{3S}{3OH^-}$

$$K_{SP} = 27\ S^4$$

$$\therefore \quad S = \sqrt[4]{\frac{K_{SP}}{27}} = \sqrt[3]{\frac{1.0 \times 10^{-38}}{27}} = \mathbf{1.39 \times 10^{-10}}\ \boldsymbol{M}$$

$$\therefore \quad [Fe^{3+}] = \mathbf{1.39 \times 10^{-10}}\ \boldsymbol{M}$$

$$[OH^-] = 1.39 \times 10^{-10} \times 3 = \mathbf{4.17 \times 10^{-10}}\ \boldsymbol{M}$$

For $PbCl_2$: $PbCl_2 \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{2S}{2Cl^-}$

$$K_{SP} = 4S^3$$

$$\therefore \quad S = \sqrt[3]{\frac{K_{SP}}{4}} = \sqrt[3]{\frac{1.6 \times 10^{-5}}{4}} = \mathbf{1.59 \times 10^{-2}}\ M$$

$$[Pb^{2+}] = \mathbf{1.59 \times 10^{-2}}\ M$$

$$[Cl^-] = 2 \times 1.59 \times 10^{-2} = \mathbf{3.18 \times 10^{-2}}\ M$$

For Hg_2I_2 : $$Hg_2I_2 \rightleftharpoons \underset{S}{Hg_2^{2+}} + \underset{2S}{2I^-}$$

$$K_{SP} = 4S^3$$

$$S = \sqrt[3]{\frac{K_{SP}}{4}} = \sqrt[3]{\frac{4.5 \times 10^{-29}}{4}} = \mathbf{2.24 \times 10^{-10}}\ M$$

$$[Hg_2^{2+}] = \mathbf{2.24 \times 10^{-10}}\ M$$

$$[I^-] = 2 \times 2.24 \times 10^{-10}$$

$$= \mathbf{4.48 \times 10^{-10}}\ M$$

Solution 36. $$BaSO_4 \rightleftharpoons \underset{S}{Ba^{2+}} + \underset{S}{SO_4^{2-}}$$ (where S M/litre is solubility of $BaSO_4$)

(i) $$K_{SP} = S \times S$$

$$\therefore \quad S = \sqrt{K_{SP}} = \sqrt{1.5 \times 10^{-9}} = 3.87 \times 10^{-5} \text{ mole litre}^{-1}$$

(ii) In presence of $0.10\ M$ $BaCl_2$, let S mole/litre $BaSO_4$ is disolved

$$K_{SP} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$1.5 \times 10^{-9} = (0.1 + S)\,(S) \qquad [(0.1 + S) = 0.1 \text{ as } S <<< 0.1]$$

$$\therefore \quad \mathbf{S = 1.5 \times 10^{-8}}\ M$$

Solution 37. $$FeSO_4 + Na_2S \longrightarrow FeS + Na_2SO_4$$

Let V mL of a molar solution are mixed so that no precipitation of FeS is noticed. Let molarity of $FeSO_4$ and Na_2S be a M.

Thus, $$[Fe^{2+}][S^{2-}] = K_{SP} = 6.3 \times 10^{-18}$$

$$\left[\frac{a \times V}{2V}\right]\left[\frac{a \times V}{2V}\right] = 6.3 \times 10^{-18}; \qquad \therefore \qquad a = \mathbf{5.02 \times 10^{-9}}\ M$$

Solution 38. $$2NaIO_4 + Cu(ClO_4)_2 \longrightarrow Cu(IO_4)_2 + 2NaClO_4$$

Meq. on mixing $0.002 \times V$ $\quad$ $0.002 \times V$ $\quad$ (Let V mL of each mixed)

For $Cu(IO_4)_2$: $$Q = [Cu^{2+}][IO_4^-]^2$$

$$Q = \left[\frac{0.002 \times V}{2\ V}\right]\left[\frac{0.002 \times V}{2\ V}\right]^2 = 10^{-9}$$

The numerical value of $Q(10^{-9})$ is lesser than K_{SP} of $Cu(IO_4)_2$ and thus **no precipitation.**

Solution 39. For $CaSO_4$, Let solubility be S mol/litre

$$\text{Them } S = \sqrt{(K_{SP})} = \sqrt{(9.1 \times 10^{-6})} = 3.02 \times 10^{-3} \text{ mol litre}^{-1}$$

Thus, 3.02×10^{-3} mole of $CaSO_4$ is soluble in water = 1 litre

$$\therefore \quad \frac{1}{136} \text{ mole (1 g) of } CaSO_4 \text{ is soluble in } = \frac{1}{136 \times 3.02 \times 10^{-3}} \text{ litre}$$

$$= \mathbf{2.43 \text{ litre water}}$$

Solution 40. For

$$\underset{}{Ag_2CrO_4} \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$$

$$K_{SP} = 4S^3$$

$$\therefore \quad S = \sqrt[3]{\frac{K_{SP}}{4}} = \sqrt[3]{\frac{16 \times 10^{-12}}{4}}$$

$$= 0.736 \times 10^{-4} \text{ mol litre}^{-1}$$

$$\therefore \quad [CrO_4^{2-}] = 0.736 \times 10^{-4}\, M = 0.736 \times 10^{-4} \times 2\, N$$

$$(N = \text{Valence factor} \times M)$$

Also, Meq. of $Pb(NO_3)_2$ = Meq. of CrO_4^{2-}

$$\therefore \quad X \times 2 \times 20 = 0.736 \times 2 \times 10^{-4} \times 50$$

$$\mathbf{X = 1.84 \times 10^{-4}\, M}$$

Solution 41. Let solubility of $Mg(OH)_2$ be S mol litre^{-1}

$$Mg(OH)_2 \rightleftharpoons \underset{S}{Mg^{2+}} + \underset{2S}{2OH^-}$$

$$\therefore \quad [Mg^{2+}][OH^-]^2 = K_{sp}$$

$$4S^3 = 8.9 \times 10^{-12}$$

$$\therefore \quad S = 1.305 \times 10^{-4} \text{ mol litre}^{-1}$$

$$\therefore \quad [OH^-] = 2 \times 1.305 \times 10^{-4} \text{ mol litre}^{-1}$$

$$\therefore \quad pOH = 3.5832$$

$$pH = \mathbf{10.4168}$$

Solution 42. NH_4^+ ion of NH_4Cl salt on dissolution in water undergoes hydrolysis as

$$\underset{\substack{1\\(1-h)}}{NH_4^+} + H_2O \rightleftharpoons \underset{\substack{0\\h}}{NH_4OH} + \underset{\substack{0\\h}}{H^+}$$

Where h is degree of hydrolysis of NH_4Cl

$$K_H = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.77 \times 10^{-5}} = \mathbf{5.65 \times 10^{-10}}$$

Also $$[H^+] = c \cdot h = c \cdot \sqrt{\frac{K_H}{c}} = \sqrt{K_H \cdot c} = \sqrt{5.65 \times 10^{-10} \times 0.04}$$

$$[H^+] = 4.75 \times 10^{-6}$$

$$\therefore \quad pH = -\log [H^+] = -\log 4.75 \times 10^{-6}$$
$$= \mathbf{5.32}$$

Solution 43. CH_3COO^- ion of CH_3COONa hydrolysis in water as :

$$\begin{array}{cccccc} CH_3COO^- & + & H_2O & \rightleftharpoons & CH_3COOH & + & OH^- \\ 1 & & & & 0 & & 0 \\ (1-h) & & & & h & & h \end{array}$$

Where h is degree of hydrolysis of CH_3COONa. Also $pKa = 4.74$ and thus $-\log K_a = 4.74$ or $K_a = 1.82 \times 10^{-5}$

$$\therefore \quad [OH^-] = c \cdot h = c \cdot \sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \cdot c}{K_a}} = \sqrt{\frac{10^{-14} \times 0.05}{1.82 \times 10^{-5}}}$$
$$= 5.24 \times 10^{-6}$$

$$\therefore \quad pOH = -\log [OH^-] = -\log 5.24 \times 10^{-6}$$
$$= 5.2805$$

$$\therefore \quad pH = 14 - pOH = 14 - 5.2805 = \mathbf{8.7195}$$

Solution 44. Both NH_4^+ and CH_3COO^- ion of CH_3COONH_4 shows hydrolysis as :

$$\begin{array}{cccccc} CH_3COO^-NH_4^+ & + & H_2O & \rightleftharpoons & CH_3COOH & + & NH_4OH \\ 1 & & & & 0 & & 0 \\ (1-h) & & & & h & & h \end{array}$$

Given

pK_a $CH_3COOH = 4.76$ $\quad \therefore \quad -\log K_a = 4.76$ or $K_a = 1.74 \times 10^{-5}$

pK_b $NH_4OH = 4.75$ $\quad \therefore \quad -\log K_b = 4.75$ or $K_b = 1.78 \times 10^{-5}$

$$K_H \text{ for } CH_3COONH_4 = \frac{K_w}{K_a \times K_b} = \frac{10^{-14}}{1.74 \times 10^{-5} \times 1.78 \times 10^{-5}}$$
$$= \mathbf{3.23 \times 10^{-5}}$$

$$\text{Also } h \text{ for } CH_3COONH_4 = \sqrt{K_H} = \sqrt{3.23 \times 10^{-5}}$$
$$= \mathbf{5.68 \times 10^{-3}}$$

Now for dissociation of CH_3COOH

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c(1-h)\,[H^+]}{ch}$$

$$[H^+] = K_a \times \frac{h}{(1-h)} = K_a \times \sqrt{K_H}$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}} = \sqrt{\frac{10^{-14} \times 1.74 \times 10^{-5}}{1.78 \times 10^{-5}}}$$

$$[H^+] = 9.88 \times 10^{-8}$$

or $\quad$ pH = **7.005** $\quad$ (pH and h are independent of initial conc. of salt)

Solution 45. $\quad NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$\qquad c(1-h) \qquad\qquad ch \qquad ch \quad$ where h is degree of hydrolysis

$$[OH^-] = ch\ ;$$

Also, $\quad h = \sqrt{\dfrac{K_H}{c}} = \sqrt{\dfrac{K_w}{K_a.c}} = \sqrt{\dfrac{10^{-14}}{4.5 \times 10^{-4} \times 0.04}} = \mathbf{2.36 \times 10^{-5}}$

$\therefore \quad [OH^-] = 0.04 \times 2.36 \times 10^{-5} \quad$ or $\quad$ pOH = 6.025

$\therefore \quad$ pH = 14 – pOH = **7.975**

Solution 46. $\quad P_yH^+ + H_2O \rightleftharpoons P_yH^+OH^- + H^+$

$\qquad c(1-h) \qquad\qquad ch \qquad ch$

$$[H^+] = ch = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{c \cdot K_w}{K_b}} = 3.63 \times 10^{-4}$$

$$(\because \text{pH} = 3.44 \ \therefore \ [H^+] = 3.63 \times 10^{-4})$$

$\therefore \quad K_b = \dfrac{0.02 \times 10^{-14}}{(3.63 \times 10^{-4})^2} = \mathbf{1.52 \times 10^{-9}}$

Selected Problems with Solutions

➤ **Problem 1.** Prove that degree of dissociation of a weak acid is given by:

$$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$

where K_a is its dissociation constant.

➤ **Problem 2.** Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid $= 2.6 \times 10^{-3}$.

➤ **Problem 3.** Diborane, B_2H_6 reacts with water to form boric acid and hydrogen. What is the pH of solution which results when 1.0 g B_2H_6 reacts with 100 mL water. Assume that final volume be 100 mL water.

K_a for $H_3BO_3 = 7.3 \times 10^{-10}$.

➤ **Problem 4.** Liquid ammonia ionises to a slight extent. At – 50°C, its self ionisation constant, $K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-30}$. How many amide ions are present per cm^3 of pure liquid ammonia? Assume $N = 6.0 \times 10^{23}$.

➤ **Problem 5.** The self ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is $1.22\ g/cm^3$.

➤ **Problem 6.** Calculate the dissociation constant of NH_4OH at 25°C. If $\Delta H°$ and $\Delta S°$ for the given changes are as follows:

$$NH_3 + H^+ \rightleftharpoons NH_4^+; \qquad \Delta H° = -52.2\ kJ\ mol^{-1}; \quad \Delta S° = +1.67\ JK^{-1}\ mol^{-1}$$

$$H_2O \rightleftharpoons H^+ + OH^-; \qquad \Delta H° = 56.6\ kJ\ mol^{-1}; \quad \Delta S° = -78.2\ JK^{-1}\ mol^{-1}$$

➤ **Problem 7.** Calculate the concentrations of all species of significant concentrations present in 0.1 M H_3PO_4 solution. $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 3.6 \times 10^{-3}$.

➤ **Problem 8.** If CH_3COOH ($K_a = 10^{-5}$) reacts with NaOH at 298 K, then find out the value of the maximum rate constant of the reverse reaction at 298 K at the end point of the reaction. Given that the rate constant of the forward reaction is 10^{-11} mol^{-1} L sec^{-1} at 298 K. Also calculate Arrhenius parameter for backward reaction if $\Delta H_{298} = 44$ kcal and $E_{a(f)} = 94$ kcal.

➤ **Problem 9.** The K_w of water at two temperature 25°C and 50°C are 1.08×10^{-14}, 5.474×10^{-14} respectively. Assuming ΔH of any reaction is independent of temperature, calculate enthalpy of neutralisation of a strong acid with strong base.

➤ **Problem 10.** The pH of pure water at 25°C and 35°C are 7 and 6 respectively. Calculate the heat of formation of water from H^+ and OH^-.

➤ **Problem 11.** For an organic monoprotic acid solution of concentration Co mole litre^{-1}, if K_a has a value comparable to K_w, show that the hydronium ion concentration is given by:

$$[H^+] = \left[\frac{K_w}{[H^+]} + \frac{K_a \, Co}{[K_a + H^+]}\right]$$

If $[H^+] = 10^{-3}\ M$ and $Co = 10^{-1}\ M$ in a solution of some organic monoprotic acid, what according to the above equation must be the order of magnitude of K_a.

➤ **Problem 12.** The K_w for $2H_2O \rightleftharpoons H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. What is pH of water at 60°C? What happens to its neutrality?

➤ **Problem 13.** For the indicator thymol blue, pH is 2.0 when half of the indicator is in unionised form. Find the % of indicator in unionised form in a solution with $[H^+] = 4 \times 10^{-3}\ M$.

➤ **Problem 14.** Calculate the per cent error in hydronium ion concentration made by neglecting the ionisation of water in $1.0 \times 10^{-6}\ M$ NaOH.

➤ **Problem 15.** Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4.

➤ **Problem 16.** What should be the pH at the equivalence point for the titration of 0.10 M KH_2BO_3 with 0.10 M HCl. K_a $H_3BO_3 = 7.2 \times 10^{-10}$.

➤ **Problem 17.** Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

➤ **Problem 18.** Calculate $[H^+]$ in a solution containing 0.1 M HCOOH and 0.1 M HOCN. K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}.

➤ **Problem 19.** What are $[H^+]$, $[A^-]$ and $[B^-]$ in a solution that is 0.03 M HA and 0.1M HB? K_a for HA and HB are 1.38×10^{-4} and 1.05×10^{-10} respectively.

➤ **Problem 20.** Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M HCl and 0.01 M in $CHCl_2COOH$. (K_a $CHCl_2COOH = 5 \times 10^{-2}$).

➤ **Problem 21.** Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_8O_2^-]$ in a solution that is 0.02 M in acetic acid and 0.01 M in benzoic acid. $K_{a_{AA}} = 1.8 \times 10^{-5}$; $K_{a_{BA}} = 6.4 \times 10^{-5}$.

➤ **Problem 22.** A solution contains 0.09 M HCl, 0.09 M $CHCl_2COOH$ and 0.1 M CH_3COOH. pH of this solution is 1. If K_a for acetic acid is 10^{-5}, calculate K_a for $CHCl_2COOH$.

➤ **Problem 23.** 100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, V.P. of H_2O at 25°C is 23.7 mm.

➤ **Problem 24.** Calculate the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1 *M* HCl. K_a for $HCO_3^- = 5.63 \times 10^{-11}$.

➤ **Problem 25.** Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre.

➤ **Problem 26.** A 0.1 *M* solution of weak acid H*A* is 1% dissociated at 25°C. What is its K_a? If this solution is with respect to Na*A* 0.2 *M*, what will be the new degree of dissociation of H*A* and pH?

➤ **Problem 27.** Calculate the amount of $(NH_4)_2SO_4$ in g which must be added to 500 mL of 0.2 *M* NH_3 to yield a solution of pH = 9.35. K_b for $NH_3 = 1.78 \times 10^{-5}$.

➤ **Problem 28.** 0.00050 mole of $NaHCO_3$ is added to a large volume of a solution buffered at pH = 8.00. How much material will exist in each of the three forms, H_2CO_3, HCO_3^- and CO_3^{2-}. K_1 and K_2 for H_2CO_3 are 4.5×10^{-7} and 4.5×10^{-11} respectively.

➤ **Problem 29.** 0.1 *M* CH_3COOH solution is titrated against 0.05 *M* NaOH solution. Calculate pH at 1/4th and 3/4th stages of neutralization of acid. The pH for 0.1 *M* CH_3COOH is 3.

➤ **Problem 30.** A solution of weak acid was titrated with base NaOH. The equivalence point was reached when 36.12 mL of 0.1 *M* NaOH have been added. Now 18.06 mL 0.1 *M* HCl were added to titrated solution, the pH was found to be 4.92. What is K_a of acid?

➤ **Problem 31.** A weak acid H*A* after treatment with 12 mL of 0.1 *M* strong base *B*OH has a pH of 5. At the end point, the volume of same base required is 26.6 mL. Calculate K_a of acid.

➤ **Problem 32.** To a solution of acetic acid, solid sodium acetate is added gradually. When *x* mole of salt is added, the pH has a certain value. If *y* mole of salt is added, the pH is this time changes by 0.6 units to previous pH. What is the ratio of *x* and *y*. If the solution is diluted after addition of *y* mole salt, what will be the change in pH. Given that $y > x$.

➤ **Problem 33.** When 40 mL of a 0.1 *M* weak monoacid base is titrated with 0.16 *M* HCl, the pH of solution at the end point is 5.23. Calculate K_b what will be the pH if 15 mL of 0.12 *M* NaOH is added to the resulting solution.

➤ **Problem 34.** The $[Ag^+]$ ion in a saturated solution of Ag_2CrO_4 at 25°C is 1.5×10^{-4} *M*. Determine K_{SP} of Ag_2CrO_4 at 25°C.

➤ **Problem 35.** K_{SP} of $PbBr_2$ is 8×10^{-5}. If the salt is 80% dissociated in solution, calculate the solubility of salt in g per litre.

➤ **Problem 36.** K_{SP} for $PbCl_2$ is 10^{-13}. What will be $[Pb^{2+}]$ in a solution prepared by mixing 100 mL of 0.1 *M* $Pb(NO_3)_2$ and 1 mL of 1 *M* HCl?

➤ **Problem 37.** Calculate simultaneous solubility of AgCNS and AgBr in a solution of water. K_{SP} of $AgBr = 5 \times 10^{-13}$ and K_{SP} of $AgCNS = 1 \times 10^{-12}$.

➤ **Problem 38.** $BaSO_4$ and $BaCrO_4$ have solubility product values in the ratio 1 : 2.5 at 25°C. When pure water is saturated with both solids simultaneously, the total concentration of Ba^{2+} ion in the solution is 1.4×10^{-5} *M*. Calculate the solubility product of $BaCrO_4$. Calculate also the solubility of $BaSO_4$ in 0.01 *M* Na_2SO_4 solution.

➤ **Problem 39.** A mixture of water and AgCl is shaken until a saturated solution is obtained. Now the solution is filtered and 100 mL of clear solution of filtrate is mixed with 100 mL of 0.03 *M* NaBr. Should a precipitate form? K_{SP} of AgCl and AgBr are 1×10^{-10} and 5×10^{-13}.

➤ **Problem 40.** Zn salt is mixed with $(NH_4)_2S$ of molarity 0.021 *M*. What amount of Zn^{2+} will remain unprecipitated in 12 mL of the solution? K_{SP} of $ZnS = 4.51 \times 10^{-24}$.

➤ **Problem 41.** A particular water sample has 131 ppm $CaSO_4$. What fraction of the water must be evaporated in a container before solid $CaSO_4$ begins to deposit K_{SP} of $CaSO_4 = 9.0 \times 10^{-6}$?

➤ **Problem 42.** To a solution of 0.1 *M* Mg^{2+} and 0.8 *M* NH_4Cl, an equal volume of NH_3 is added which just gives precipitate. Calculate $[NH_3]$ in solution. K_{SP} of $Mg(OH)_2 = 1.4 \times 10^{-11}$ and K_b of $NH_4OH = 1.8 \times 10^{-5}$.

➤ **Problem 43.** What is the molar solubility of $AgCl_{(s)}$ in 0.100 *M* $NH_{3(aq)}$. Given K_{SP} of $AgCl = 1.8 \times 10^{-10}$; K_f of $[Ag(NH_3)_2]^+ = 1.6 \times 10^7$.

➤ **Problem 44.** 10 mL of 0.3 *M* Na_2SO_4 are mixed with 20 mL solution having initially 0.1 *M* Ca^{2+} and 0.1 *M* Sr^{2+} in it. What are the final concentration of Ca^{2+}, Sr^{2+} and SO_4^{2-} in solution? Given K_{SP} of $SrSO_4 = 7.6 \times 10^{-7}$ and K_{SP} of $CaSO_4 = 2.4 \times 10^{-5}$.

➤ **Problem 45.** The solubility of $CaCO_3$ is 7 mg/litre. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{2+} and Ba^{2+}, no precipitate is formed until 90% of Ba^{2+} has been precipitated as $BaCO_3$.

➤ **Problem 46.** Calculate the solubility of AgCN in a buffer solution of pH = 3. Given K_{SP} of $AgCN = 1.2 \times 10^{-16}$ and K_a for $HCN = 4.8 \times 10^{-10}$.

➤ **Problem 47.** 2 *M* solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2. Very little amount of $CaCO_3$ and NaF are formed. If the solubility product of $CaCO_3$ is *x* and molar solubility of CaF_2 is *y*, find the molar concentration of F^- in the resulting solution after equilibrium is attained.

➤ **Problem 48.** 100.0 mL of a clear saturated solution of Ag_2SO_4 is added to 250.0 mL of a clear saturated solution of $PbCrO_4$. Will any precipitate form and if so what? Given K_{SP} values for Ag_2SO_4, Ag_2CrO_4, $PbCrO_4$ and $PbSO_4$ are 1.4×10^{-5}, 2.4×10^{-12}, 2.8×10^{-13} and 1.6×10^{-8} respectively.

➤ **Problem 49.** 25.0 mL clear saturated solution of $PbI_2(aq)$ requires 13.3 mL of $AgNO_3(aq)$ solution for complete precipitation. What is molarity of $AgNO_3$ solution? K_{SP} of PbI_2 is 7.1×10^{-9}.

➤ **Problem 50.** K_{SP} for $SrF_2 = 2.8 \times 10^{-9}$ at 25°C. How much NaF should be added to 100 mL of solution having 0.016 M in Sr^{2+} ions to reduce its concentration to 2.5×10^{-3} M?

➤ **Problem 51.** H_2S is bubbled into 0.2 M NaCN solution which is 0.02 M in each $[Cd(CN)_4]^2$ and $[Ag(CN)_2]^-$. Determine which sulphide will precipitate first?

Given, $K_{SP\ Ag_2S} = 1 \times 10^{-50}\ M^3$

$K_{SP\ CdS} = 7.1 \times 10^{-28}\ M^2$

$K_{inst\ [Ag(CN)_2]^{1-}} = 1 \times 10^{-20}\ M^2$

$K_{inst\ [Cd(CN)_4]^{2-}} = 7.8 \times 10^{-18}\ M^4$

➤ **Problem 52.** 338 mL clear saturated solution of $AgBrO_3$ requires just 30.4 mL of $H_2S_{(g)}$ at 23°C and 748 mm Hg to precipitate all the Ag^+ ions into Ag_2S. What will be K_{SP} of $AgBrO_3$?

➤ **Problem 53.** 0.10 mole of AgCl(s) is added to 1 litre of H_2O. Next crystal of NaBr are added until 75% of the AgCl is converted to AgBr(s), the less soluble silver halide. What is Br^- at this point? K_{SP} of AgCl is 1.78×10^{-10} and K_{SP} of AgBr is 5.25×10^{-13}.

➤ **Problem 54.** Calculate pH of the following mixtures. Given that K_a 1.8×10^{-5} and $K_b = 1.8 \times 10^{-5}$.

(a) 50 mL of 0.10 M NaOH + 50 mL of 0.05 M CH_3COOH.

(b) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH.

(c) 50 mL of 0.10 M NaOH + 50 mL of 0.10 M CH_3COOH.

(d) 50 mL of 0.10 M NH_4OH + 50 mL of 0.05 M HCl.

(e) 50 mL of 0.05 M NH_4OH + 50 mL of 0.01 M HCl.

(f) 50 mL of 0.10 M NH_4OH + 50 mL of 0.10 M HCl.

(g) 50 mL of 0.05 M NH_4OH + 50 mL of 0.05 M CH_3COOH.

➤ **Problem 55.** Calculate $[H^+]$ in a 0.20 M solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.

➤ **Problem 56.** 10 g of NH_4Cl (mol. wt. 53.5) when dissolved in 1000g water lowered the freezing point by 0.637°C. Calculate the degree of hydrolysis of the salt if its degree of dissociation is 0.75. The molal depression constant of water is 1.86 K molality^{-1}.

➤ **Problem 57.** At 18°C aniline and acetic acid have dissociation constants 5×10^{-10} and 1.8×10^{-5} respectively. An aqueous solution of anilium acetate is hydrolysed to the extent of x% under equilibrium, what is the pH of the solution. $K_w = 10^{-14}$.

➤ **Problem 58.** Calculate the extent of hydrolysis of 0.005 M K_2CrO_4. $K_2 = 3.1 \times 10^{-7}$ for H_2CrO_4. (H_2CrO_4 is strong for first ionisation and $K_1 = 1.6$).

➤ **Problem 59.** A solution made up to be 0.0100 M $Co(NO_3)_2$ and 0.0200 M N_2H_4 was found to have an equilibrium $[Co^{2+}]$ of 6.2×10^{-3}. Assuming that the only complex formed was $Co(N_2H_4)^{2+}$, what is the apparent K_1 for complex formation?

➤ **Problem 60.** The vapour pressure of 0.01 molal solution of weak base BOH in water at 20°C is 17.536 mm. Calculate K_b for base. Aqueous tension at 20°C is 17.540 mm. Assume molality and molarity same.

➤ **Problem 61.** A 0.01 M aqueous solution of weak acid HA has an osmotic pressure 0.293 atm at 25°C. Another 0.01 M aqueous solution of other weak acid HB has an osmotic pressure of 0.345 atm under the same conditions. Calculate equilibrium constants of two acids for their dissociation.

➤ **Problem 62.** The freezing point of 3.75×10^{-2} M aqueous solution of weak acid HA is 272.9 K. The molality of the solution was found to be 0.0384 molal. Find the $[H^+]$ of the solution on adding 3.75×10^{-2} moles of NaA to one litre of the above solution. K_f of water = 1.86 K molal^{-1}.

➤ **Problem 63.** Calculate 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. Also report the pH at which coloured ion is 80% present.

➤ **Problem 64.** A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be pH of resulting solution?

➤ **Problem 65.** Calculate the pH of 0.010 M $NaHCO_3$ solution.

$K_1 = 4.5 \times 10^{-7}$; $K_2 = 4.7 \times 10^{-11}$ for carbonic acid.

➤ **Problem 66.** Show that solubility of a sparingly soluble salt $M^{2+}A^{2-}$ in which A^{2-} ion undergoes hydrolysis is given by :

$$S = \sqrt{K_{SP}\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)}$$

where K_1 and K_2 are the dissociation constant of acid HA_2. K_{SP} is solubility product of MA.

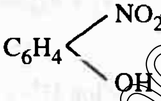
➤ **Problem 67.** A solution of volume V contains a mole of MCl and b mole of NCl where MOH and NOH are two weak bases having dissociation constants K_1 and K_2 respectively. Show that the pH of the solution can be expressed as $\text{pH} = \frac{1}{2}\log_{10}\left[\frac{K_1K_2}{K_w} \times \frac{V}{aK_2 + bK_1}\right]$

Answers

1. See solution ;
2. $2.37 \times 10^{-3}\ M$;
3. 4.6401
4. 6×10^5 ions ;
5. 0.004% ;
6. 1.7×10^{-5} ;
7. See solution ;
8. 10^{-20}, $2.71 \times 10^{+16}$;
9. -12.5×10^3 cal ;
10. 84.551 kcal/mol ;
11. 10^{-5} ;
12. 6.51, See solution ;
13. 0.2857 ;
14. 1% ;
15. 0.4685 ;
16. 5.22 ;
17. 3.0409 ;
18. $7.13 \times 10^{-3}\ M$;
19. $[H^+] = [A^-] = 2.04 \times 10^{-3}\ M$, $[B^-] = 5.15 \times 10^{-9}\ M$;
20. $[H^+] = 0.0174\ M$, $[CHCl_2COO^-] = 7.416 \times 10^{-3}\ M$;
21. $[H^+] = 10^{-3}\ M$, $[CH_3COO^-] = 3.6 \times 10^{-4}\ M$, $[C_7H_5O_2] = 6.4 \times 10^{-4}\ M$;
22. 1.25×10^{-2} ;
23. 2.4142 ;
24. 10.197 ;
25. 1 : 2 ;
26. 10^{-5}, 5×10^{-5}, pH = 5.3010 ;
27. 5.248 g ;
28. $n_{H_2CO_3} = 1.069 \times 10^{-5}$, $n_{HCO_3^-} = 4.86 \times 10^{-4}$, $n_{CO_3^-} = 2.28 \times 10^{-5}$;
29. 4.5228 , 5.4771 ;
30. 1.2×10^{-5} ;
31. 8.219×10^{-6} ;
32. 1 : 3.98 ;
33. 1.775×10^{-5}, 9.1621 ;

34. 1.688×10^{-12} mol^{3} litre^{-3} ;
35. 12.48 g litre^{-1} ;
36. 9.4×10^{-2} mol litre^{-1} ;
37. 8.16×10^{-7} mol litre^{-1}, 4×10^{-7} mol litre^{-1} ;
38. $1.4 \times 10^{-10}\, M^2$, $5.6 \times 10^{-9}\, M$;
39. See solution ;
40. 1.677×10^{-22} g/12 mL ;
41. 68% ;
42. $0.3710\, M$;
43. $5.36 \times 10^{-3}\, M$;
44. $[Ca^{2+}] = 3.3 \times 10^{-2}\, M$, $[Sr^{2+}] = 1.05 \times 10^{-3}\, M$, $[SO_4^{2-}] = 7.17 \times 10^{-4}\, M$;
45. 4.9×10^{-10} ;
46. 1.58×10^{-5} mol litre^{-1} ;
47. $\sqrt{\frac{8y^3}{x}}$;
48. See solution ;
49. 4.55×10^{-3} ;
50. 0.1178 g ;
51. CdS ;
52. 5.29×10^{-5} ;
53. $2.2 \times 10^{-4}\, M$;
54. (a) 12.3979, (b) 4.7447, (c) 8.7218, (d) 9.2553,
(e) 1.6021, (f) 5.2782, (g) 7 ;
55. 0.05 ;
56. 0.106 ;
57. 4.7219 ;
58. 0.253% ;
59. 37.8 ;
60. 9.74×10^{-4} ;
61. $HA = 4.77 \times 10^{-4}$, $HB = 2.85 \times 10^{-3}$;
62. $6.89 \times 10^{-3}\, M$;
63. 5, 5.6020 ;
64. 6.9788 ;
65. 8.34 ;
66. See solution
67. See solution

Problems for Self Assessment

1. What dissociation constant must you pick for an acid H*A* so that it will be 1% dissociated in a solution having H_3O^+ fixed at 0.1 *M*. Also if 1 *N* solution of H*A* is 4.5% dissociated. What will be its dissociation constant?
2. A saturated solution of *o*-nitrophenol  $C_6H_4\langle^{NO_2}_{OH}$ has pH = 4.53. Calculate its solubility in g L^{-1}. pK_a of *o*-nitrophenol = 7.23.
3. A solution was made upto be 0.010 *M* in chloroacetic acid ($ClCH_2COOH$) and also 0.0020 *M* in sodium chloro-acetate ($ClCH_2COONa$). What is $[H^+]$ of the solution. K_a for $ClCH_2COOH$ is 1.5×10^{-3}.
4. How much solid sodium dichloro-acetate should be added to a litre of 0.100 *M* dichloro-acetic acid to reduce $[H^+]$ to 0.030. Neglect the increase in volume of the solution on addition of salt.
5. The degree of dissociation of pure water is 1.8×10^{-9} at 28°C. Find K_w and K_a for H_2O.
6. Calculate the number of H^+ present in 1 mL solution whose pH = 13.
7. 25 mL of a saturated solution of phenyl acetic acid requires 17.70 mL of 0.1850 *M* NaOH for its neutralisation. What is the pH of saturated solution of phenyl acetic acid. Assume K_a for the acid = 5.56×10^{-5}.
8. How many mole of $Ca(OH)_2$ must be dissolved to produce 250 mL of an aqueous solution of pH 10.65, assuming complete dissociation?
9. Compute the pH of a solution at 25°C which is twice as alkaline as pure water.
10. Calculate the pH of a solution made by mixing 50 mL of 0.01 *M* $Ba(OH)_2$ with 50 mL water.
11. 0.12 mL of a solution of KOH (50% by weight of KOH), specific gravity 1.5 g/cm^3, is diluted to 250 mL. Calculate its pH.
12. Find the pH and % dissociation of HAc in a solution obtained by mixing 25 mL of 0.2 *M* HCl and 25 mL of 0.2 *M* NaAc. Given K_a for HAc = 1.78×10^{-5}.
13. How many mL of 0.001 *M* HCl should be added to 10 cm^3 of 0.001 *N* NaOH to change its pH by one unit?
14. Calculate the decrease in % in $[H^+]$ when pH increases by 0.1 unit.
15. The pH of blood is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 *M* $NaHCO_3$ solution should be mixed with 10 mL sample of blood which is 2 *M* in $H_2C_2O_3$ in order to maintain a pH of 7.4? Given K_1 for H_2CO_3 is 7.3×10^{-7}.

16. Calculate weight in g for HCl added to 100 mL of 0.1 *N* *B*OH to have its pH = 6.6 and $K_b = 5.6 \times 10^{-8}$.

17. A buffer solution is made by adding 0.1 mole of sodium acetate to one litre of 0.1 *M* CH_3COOH. What is the maximum amount of HCl that can be added to solution without changing pH by:
(a) more than 0.5 units,
(b) more than 0.3 units?

18. The following pairs of solutions are mixed. Show whether or not precipitation occurs.
(a) 100 mL of 0.01 *M* Na_2SO_4 + 100 mL of 0.01 *M* $Pb(NO_3)_2$
(b) 50 mL of 10^{-4} *M* $AgNO_3$ + 100 mL of 10^{-4} *M* NaCl
K_{SP} of $PbSO_4 = 1.3 \times 10^{-8}$, K_{SP} of AgCl $= 1.7 \times 10^{-10}$

19. The solubility of $Li_3Na_3(AlF_6)_2$ is 0.075 g per 100 mL 25°C. Calculate K_{SP} of salt at 25°C.

20. A particular water sample is saturated with CaF_2 having total Ca^{2+} content as 115 ppm (or 115 g Ca^{2+} in 10^6 g H_2O). What is the F^- ion content of the water in ppm? Given K_{SP} for $CaF_2 = 5.3 \times 10^{-9}$. At. wt. of Ca^{2+} and F^- are 40 and 20 respectively.

21. What is the solubility of M_2Y in following solution if K_{SP} of M_2Y is 2×10^{-13}
(a) 0.1 *M* solution of Na_2Y
(b) 0.1 *M* solution of M_2X.

22. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g litre^{-1}. Calculate its solubility in g litre^{-1} in 0.02 *M* $Mg(NO_3)_2$.

23. Solid $AgNO_3$ is gradually added to a solution containing equimolar concentration of Cl^- and I^-. If K_{SP} of AgCl and AgI are 1.7×10^{-10} and 1.5×10^{-16} respectively, which one will precipitate first? Also find the relative concentration of I^- to Cl^- just before the precipitation of AgCl.

24. A 50.0 mL sample of 0.1 *M* $La(NO_3)_3$ is mixed with 50.0 mL of a NH_4^+/NH_3 buffer having 0.20 *M* in NH_4^+ and 0.40 *M* in NH_3. What percentage of the original La^{3+} has been precipitated as $La(OH)_3$ at equilibrium? Given K_{SP} of $La(OH)_3 = 1 \times 10^{-19}$; pK_b for $NH_3 = 4.74$.

25. A saturated solution of sparingly soluble salt MCl_2 has a vapour pressure of 31.78 mm of Hg at 30°C. Pure water exerts a pressure of 31.82 mm of Hg at 30°C. Calculate K_{SP} of MCl_2. Assume molarity equal to molality and MCl_2 is 100% dissociated in solution.

26. The concentration of Fe^{3+} ions in a sample of water is found to be 50×10^{-5} *M*. Calculate the pH at which 99% of Fe^{3+} will be precipitated. K_{SP} of $Fe(OH)_3 = 10^{-36}$.

27. A solution contains 0.1 *M* Pb^{2+} and 0.28 *M* HCl which is 94% ionised. H_2S is passed in solution to saturate the solution. How much of Pb^{2+} ions will remain in solution? K_{SP} of PbS is 4×10^{-28} and of H_2S is 1.1×10^{-23}.

28. Calculate solubility of $CaF_{2(s)}$ in a buffer solution with pH = 3.0. Given,

$K_{SP\,CaF_2} = 5.3 \times 10^{-9}$ and $K_{a\,HF} = 6.7 \times 10^{-4}$

29. The solubility of silver acetate in pure water at 25°C is 8.25 g/litre and 66 g/litre in an acid buffer of pH = 3. Calculate,

(a) K_{SP} of silver acetate assuming its negligible hydrolysis.

(b) K_a for acetic acid.

30. A mixture of salt containing $Cu_3(AsO_4)_2$ and $Pb_3(AsO_4)_2$ is shaken with water calculate the concentration of each ion present in the solution at equilibrium. K_{SP} of $Cu_3(AsO_4)_2$ and $Pb_3(AsO_4)_2$ are 8×10^{-36} and 4.096×10^{-36} respectively. Neglect the hydrolysis.

31. 0.01 *M* solution of $PuO_2(NO_3)_2$ was found to have a pH of 3.8. What is the hydrolysis constant for PuO_2^{2+} and dissociation constant for $PuO_2 \cdot OH^-$?

32. Calculate the $[H^+]$ for the 0.16 *M* solution of $N_2H_5^+$ in water. Given that K_a for $N_2H_5^+$ is 10^{-8}. Also $N_2H_5^+ + H_2O \rightleftharpoons N_2H_5OH + H^+$. Report the change in pH of solution if 0.16 mole of N_2H_5OH is added to 1 litre of this solution.

33. The hydrolysis constant for $Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$ is 1.7×10^{-10}, what is $[H^+]$ in 0.1 *M* $AlCl_3$ solution?

34. Calculate the pH of a solution containing 1.8 g $NaHSO_4$ per 100 mL. K_a for $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ is 1.26×10^{-2}.

35. K_1 and K_2 for oxalic acid are 5.6×10^{-2} and 5.4×10^{-5}. Calculate $[OH^-]$ in a 0.005 *M* solution of $Na_2C_2O_4$.

36. In 0.1 *M* solution of salt K*A*, the anion is 8% hydrolysed. What is dissociation constant of acid H*A*?

37. A certain acid-base indicator is red in acid solution and blue is basic solution. 75% of the indicator is present in the solution in its blue form at pH = 5. Calculate K_a for the indicator. Also calculate the pH at which the indicator shows:

(i) 90% red form,

(ii) 90% blue form.

Answers

1. 1.0×10^{-3}, 2.02×10^{-3} ;

2. 2.05 g L^{-1} ;

3. 2.4×10^{-3} ;

4. 0.087 mole ;

5. $1 \times 10^{-14} \text{ (m/L)}^2$, 1.8×10^{-16} m/L ;

6. 6.023×10^{7} ;

7. pH = 2.57 ;

8. 5.6×10^{-5} mole ;

9. 7.3 ;

10. 12 ;

11. 11.80 ;

12. $\alpha = 1.33\%$, pH = 2.8761 ;

13. 8.18 mL ;

14. 20.56% ;

15. 78.36 mL ;

16. 0.214 g ;

17. (a) 5.2×10^{-2} *M*, (b) 3.3×10^{-3} *M* ;

18. (a) yes, (b) yes ;

19. 7.96×10^{-19} ;

20. 27 ppm ;

21. (a) 7×10^{-7} *M*, (b) 5×10^{-12} *M* ;

22. 8.7×10^{-4} g/litre ;

23. AgI, $\dfrac{[\text{I}^-]}{[\text{Cl}^-]} = 8.8 \times 10^{-7}$;

24. 99.99% ;

25. 5×10^{-5} ;

26. 3.767 ;

27. 2.51×10^{-6} *M* ;

28. 1.434×10^{-3} mol litre^{-1} ;

29. (a) 2.44×10^{-3}, (b) 1.564×10^{-5} ;

30. $[\text{Cu}^{2+}] = 8.91 \times 10^{-8}$ *M*, $[\text{Pb}^{2+}] = 7.13 \times 10^{-8}$ *M*,
$[\text{AsO}_4^{3-}] = 1.07 \times 10^{-7}$ *M* ;

31. $K_H = 2.5 \times 10^{-6}$, $K_b = 4 \times 10^{-9}$;

32. 4×10^{-5}, $\Delta\text{pH} = 3.6021$;

33. 4.12×10^{-6} ;

34. 1.36 ;

35. 9.6×10^{-7} *M* ;

36. 1.43×10^{-11} ;

37. $K_a = 3 \times 10^{-5}$, (i) 3.56, (ii) 5.47.

12

Thermodynamics

Chapter at a Glance

I Law of Thermodynamics

For a finite change: $q = \Delta E - W = \Delta E - P\Delta V$

where q is heat given to system, ΔE is change in internal energy and $-W$ is work done by the system.

$$dq = dE - dW = dE - PdV$$

Work done in an Irreversible process

$$W = -P_{ext} \times \Delta V = -P_{ext} \times (V_2 - V_1) = -P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right]$$

P_{ext} is the pressure against which volume changes from V_1 to V_2

Work done in reversible process, *i.e.*, Maximum work

Isothermal Conditions

$$W_{rev} = -2.303\, nRT \log_{10}(V_2/V_1)$$
$$W_{rev} = -2.303\, nRT \log_{10}(P_1/P_2)$$

W_{rev} is maximum work done.

Adiabatic Conditions

$$W_{rev} = [nR/(\gamma - 1)]\,[T_2 - T_1]$$

γ is poisson's ratio.

Also for adiabatic process, following conditions hold good:

$$PV^{\gamma} = \text{constant}$$
$$T^{\gamma}P^{1-\gamma} = \text{constant}$$
$$V^{\gamma-1}T = \text{constant}$$

Heat Capacities

At constant pressure $C_p = (\delta H/\delta T)_p$

C_p is molar heat capacity at constant pressure.

At constant volume $C_v = (\delta E/\delta T)_v$

C_v is molar heat capacity at constant volume.

$$C_p \times c_p \times M \text{ and } C_v = c_v \times M$$

and $C_p - C_v = R$

$$c_p - c_v = R/M$$

$$C_p/C_v = c_p/c_v = \gamma \quad \text{(The poisson's ratio)}$$

c_p and c_v are specific heats at constant pressure and volume respectively.

Entropy

$$\Delta S = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$$

$$\Delta S = q_{\text{rev}}/T = 2.303\ nR \log_{10}(V_2/V_1) = 2.303\ nR \log_{10}(P_1/P_2)$$

$$\Delta S_{\text{fusion}} = \Delta H_{\text{fusion}}/T$$

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$$

ΔS is entropy change.

Free Energy

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ and } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{(In standard state)}$$

At equilibrium, $\Delta G = 0$

$$-\Delta G^\circ = RT \ln K_p \quad (\text{or } K_C)$$

$$= 2.303\ RT \log_{10} K_p \quad (\text{or } K_C)$$

ΔG is free energy change and ΔG° is standard free energy change. K_C and K_p are equilibrium constants in terms of concentration and pressure respectively.

The Basic Problems with Solution

➤ Problem 1. During 200 J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

➤ Problem 2. A system does 40 J work on surrounding as well as gives out 20 J energy. Calculate the change in internal energy.

➤ Problem 3. A system does 100 J work on surroundings by absorbing 150 J of heat. Calculate the change in internal energy.

➤ Problem 4. A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre to 1.0 litre. Calculate the change in internal energy.

➤ Problem 5. Calculate the work done during the process when one mole of gas is allowed to expand freely into vacuum.

➤ Problem 6. Two litre of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

➤ Problem 7. The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.

➤ Problem 8. In a fuel cell (a device for producing electricity directly from chemical reaction), methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is,

$$CH_3OH_{(l)} + 3/2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

Calculate the standard Gibbs energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is –726 kJ mol^{-1}, calculate the efficiency of conversion of Gibbs energy into useful work.

($\Delta_f G°$ for CO_2, H_2O, CH_3OH, O_2 are –394.36, –237.13, –166.27 and zero respectively.)

➤ Problem 9. For the water gas reaction :

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)},$$

the standard Gibbs energy of reaction (at 1000 K) is –8.1 kJ mol^{-1}. Calculate its equilibrium constant.

➤ Problem 10. The standard Gibbs energies for the reactions at 1773 K are given below :

$$C + O_2 \longrightarrow CO_2 ; \quad \Delta_r G° = -380 \text{ kJ mol}^{-1}$$

$$2C + O_2 \rightleftharpoons 2CO ; \quad \Delta_r G° = -500 \text{ kJ mol}^{-1}$$

Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3\ ;\ \Delta_r G^- = -22500 \text{ kJ mol}^{-1}$$

$$2Pb + O_2 \longrightarrow 2PbO\ ;\ \Delta_r G^- = -120 \text{ kJ mol}^{-1}$$

➤ **Problem 11.** Calculate the free energy change for the reaction given below :

$$Zn_{(s)} + Cu^{2+}_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

Given that standard free energy ($G°$) for $Zn^{2+}_{(aq.)}$, $Cu^{2+}_{(aq.)}$, are -147.2 kJ mol^{-1} and 65.0 kJ mol^{-1}.

➤ **Problem 12.** Find out whether it is possible to reduce MgO using carbon at 298 K. If not, at what temperature it becomes spontaneous. For reaction, $MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$, $\Delta H° = +491.18$ kJ mol^{-1} and $\Delta S^0 = 197.67$ JK^{-1} mol^{-1}.

➤ **Problem 13.** Calculate the change of entropy, $\Delta_r S°$ at 298K for the reaction in which urea is formed from NH_3 and CO_2.

$2NH_3(g) + CO_2(g) \longrightarrow NH_2CONH_2(aq) + H_2O(l)$. 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 JK^{-1} mol^{-1} respectively.

➤ **Problem 14.** Calculate free energy change for the conversion of oxygen to ozone at 298 K, if K_p for the change $\frac{3}{2}O_2(g) \longrightarrow O_3(g)$ at 298K is $2.47 \times 10^{-29}\ (atm)^{-½}$.

➤ **Problem 15.** Calculate the equilibrium constant K_p for the reaction given below if $\Delta G° = -10.632$ kJ at 300 K.

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

➤ **Problem 16.** The enthalpy of vaporisation of liquid diethyl ether $-(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS for conversion of : (a) liquid to vapour, and (b) vapour to liquid at 35°C.

➤ **Problem 17.** Ethanol boils at 78.4°C and the enthalpy of vaporisation of ethanol is 42.4 kJ mol^{-1}. Calculate the entropy of vaporisation of ethanol.

➤ **Problem 18.** Calculate the entropy change for the conversion of following :

(a) 1 g ice to water at 273 K, ΔH_f for ice = 6.025 kJ mol^{-1}.

(b) 36 g water to vapour at 373 K; ΔH_v for H_2O = 40.63 kJ mol^{-1}.

➤ **Problem 19.** Calculate the value of ΔG at 700 K for the reaction $nX \longrightarrow mB$. Given that value of $\Delta H = -113$ kJ mol^{-1} and $\Delta S = -145$ JK mol^{-1}.

➤ **Problem 20.** Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25°C. Lattice energy of NaCl = 777.8 kJ mol^{-1} ; ΔS for dissolution = 0.043 kJ mol^{-1} and hydration energy of NaCl = -774.1 kJ mol^{-1}.

➤ **Problem 21.** Calculate the standard free energy change for the reaction,

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)} \text{ at } 298 \text{ K.}$$

Given $\Delta H^\circ = -92.4$ kJ and $\Delta S^\circ = -198.3$ JK^{-1}. Also, comment on the result.

➤ **Problem 22.** For the reaction, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$; $\Delta H = -95.4$ kJ and $\Delta S = -198.3$ JK^{-1}. Calculate the maximum temperature at which the reaction will proceed in forward direction.

➤ **Problem 23.** The equilibrium constant for the reaction given below is 2.0×10^{-7} at 300 K. Calculate the standard free energy change for the reaction;

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Also, calculate the standard entropy change if $\Delta H^\circ = 28.40$ kJ mol^{-1}.

Answers

1. + 60 J ;
2. − 60 J ;
3. + 50 J ;
4. +124.025 J ;
5. 0 ;
6. − 810.10 Joule ;
7. 0.20972 kJ mol^{-1} ;
8. − 702.35 kJ mol^{-1}, 96.7% ;
9. 2.648 ;
10. See solution ;
11. −212.2 kJ ;
12. T > 2484.8 K ;
13. −354.4 JK^{-1} mol^{-1} ;
14. 163.229 kJ ;
15. 70.95 ;
16. (a) + 84.41 JK^{-1} mol^{-1}, (b) − 84.41 JK^{-1} mol^{-1} ;
17. 120.66 JK^{-1} mol^{-1}, 22.1 JK^{-1} mol^{-1} ;
18. (a) 1.227 JK^{-1}, (b) 217.85 JK^{-1} ;
19. −11.50 kJ mol^{-1} ,
20. −9.114 kJ mol^{-1} ;
21. −33.306 kJ ;
22. $T < 481.8$
23. + 38.48 kJ mol^{-1}, −33.6 JK^{-1}

Solutions

Solution 1. $w = 200$ J; $q = -140$ J;

$\because$ $q = \Delta E + (-w)$; where $-w$ is work done by the system.

$$\Delta E = q + w$$
$$\Delta E = -140 + 200 = \mathbf{+60\ J}$$

Solution 2. $w = -40$ J; $q = -20$ J

$$\Delta E = q + w$$
$$\Delta E = -20 + (-40) = \mathbf{-60\ J}$$

Solution 3. $w = -100$ J; $q = 150$ J; $\Delta E = q + w$

$$\therefore \quad \Delta E = 150 - 100 = \mathbf{+50\ J}$$

Solution 4.

$$w = -P\Delta V = -1.5 \times (1.0 - 0.5) = -0.75 \text{ litre atm}$$
$$= -0.75 \times 101.3 \text{ J} = -75.975 \text{ J}$$

$\because$ 1 litre atm $= 101.3$ J

Now, $\Delta E = 200 - 75.975 = \mathbf{+124.025\ J}$

Solution 5. Gas expands in vacuum *i.e.*, $P_{ext} = 0$ and thus, irreversible process

Therefore, $W = -P_{ext}(V_2 - V_1) = 0$

Solution 6. Since the external pressure is greatly different from the pressure of N_2 and thus, process is irreversible.

$$W = -P_{ext}(V_2 - V_1)$$
$$W = -1 \times (V_2 - V_1)$$

Given, $V_1 = 2$ litre $\quad V_2 = ? \quad T = 273$ K
$P_1 = 5$ atm $\quad P_2 = 1$ atm

$$\therefore \quad P_1V_1 = P_2V_2$$
$$\therefore \quad V_2 = \frac{2 \times 5}{1} = 10 \text{ litre}$$
$$\therefore \quad W = -1 \times (10 - 2) = -8 \text{ litre atm}$$
$$= -\frac{8 \times 1.987}{0.0821} \text{ calorie}$$
$$= -\frac{8 \times 1.987 \times 4.184}{0.0821} \text{ J}$$
$$= \mathbf{-810.10\ joule}$$

Solution 7.

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

Given $\Delta E = +0.21 \text{ kJ mol}^{-1} = 0.21 \times 10^3 \text{ J mol}^{-1}$
$P = 1 \text{ bar} = 1.0 \times 10^5 \text{ Pa}$

$$\Delta V = V_{(\text{aragonite})} - V_{(\text{calcite})} \qquad (\text{mol. wt. of } CaCO_3 = 100)$$

$$= \left(\frac{100}{2.93} - \frac{100}{2.71}\right) \text{cm}^3\ \text{mol}^{-1} \text{ of } CaCO_3$$

$$= -2.77\ \text{cm}^3 = -2.77 \times 10^{-6}\ \text{m}^3$$

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

$$\Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6}$$

$$\mathbf{= 209.72\ J\ mol^{-1}}$$

$$\mathbf{= 0.20972\ kJ\ mol^{-1}}$$

Solution 8. $CH_3OH_{(l)} + 3/2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

$$\Delta_r G^\circ = \Delta_f G^\circ_{CO_2} + 2 \times \Delta_f G^\circ_{H_2O} - \Delta_f G^\circ_{CH_3OH} - 3/2 \times \Delta_f G^\circ_{O_2}$$

$$= -394.36 + 2 \times (-237.13) - (-166.27) - 3/2 \times 0$$

$$\mathbf{\Delta_r G^\circ = -702.35\ kJ\ mol^{-1}}$$

The efficiency of conversion of Gibbs free energy into useful work

$$= \frac{\Delta_r G^\circ}{\Delta H^\circ} \times 100$$

or $\quad$ efficiency $= \dfrac{-702.35}{-726} \times 100 = \mathbf{96.7\%}$

i.e., 96.7% of Gibbs free energy can be converted into useful work.

Solution 9.

$$-\Delta G^\circ = 2.303\ RT \log K_C$$

$$+8.1 \times 10^3 = 2.303 \times 8.314 \times 1000 \log K_C$$

$$\therefore \quad \mathbf{K_C = 2.648\ mol\ litre^{-1}}$$

Solution 10.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3\ ; \quad \Delta_r G^\circ = -22500\ \text{kJ mol}^{-1} \qquad ...(1)$$

$$3C + 3O_2 \longrightarrow 3CO_2\ ; \quad \Delta_r G^\circ = -380 \times 3\ \text{kJ mol}^{-1} \qquad ...(2)$$

By eq. (2)–(1)

$$3C + 2Al_2O_3 \longrightarrow 3CO_2 + 4Al;$$

$$\Delta_r G^\circ = -1140 - (-22500)$$

$$= +21360\ \text{kJ mol}^{-1}$$

Since $\Delta_r G^\circ$ is positive, the reaction will not take place or Al_2O_3 will not be reduced by carbon.

$$2Pb + O_2 \longrightarrow 2PbO\ ; \quad \Delta_r G^\circ = -120\ \text{kJ mol}^{-1} \qquad ...(3)$$

$$C + O_2 \longrightarrow CO_2\ ; \quad \Delta_r G^\circ = -380\ \text{kJ mol}^{-1} \qquad ...(4)$$

By eq. (4)–(3);

$$C + 2PbO \longrightarrow CO_2 + 2Pb\ ;$$

$$\Delta_r G^\circ = -380 - (-120) = -260\ \text{kJ}$$

Thus, reaction will be spontaneous and PbO will be reduced by carbon.

Solution 11.

$$\Delta G^\circ = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

$$= [0 + (-147.2) - (0 + 65.0)] = \mathbf{-212.2\ kJ}$$

Solution 12. $MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= 491.18 - 298 \times [197.67 \times 10^{-3}]$$
$$= 432.27 \text{ kJ}$$

Thus reaction is non-spontaneous at 298. For spontaneouc nature $\Delta G^\circ = -\text{ve}$ *i.e.*, $T\Delta S^\circ > \Delta H^\circ$

or $T \times [197.67 \times 10^{-3}] > 491.18$

or $$T > \frac{491.18}{197.67 \times 10^{-3}} > \mathbf{2484.8\ K}$$

Solution 13. For the given change

$$\Delta_r S^\circ = \Sigma n_P S^\circ_P - \Sigma n_R S^\circ_R$$
$$= S^\circ_{NH_2CONH_2} + S^\circ_{H_2O} - \left[2 \times S^\circ_{NH_3} + S^\circ_{CO_2}\right]$$
$$= 174.0 + 69.9 - [2 \times 192.3 + 213.7]$$
$$= \mathbf{-354.4\ JK^{-1}\ mol^{-1}}$$

Solution 14.

$$\Delta G^\circ = -2.303\ RT \log_{10} K_P$$
$$= -2.303 \times 8.314 \times 298 \times \log 2.47 \times 10^{-29}$$
$$= 163229 \text{ J}$$
$$= \mathbf{163.229\ kJ}$$

Solution 15.

$$\Delta G^\circ = -2.303\ RT \log K_p$$

or $$-10.632 \times 10^3 = -2.303 \times 8.314 \times 300 \log K_p$$

$\therefore$ $$K_p = \mathbf{70.95}$$

Solution 16. (a) $$\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T} = \frac{26 \times 10^3}{308}$$
$$= \mathbf{+84.41\ JK^{-1}\ mol^{-1}}$$

(b) $$\Delta S_{cond.} = \frac{\Delta H_{cond.}}{T} = -\frac{26 \times 10^3}{308} \qquad (\because H_{cond} = -26 \text{ kJ})$$
$$= \mathbf{-84.41\ JK^{-1}\ mol^{-1}}$$

Solution 17. $$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{42.4 \times 10^3}{351.4} = \mathbf{120.66\ JK^{-1}\ mol^{-1}}$$

Solution 18. (a) $$\Delta S_{fusion} = \frac{\Delta H_f}{T} = \frac{6.025 \times 10^3}{273} = \mathbf{22.1\ JK^{-1}\ mol^{-1}}$$

Now 18 g ice melts showing a change in entropy = 22.1

$\therefore$ 1 g ice melts showing a change in entropy $= \frac{22.1}{18} \times 1$

$= \mathbf{1.227\ JK^{-1}}$.

(b) $$\Delta S_v = \frac{\Delta H_v}{T} = \frac{40.63 \times 10^3}{373} = \mathbf{108.9\ JK^{-1}\ mol^{-1}}$$

18 g H_2O vaporises to show a change in entropy = 108.9

∴ 36 g H_2O vaporises to show a change in entropy $= \frac{108.9 \times 36}{18}$

$= \mathbf{217.85\ JK^{-1}}$

Solution 19. $\Delta G = \Delta H - T\Delta S = -113 \times 10^3 - 700 \times (-145)\ \text{J mol}^{-1}$

$\Delta G = -113000 + 101500 = -11500\ \text{J mol}^{-1}$

$\Delta G = \mathbf{-11.50\ kJ\ mol^{-1}}$

Solution 20. $\Delta H_{\text{disolution}}$ = Lattice energy + Hydration energy

$= 777.8 - 774.1 = 3.7\ \text{kJ mol}^{-1}$

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

$= 3.7 - 298 \times 0.043 = 3.7 - 12.814$

$\Delta G = \mathbf{-9.114\ kJ\ mol^{-1}}$

Solution 21. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -92.4 - 298 \times (-198.3) \times 10^{-3}$ ($\because \Delta S^\circ = -198.3 \times 10^{-3}\ \text{kJK}^{-1}$)

$= \mathbf{-33.306\ kJ}$

Since ΔG° is negative, it means that a mixture of H_2 and N_2 at 25°C, each present at a pressure of 1 atm would react spontaneously to form ammonia.

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

For a reaction to be spontaneous, $\Delta G = -ve$ and therefore,

$$\Delta H - T\Delta S = -ve \text{ or } \Delta H > T\Delta S \text{ or } \frac{\Delta H}{\Delta S} > T \text{ or } \frac{-95.4 \times 10^{+3}}{-198.3} > T$$

or $\mathbf{481.0 > \mathit{T}}$

Thus, if temperature of system is lesser than 481 K, the reaction would be spontaneous. Also at 481 K, the reaction will be in equilibrium. An increase in temperature above 481.0 will develop non-spontaneity for the reaction.

Solution 23. $\Delta G^\circ = -2.303 \times 8.314 \times 300 \log [2.0 \times 10^{-7}]$

$= +38479.8\ \text{J mol}^{-1} = \mathbf{+\ 38.48\ kJ\ mol^{-1}}$

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\therefore \quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{28.40 - 38.48}{300}$$

$= -0.0336\ \text{kJ} = \mathbf{-33.6\ JK^{-1}}$

Selected Problems with Solutions

➤ **Problem 1.** A gas occupies 2 litre at STP. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm. Calculate change in its internal energy.

➤ **Problem 2.** Calculate the work done during the process when one mole of gas is allowed to expand freely into vacuum.

➤ **Problem 3.** 2.8 g of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate ΔE, q and W for gas.

➤ **Problem 4.** At 27°C, one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate ΔE and q.

➤ **Problem 5.** One mole of an ideal gas is heated at constant pressure from 0°C to 100°C.

(a) Calculate work done.

(b) If the gas were expanded isothermally and reversibly at 0°C from 1 atm to some other pressure P_f, what must be the final pressure if the maximum work is equal to the work involved in (a)?

➤ **Problem 6.** 1 mole of an ideal gas at 25°C is subjected to expand reversibly ten times of its initial volume. Calculate the change in entropy of expansions.

➤ **Problem 7.** An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T, while the other portion is a perfect vacuum. If a hole is opened between the two portions, calculate the:

(a) change in internal energy of the gas,

(b) change in temperature of the gas.

➤ **Problem 8.** The temperature of a bomb calorimeter was found to rise by 1.617 K, when a current of 3.20 A was passed for 27.0 second from a 12.0 V source. Calculate the calorimeters constant.

➤ **Problem 9.** 1 litre flask containing $NH_{3(g)}$ at 2.0 atm at 200 K is connected by a narrow tube of negligible volume to another 800 mL flask containing $HCl_{(g)}$ at 8.0 atm at 200 K. The two gases react according to equation

$$NH_{3_{(g)}} + HCl_{(g)} \longrightarrow NH_4Cl_{(S)}\,; \quad \Delta H = -43\ \text{kJ/mol}$$

If heat capacity of $HCl_{(g)}$ C_v is 20 J K^{-1} mol^{-1}, determine the heat produced, final temperature and final pressure inside the flask. The heat capacity of flask and volume of solid NH_4Cl in flask is negligible.

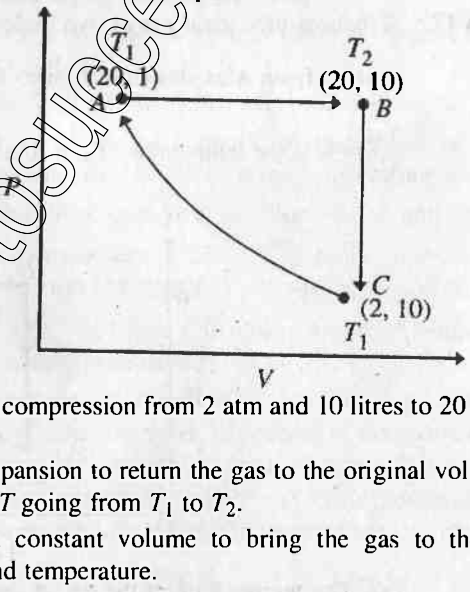
➤ **Problem 10.** The specific heat of a liquid was measured by placing 100 g of the liquid in a calorimeter. The liquid was heated by an electric immersion coil. The heat capacity of the calorimeter together with the coil was previously determined to be 31.4 J/K. With the 100 g sample placed in the calorimeter, a current of 0.5 ampere was passed through the immersion coil for exactly 3 minutes. The voltage across the terminal of coil was measured to be 1.50 V. The temperature of the sample rose by 0.8°C. Find the specific capacity of liquid.

➤ **Problem 11.** A sample of 3.0 mole of perfect gas at 200 K and 2.0 atm is compressed reversibly and adiabatically until the temperature reaches 250 K. Given that molar heat capacity at 27.5 J K^{-1} mol^{-1} at constant volume, calculate q, W, ΔE, ΔH and the final pressure and volume.

➤ **Problem 12.** One mole of a monoatomic ideal gas is heated at constant pressure from 25°C to 300°C. Calculate the ΔH , ΔE, workdone and entropy change during the process. Given $C_V = \frac{3}{2}R$.

➤ **Problem 13.** Calculate the final temperature of a sample of CO_2 gas (16 g) that is expanded reversibly and adiabatically from 0.5 litre to 2.0 litre at 298 K. Also calculate the work done by the gas. If $C_{v,m.}$ for CO_2 is 42 J K^{-1} mol^{-1}. Calculate the enthalpy change in the process. Take C_p/c_v for CO_2 as 1.33.

➤ **Problem 14.** One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps:



(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2.

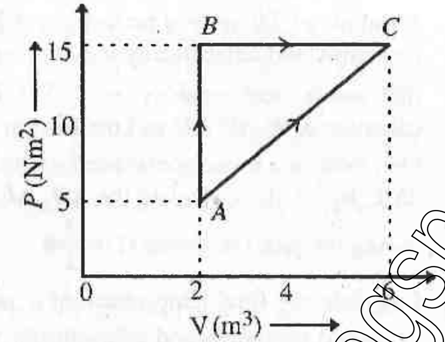
(b) Calculate ΔE, q and W in calories, for each step and for the cycle.

➤ **Problem 15.** 1 g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere, the volume increases from 1 mL to 1671 mL. The heat of vaporisation at this pressure is 540 cal/g. Find the:

(a) Work done (in J) during phase change.

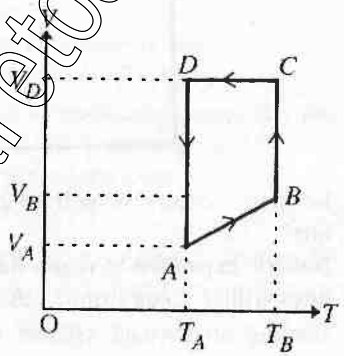
(b) Increase in internal energy of water.

➤ **Problem 16.** The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the:



(a) Path along which work done is least.
(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.
(c) Amount of heat supplied to the gas to go from A to B, if internal energy of gas at state B is 10 J.

➤ **Problem 17.** A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C, calculate:



(a) The temperature of the gas at point B.
(b) Heat absorbed or released by the gas in each process.
(c) The total work done by the gas during complete cycle.

➤ **Problem 18.** Two moles of helium gas ($r = 5/3$) are initially at a temperature of 27°C and occupy a volume of 20 litre. The gas is first expanded at constant pressure until the volume is doubled. It then undergoes adiabatic change until the temperature returns to its initial value.
(a) Sketch the process on P—V diagram.
(b) What are final pressure and final volume of gas.
(c) What is the work done by the gas.

➤ **Problem 19.** An ideal gas has a specific heat at constant pressure $C_p = \frac{5}{2}R$. The gas is kept in a closed vessel of volume 0.0083 m^3, at a temperature of 300 K and pressure 1.6×10^6 N/m^2. An amount of 2.49×10^4 J of energy is supplied to the gas. Calculate the final temperature and pressure of the gas.

➤ **Problem 20.** A strip of magnesium of mass 15 g is dropped into an open beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of reaction. The atmospheric pressure is 1.0 atm and temperature is 25°C. Also calculate the work done if the reaction is carried out in closed beaker.

➤ **Problem 21.** Calculate the work done when 50 g of iron reacts with hydrochloric acid in:

(i) a closed vessel of fixed volume,

(ii) an open beaker at 25°C.

➤ **Problem 22.** The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively.

➤ **Problem 23.** Calculate the work done when a system raises a column of water of radius 5.0 mm through 10 cm.

➤ **Problem 24.** A bulb of 100 watt is switched on in a room of dimensions $5 \times 4 \times 3$ m^3. What will be the increase in temperature of room after 15 minute, if specific heat of air at room temperature and 1 atm is 0.71 J g^{-1} K^{-1} and heat capacity of four walls and the roof is 50×10^3 J K^{-1} (density of air = 1.22×10^{-6} kg mL^{-1})?

➤ **Problem 25.** 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. Calculate upto which temperature, the reaction would not be spontaneous.

➤ **Problem 26.** Consider a class room of dimensions $5 \times 10 \times 3$ m^3 at temperature 20°C and pressure 1 atm. There are 50 peoples in the room, each losing energy at the average of 150 watt. Assuming that the walls, ceilling, floor and furniture perfectly insulated and none of them obsorbing heat, how much time will be needed for rising the temperature of air in the room to body temperature, *i.e.*, 37°C. For air $C_p = \frac{7}{2}R$. Loss of air to the outside as the temperature rises may be neglected.

➤ **Problem 27.** An athelete in a gymansium room lifts a 50 kg mass through a vertical distance of 2.0 m; $g = 9.8$ ms^{-2}. The mass is allowed to fall through 2.0 m distance while coupled to an electrical generator. The electrical generator produces an equal amount of electrical work. This electrical work is used to produce aluminium by Hall's process involving the change,

$$Al_2O_3\,(\text{molten}) + 3C(s) \longrightarrow 2Al(l) + 3CO(g)$$

The reaction require standard free energy change equal to 593 kJ. How many times must the athelete life the 50 kg mass and to drop and couple with generator to produce sufficient Gibbs free energy to produce 27 g Al?

➤ Problem 28. An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 metre. Its engine run with pure normal octane (C_8H_{18}) has a 30% efficiency. Calculate the fuel cost of the flight if octane sells at Rs. 3/- per litre. Given density of octane = 0.705 g mL^{-1}, heat of combustion of octane = $1300 \text{ kcal mol}^{-1}$. ($g = 981$)

➤ Problem 29. Titanium metal is extensively used in aerospace industry because the metal imparts strength to structures but does not unduly add to their masses. The metal is produced by the reduction of $TiCl_4(l)$ which in turn is produced from mineral rutile [$TiO_2(s)$]. Can the following reaction for production of $TiCl_4(l)$ be carried out at 25°C?

$$TiO_2(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + O_2(g)$$

Given that H_f° for $TiO_2(s)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are -944.7, -804.2, 0.0, 0.0 kJ mol^{-1}. Also S° for $TiO_2(g)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are 50.3, 252.3, 233.0, 205.1 $\text{J mol}^{-1} \text{K}^{-1}$ respectively.

➤ Problem 30. A lead bullet weighing 18.0 g and travelling at 500 m/s is embedded in a wooden block of 1.00 kg. If both the bullet and the block were initially at 25.0°C, what is the final temperature of block containing bullet? Assume no temperature loss to the surroundings. (Heat capacity of wood = 0.5 kcal/kg-K; of lead = 0.030 kcal/kg-K)

➤ Problem 31. The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$\Delta H^\circ_{300\text{ K}} = -41.16 \text{ kJ mol}^{-1}; \qquad \Delta S^\circ_{300\text{ K}} = -4.24 \times 10^{-2} \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{1200\text{ K}} = -32.93 \text{ kJ mol}^{-1}; \qquad \Delta S^\circ_{1200\text{ K}} = -2.96 \times 10^{-2} \text{ kJ mol}^{-1}$$

Calculate K_p at each temperature and predict the direction of reaction at 300 K and 1200 K, when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1$ atm at initial state.

Answers

1. 249.37 joule ;
2. 0 ;
3. $\Delta E = 0$, $q = 236.95$ J, $W = -236.95$ J ;
4. $\Delta E = 0$, $q = -965.84$ cal ;
5. (a) -198.7 cal, (b) 0.694 atm ;
6. 19.15 JK^{-1} mol^{-1} ;
7. No change in T and E ;
8. 641.18 JK^{-1} ;
9. 14.39 atm
10. 1.37 J/g-K ;
11. $q = 0$, $W = +4.157$ kJ, $\Delta E = +4.157$ kJ,
$\Delta H = 5.372$ kJ, 5.2 atm, 11.8 litre ;
12. 3.269 cal K^{-1} mol^{-1}
13. 188.6 K, 1.002 kJ, 2.002 kJ ;
14. (i) $T_1 = 243.60$ K, $T_2 = 2436.0$ K,
(ii) in path CA $W = +1122.02$ cal, $\Delta E = 0$, $q = W$,
in path AB $W = -4384.9$ cal, $\Delta E = +6577.2$ cal, $q = 10962.1$ cal
in path BC $W = 0$, $q = \Delta E = -6577.2$;
15. (a) -168.67 J, (b) 2088.53 J ;
16. (a) AC is least, (b) 170 J, (c) 10 J ;
17. (a) 600 K, (b) (i) +3000 cal, (ii) $+1.663 \times 10^3$ cal, (iii) -1800 cal,
(iv) 1200 cal, (c) 1200 cal ;
18. (a) See solution (b) 2.46 atm, 113.13 litre (c) 3000 cal ;
19. $T = 675$ K, $P = 3.58 \times 10^6$ N/m^2 ;
20. -1.548 kJ, 0
21. (i) 0, (ii) -2212.22 J ;
22. 0.20972 kJ mol^{-1} ;
23. -3.85×10^{-3} J ;
24. 0.88 K ;
25. $T < 428.57$ K ;
26. 411.3 second ;
27. 303 ;
28. 1472.4 Rs. ;
29. 158.06 kJ ;
30. 26.08°C ;
31. at 300 K $\Delta G° = -28.44$ kJ , $K_p = 8.94 \times 10^4$,
at 1200 K $\Delta G° = +2.59$ kJ, $K_p = 0.77$.

Problems for Self Assessment

1. A sample consisting of 1.0 mole $CaCO_{3(s)}$ was heated to 800°C when it decomposed. The heating was carried out in a container fitted with a piston which was initially resting on solid. Calculate the work done during complete decomposition of $CaCO_3$ at 1 atm. What work would be done if instead of having a piston, the container were open to the atmosphere. Also calculate the work done if piston is removed and reaction is made in closed container.
2. When 229 J of energy is supplied as heat at constant pressure to 3.0 mole of argon gas, the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.
3. A sample of liquid of mass 30.5 g is cooled from 290 K to 275 K at constant pressure by the extraction of 1.2 kJ of energy as heat. Calculate q and ΔH and estimate the heat capacity of the sample. Also if liquid has mol. wt. of 90, calculate its molar heat capacity.
4. A sample of 4.0 mole O_2 is originally confined in 20 L at 270 K is subjected to reversible adiabatic expansion against a constant pressure until the volume has been increased by a factor 3.0. Calculate q, W, ΔT, ΔE, ΔH and final pressure. Assume $C_p/C_v = 1.40$ for O_2.
5. Calculate the final volume of one mole of an ideal gas initially at 0°C and 1 atm pressure, if it absorbs 1000 cal of heat during a reversible isothermal expansion.
6. 10 moles of an ideal gas expands isothermally and reversibly from a pressure of 10 atm to 2 atm at 300 K. What is the largest mass which can be lifted through a height of 1 meter in this expansion.
7. Calculate ΔE and ΔH when 100 dm^3 of helium at STP are heated to 373 K in a closed container. Assume that gas behaves ideally and it C_{vm} is 12.55 J mol^{-1} K^{-1}.
8. One mole of an ideal monoatomic gas is carried through the cycle of the given fig., consisting of steps A, B and C and involving states 1, 2 and 3. Fill in blank space in the tables given below. Assume reversible steps.

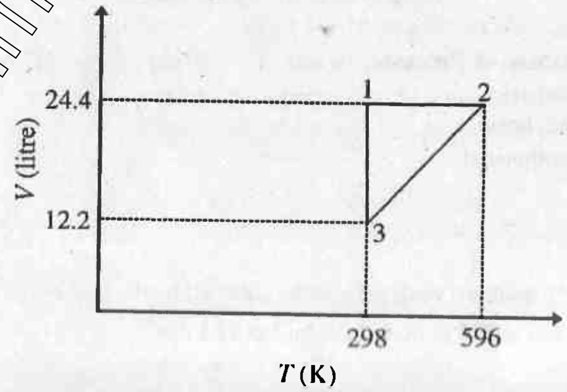


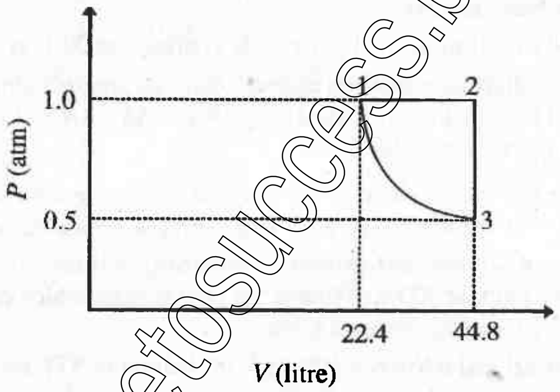
Table-1

State	*P* atm	*V* litre	*T* K
1	——	22.4	273
2	——	22.4	546
3	——	44.8	546

Table-2

Step	Name of Process	*q* cal	*W* cal	Δ*E* cal
A	——————	——	——	——
B	——————	——	——	——
C	——————	——	——	——
	Cycle			

9. One mole of a monoatomic ideal gas is put through the reversible cycle shown in the figure. Fill in the blank spaces in the table given below.

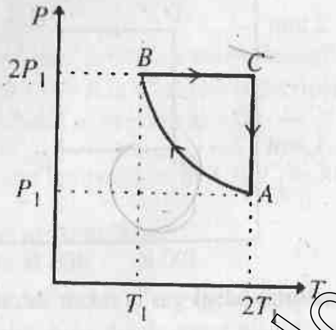


Stage	*P* atm	*V* litres	*T* K
1	1	——	298
2	1	——	596
3	2	——	596

Step	Nature of Process	*q* cal	*W* cal	Δ*E* cal	Δ*H* cal
1 → 2	Isobaric	——	——	——	——
2 → 3	Isochoric	——	——	——	——
3 → 1	Isothermal	——	——	——	——
Total cycle		——	——	——	——

10. What is the maximum work that can be obtained by the isothermal expansion of 1 mole of an ideal gas at 273 K from 2.24 dm^3 to 22.4 dm^3?

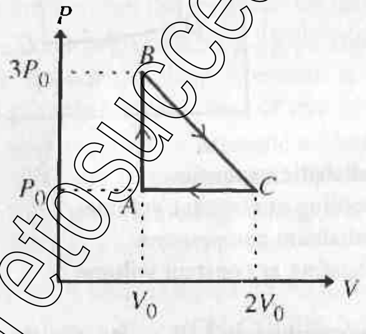
11. Two moles of an ideal monoatomic gas is taken through a cycle $ABCA$ as shown in P, T diagram. During the process AB, pressure and temperatures of the gas very such that PT = constant. If T_1 = 300 K, calculate the:



(a) Work done on the gas in the process AB.

(b) Heat absorbed or released by the gas in each of the process.

12. One mole of an ideal monoatomic gas is taken round cyclic process $ABCA$ as shown in figure. Calculate:



(a) The work done by the gas.

(b) The heat rejected by the gas in the path CA the heat absorbed by the gas in the path AB.

(c) The net heat absorbed by the gas in the path BC.

(d) The maximum temperature attained by the gas during the cycle.

13. Three moles of an ideal gas ($C_p = 7/2\,R$) at pressure P_A and temperature T_A is isothermally expanded to twice its initial volume. It is then compressed at constant pressure to its original volume. Finally the gas is compressed at constant volume to its original pressure P_A.

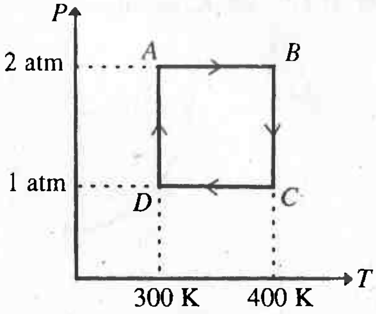
(a) Sketch P—V and P—T curves for complete process.

(b) Calculate the net work done by the gas and net heat supplied to gas during the complete process.

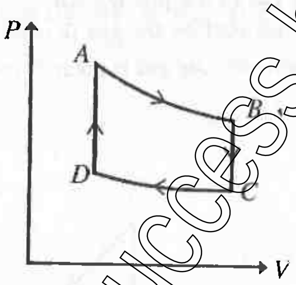
14. Two moles of helium gas undergo a cyclic process as shown in figure. Assuming the gas to be ideal, calculate:

(a) the net change in heat energy,

(b) the net work done,
(c) the net change in internal energy.



15. One mole of a monoatomic ideal gas is taken through the cycle shown in figure:



$A \longrightarrow B$: adiabatic expansion
$B \longrightarrow C$: cooling at constant volume
$C \longrightarrow D$: adiabatic compression
$D \longrightarrow A$: heating at constant volume

The pressure and temperature at $A, B \ldots$ etc. are $P_A, T_A, P_B, T_B \ldots$ respectively.

Given $T_A = 1000$ K, $P_B = \frac{2}{3} P_A$ and $P_C = \frac{1}{3} P_A$ calculate:

(a) the work done by the gas in the process $A \longrightarrow B$,
(b) the heat lost by the gas in the process $B \longrightarrow C$,
(c) the temperature T_D.

[Given, $\left(\frac{2}{3}\right)^{2/5} = 0.85$]

16. An ideal gas is taken through a cyclic thermodynamic process through four steps. The amount of heat involved in these steps are: $Q_1 = 5960$ J, $Q_2 = -5585$ J, $Q_3 = -2980$ J and $Q_4 = 3645$ J respectively. The corresponding Quantities of work involved are $W_1 = 2200$ J, $W_2 = -825$ J and $W_3 = -1100$ J and W_4 respectively. Calculate:

(a) the value of W_4,
(b) the efficiency of cycle.

17. At 27°C two moles of an ideal monoatomic gas occupy a volume V. The gas expands adiabatically to a volume $2V$. Calculate:
    (a) the final temperature of gas,
    (b) the change in internal energy,
    (c) the work done by the gas.

18. One mole of a diatomic ideal gas ($\gamma = 1.4$) is taken through a cyclic process starting from point A. The process $A \longrightarrow B$ is adiabatic compression, $B \longrightarrow C$ is isobaric expansion, $C \longrightarrow D$ is adiabatic expansion and $D \longrightarrow A$ is isochoric. The volume ratio $\frac{V_A}{V_B} = 16$ and $\frac{V_C}{V_B} = 2$ and temperature at A is $T_A = 300$ K. Calculate the:
    (a) Temperature of the gas at point B and D.
    (b) Efficiency of the cycle.

19. A track star expends 5.0×10^5 J min^{-1} energy during its running. If this energy have been used to heat water, how much water would have raised its temperature from 25°C to 100°C. Sp. heat of water = 4.18 J/g.

20. 1.0 mole of Fe_2O_3 and 2.0 mole of Al are mixed at temperature 25°C and reaction is completed to give:

$$Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(l); \quad \Delta H = -850 \text{ kJ}$$

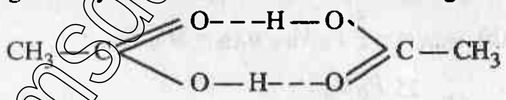
The liberated heat is retained within the products, whose combined specific heat over a broad temperature range is about 0.8 J g^{-1}K^{-1}. The melting point of iron is 1530°C. Show that the quantity of heat liberated is sufficient to raise the temperature of the product to the melting point of iron in order to get it welded.

21. Calculate the amount of work required for adiabatic reversible expansion of 1 mole of a polyatomic gas at –50°C and 10 atm to 1 atm; ($\gamma = 1.33$).

22. Predict whether at 27°C, the following change is spontaneous or not; $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$. Given,

$$\Delta H = +9080 \text{ J mol} \quad \text{and} \quad \Delta S = +35.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

23. Acetic acid CH_3COOH can form a dimer $(CH_3COOH)_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mol of dimer.



If at 25°C, the equilibrium constant for dimerisation is 1.3×10^3, calculate $\Delta S°$ for the reaction,

$$CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

24. Calculate the standard entropy change for the reaction;

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

at 25°C. Given $S°$ for H_2, Cl_2 and HCl are 0.13, 0.22 and 0.19 kJ K^{-1} mol^{-1} respectively.

25. Calculate the change in entropy when 1 mole of N_2 gas expands isothermally and reversibly from an initial volume of 1 litre to a final volume of 10 litre at 27°C.

Answers

1. –8.9 kJ, –8.9 kJ, 0 ;

2. $C_p = 29.93\ JK^{-1}\ mol^{-1}$, $C_v = 21.93\ JK^{-1}\ mol^{-1}$;

3. –1.2 kJ, –1.2 kJ, +80 JK^{-1}, 236.0 $JK^{-1}\ mol^{-1}$;

4. $W = -7.98$ kJ, $q = 0$, $\Delta E = -7.98$ kJ, $\Delta H = 11.174$ kJ, $\Delta T = 96$ K, $P = 724.6$ torr;

5. 121.25 dm^3 ; **6.** 409.29 kg ;

7. 5.226 kJ, 9.317 kJ,

8.

Table-1

State	P atm	V litre	T K
1	1	22.4	273
2	2	22.4	546
3	1	44.8	546

Table-2

Step	Name of Process	q cal	W cal	ΔE cal
A	Isochoric	819	0	819
B	Isothermal	0	748	0
C	Isobaric	–1365	–546	–819
	Cycle	202	202	0

9.

Stage	1	2	3
V litre	24.4	48.4	24.4

Step	q cal	W cal	ΔE cal	ΔH cal
1 → 2	1480	591	889	1480
2 → 3	–822	–822	0	0
3 → 1	–889	0	–889	–1480
Total cycle	231	–231	0	0

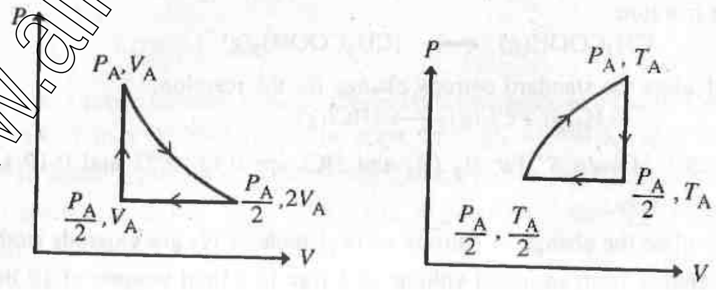
10. -5.23×10^3 J ;

11. (a) $W = -2400$ cal, (b) $Q = 1663.56$ cal ;

12. (a) $W = P_0 v_0$, (b) $q_{CA} = -\frac{5}{2} P_0 V_0$, $q_{AB} = 3P_0 V_0$,

(c) $q_{BC} = \frac{1}{2} P_0 V_0$, (d) $\frac{25}{8} \frac{P_0 V_0}{R}$;

13. (a)



(b) $q = w = 0.58 \times R \times T_A$;

14. (a) 1153.53, (b) 1153.5 J, (c) Zero ;
15. (a) 1869.75 J, (b) −5297.6 J, (c) 500 K ;
16. (a) $w_4 = 765$ J, (b) $n = 0.108$;
17. (a) 189 K, (b) −2767 J, (c) 2767 J ;
18. (a) $T_B = 909$ K, $T_C = 1818$ K, (b) 0.614 ;
19. 1.59×10^3 g ;
20. Temperature rises up to [25 + 4965]K = 4990 K, *i.e.*, much more than m.pt. of Fe ;
21. −2443.8 J ; **22.** $\Delta G = -1630$ J, ∴ Spontaneous ;
23. $-0.163\ \text{JK}^{-1}$; **24.** $30\ \text{JK}^{-1}\ \text{mol}^{-1}$;
25. $19.15\ \text{JK}^{-1}\ \text{mol}^{-1}$.

13

Thermochemistry

Chapter at a Glance

Heat changes expressed at constant pressure = ΔH
Heat changes expressed at constant volume = ΔE

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

$$\Delta H = \Delta E + \Delta nRT$$

Δn = No. of moles of product – No. of moles of reactants; as represented by stoichiometry of change.
(count only gaseous phase molecules for Δn)

Kirchoff's equation: Variation of ΔH and ΔE with temperature

$$\Delta H_2 - \Delta H_1 = \Delta C_p\,(T_2 - T_1)$$

$$\Delta E_2 - \Delta E_1 = \Delta C_v\,(T_2 - T_1)$$

$$\Delta C_p = \Sigma C_{p\ \text{Products}} - \Sigma C_{p\ \text{Reactants}}$$

$$\Delta C_v = \Sigma C_{v\ \text{Products}} - \Sigma C_{v\ \text{Reactants}}$$

ΔC_p and ΔC_v are changes in molar heat capacities at constant pressure and volume respectively during the change

Standard Heat Enthalpy ($H°$)

$$H^\circ_{(\text{Compound})} = \Delta H^\circ_{(\text{Formation of compound})}$$

Heat of Solution for Electrolytes (ΔH_s)

$$\Delta H_s = \Delta H_i + \Delta H_h$$

ΔH_i and ΔH_h are heat of ionisation and heat of hydration respectively

Heat of Neutralization

$$H^+ + OH^- \rightleftharpoons H_2O\ ;\ \Delta H\ (\text{neutralization}) = -13.7\ \text{kcal} = -57.27\ \text{kJ}$$

The Basic Problems with Solution

➤ **Problem 1.** A swimmer coming out from a pool is covered with a film of water weighing about 80 g. How much heat must be supplied to evaporate this water. If latent heat of evaporation for H_2O is 40.79 kJ mol^{-1} at 100°C.

➤ **Problem 2.** How much heat is produced when 4.50 g methane gas is burnt in a constant pressure system.

Given : $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$; $\Delta H = -802$ kJ

➤ **Problem 3.** Red phosphorus reacts with liquid bromine in an exothermic reaction, $2P(s) + 3Br_2(l) \longrightarrow 2PBr_3(g)$: $\Delta_r H^\circ = -243$ kJ. Calculate the enthalpy change when 2.63 g of phosphorus reacts with an excess of bromine in this way.

➤ **Problem 4.** Ammonium nitrate can decompose with explosion by the following reaction :

$$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(g)}; \quad \Delta H = -37.0 \text{ kJ}$$

Calculate the heat produced when 2.50 g of NH_4NO_3 decomposes.

➤ **Problem 5.** Heat of reaction for $C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(v)}$ at constant pressure is -651 kcal at 17°C. Calculate the heat of reaction at constant volume at 17°C.

➤ **Problem 6.** The enthalpy change (ΔH) for the reaction,

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is -92.38 kJ at 298 K.

What is ΔE at 298 K?

➤ **Problem 7.** The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heat of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°C?

➤ **Problem 8.** ΔH for combustion of ethane and ethyne are -341.1 and -310.0 kcal respectively. Which gas is better for welding purpose and why?

➤ **Problem 9.** ΔH_f° for Al_2O_3 is -1670 kJ. Calculate the enthalpy change for the reaction :

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

➤ **Problem 10.** Thermochemical equation for two rocket fuels are given below :

$$2Al_{(s)} + (3/2)O_{2(g)} \longrightarrow Al_2O_{3(s)}; \Delta H = -1667.8 \text{ kJ}$$

$$H_{2(g)} + \tfrac{1}{2}O_2 \longrightarrow H_2O_{(l)}; \quad \Delta H = -285.9 \text{ kJ}$$

If equal mass of Al and H_2 are used, which is a better rocket fuel?

➤ **Problem 11.** A cooking gas cylinder is assumed to contain 11.2 kg isobutane. The combustion of isobutane is given by :

$$C_4H_{10(g)} + (13/2)O_{2(g)} \longrightarrow 4CO_{2(g)} + 5H_2O_{(l)}; \quad \Delta H = -2658 \text{ kJ}$$

(a) If a family needs 15000 kJ of energy per day for cooking, how long would the cylinder last?

(b) Assuming that 30% of the gas is wasted due to incomplete combustion, how long would the cylinder last?

➤ **Problem 12.** When 3.725 g of KCl is dissolved in excess of water, the amount of heat absorbed is X kJ. Calculate the enthalpy of solution of KCl.

➤ **Problem 13.** Calculate the amount of heat released when heat of neutralization is –57.0 kJ :

(a) 0.5 mole of HNO_3 is mixed with 0.3 mole of NaOH in aqueous solution.

(b) 200 mL of 0.1 M H_2SO_4 is mixed with 150 mL of 0.2 M KOH.

➤ **Problem 14.** Calculate the heat of neutralization by mixing 200 mL of 0.1 M H_2SO_4 and 200 mL of 0.2 M KOH if heat generated by the mixing is 2.3 kJ.

➤ **Problem 15.** When a student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee cup calorimeter, the temperature of the resultant solution increases from 21.0°C to 27.5°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the total volume of the solution is 100 mL, its density 1.0 g mL^{-1} and that its specific heat is 4.18 J/g, calculate :

(a) the heat change during mixing.

(b) the enthalpy change for the reaction :

$$HCl_{(aq.)} + NaOH_{(aq.)} \longrightarrow NaCl_{(aq.)} + H_2O$$

➤ **Problem 16.** (a) Calculate the energy needed to raise the temperature of 10.0 g of iron from 25°C to 500°C if specific heat capacity of iron is 0.45 J $(°C)^{-1}$ g^{-1}.

(b) What mass of gold (of specific heat capacity 0.13 J $(°C)^{-1}$ g^{-1} can be heated through the same temperature difference when supplied with the same amount of energy as in (a)?

➤ **Problem 17.** Standard vaporization enthalpy of benzene at its boiling point is 30.8 kJ mol^{-1}; for how long would a 100 W electric heater have to operate in order to vaporize a 100 g sample of benzene at its boiling temperature?

➤ **Problem 18.** Acetic acid (ethanoic acid) and hydrochloric acid react with KOH solution. The enthalpy of neutralisation of ethanoic acid is –55.8 kJ mol^{-1} while that of hydrochloric acid is – 57.3 kJ mol^{-1}. Can you think of how are these different?

➤ **Problem 19.** Specific heat of Li(s), Na(s), K(s), Rb(s) and Cs(s) at 398 K are 3.57, 1.23, 0.756, 0.363 and 0.242 Jg^{-1} K^{-1} respectively. Compute the molar heat capacity of these elements and identify any periodic trend. If there is trend, use it to predict the molar heat capacity of Fr.

➤ Problem 20. Given S^o for $C_{Graphite}$, $H_2(g)$ and $CH_4(g)$ are 5.70, 130.7 and 186.3 J K^{-1} mol^{-1}. Also standard heat of formation of CH_4 is –74.81 kJ mol^{-1}.

Calculate the statndard free energy change for the formation of methane at 298 K.

$$C_{Graphite} + 2H_2(g) \longrightarrow CH_4(g)$$

➤ Problem 21. 0.562 g of graphite kept in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure was burnt according to the equation

$$C_{Graphite} + O_2(g) \longrightarrow CO_2(g)$$

During the reaction, temperature rises from 298 K to 298.89 K. If the heat capacity of the calorimeter and its contents is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298K and 1 atm?

➤ Problem 22. Calculate the enthalpy change during the reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g).$$

Given $e_{H-H} = 435$ kJ mol^{-1}; $e_{Br-Br} = 192$ kJ mol^{-1} and $e_{H-Br} = 368$ kJ mol^{-1}.

➤ Problem 23. Determine enthalpy change for the reaction,

$$CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$$

Bond energies for C—H, C—Cl, Cl—Cl, H—Cl are 412, 338, 242, 431 kJ mol^{-1} respectively.

➤ Problem 24. During one of his adventures Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous and contains CO in addition to O_2 and N_2. Sabu, being huge, could not enter cave. In order to save Chacha Chaudhary he started sucking the poisonous air out of the cave by mouth. In each cycle he used to fill his lungs with cave air and exhale it out in the surroundings. In the mean time fresh air (N_2 + O_2) from the surrounding effused into cave till the pressure was 1 atmosphere. Each time Sabu sucked air, the pressure in the cave dropped to ½ atm. An initial sample of air taken from the cave measured 11.2 mL at STP and give 7 J on complete combustion at constant pressure.

(a) If the safe level of CO required in cave for life is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary.

(b) Sabu should rescue Chacha Chaudhary within 10 minutes else he will die. Precious 80 second are wasted in thinking of a way to rescue him. At maximum how much time should each cycle of inhaling exhaling take. Given ΔH_{comb} CO = –280 kJ mol^{-1}. Neglect Graham's law effect during operations.

Answers

1. 181.2 kJ ;
2. −225.6 kJ;
3. −10.31 ;
4. 1.16 kJ;
5. −654.48 kcal;
6. −87.425 kJ;
7. 22.8 cal/g;
8. Ethyne;
9. −3340 kJ;
10. H_2, −142.95 kJ/g ;
11. (a) 34 day, (b) 24 day;
12. 20 *X*;
13. (a) 17.1 kJ, (b) 1.71 kJ;
14. 57.5 kJ;
15. 54.4 kJ;
16. 34.61 g;
17. 6.6 min;
18. See solution;
19. 33.5 J mol^{-1} K^{-1};
20. −50.73 kJ ;
21. -3.93×10^{-5} J ;
22. −109 kJ ;
23. −115 kJ mol^{-1};
24. 13 times, 40 sec.

Solution

Solution 1. Amount of water present on the body of swimmer = 80 g = $\frac{80}{18}$ mole

$$\text{Thus heat required to evaporate } \frac{80}{18} \text{ mole } H_2O = 40.79 \times \frac{80}{18}$$

$$= \mathbf{181.2\ kJ}$$

Solution 2. $\because$ 16 g CH_4 on burning produces heat = – 802 kJ

$\therefore$ 4.5 g CH_4 on burning produces heat = $\frac{-802 \times 4.5}{16}$ = **–225.6 kJ**

Solution 3. $\because$ 2 mole of P produces heat = 243 kJ

$$\therefore \frac{2.63}{31} \text{ mole of P produces heat} = \frac{243 \times 2.63}{31 \times 2}$$

$$= \mathbf{10.31\ kJ}$$

$\therefore$ Heat produced = 10.31 kJ

ΔH = **–10.31 kJ** (The evolution of heat is exothermic in nature.)

Solution 4. $\because$ 80 g NH_4NO_3 gives heat = 37.0 kJ

$\therefore$ 2.50 g NH_4NO_3 gives heat = (37.0 × 2.50)/80 = **1.16 kJ**

Solution 5. $\Delta H = \Delta E + \Delta nRT$ and $\Delta H = -651 \times 10^3$ cal; $R = 2$ cal; $T = 290$ K

and $\Delta n = 6 + 6 - 6 = 6$

$\therefore$ $-651 \times 10^3 = \Delta E + 6 \times 2 \times 290$

or $\Delta E = 654480$ cal = – **654.48 kcal**

Solution 6. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H = -92.38$ kJ at 298 K

$\Delta E = ?$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta n = 2 - (3 + 1) = -2$$

$$\therefore -92.38 \times 10^3 = \Delta E + 8.314 \times (-2) \times 298$$

$$\Delta E = -87424.8\ J = \mathbf{-87.425\ kJ}$$

Solution 7. $I_{2(s)} \longrightarrow I_{2(v)}$; $\Delta H = 24$ cal/g at 200°C

$\Delta cp = cp$ of product – cp of reactants = 0.031 – 0.055 = – 0.024 cal/g

$$\because \Delta H_2 - \Delta H_1 = \Delta cp\,(T_2 - T_1)$$

$$\Delta H_2 - 24 = -0.024 \times (523 - 473)$$

$$\therefore \Delta H_2 = \mathbf{22.8\ cal/g}$$

Solution 8. A better gas welder is one which possesses high calorific value *i.e.*, heat produced by 1 g of fuel.

Calorific value for ethane = (–341.1/30) = –11.37 kcal/g (mol wt. = 30)

Calorific value for ethyne = (–310.0/26) = –11.92 kcal/g (mol wt. = 26)
Thus **ethyne** is better gas welder.

Solution 9. Given : $2Al + (3/2)O_2 \longrightarrow Al_2O_3$; $\Delta H = -1670$ kJ

multiplying it by 2; $4Al + 3O_2 \longrightarrow 2Al_2O_3$; $\Delta H = 2 \times (-1670)$
$= \mathbf{-3340}$ **kJ**

Solution 10. Calorific value of Al $= \dfrac{-1667.8}{54} = -30.88$ kJ/g

Calorific value of $H_2 = \dfrac{-285.9}{2} = \mathbf{-142.95}$ **kJ/g**

Thus H_2 is better rocket fuel.

Solution 11. (a) ∵ 58 g isobutane provides energy = 2658 kJ

11.2×10^3 g isobutane provides energy $= \dfrac{2658 \times 11.2 \times 10^3}{58}$ kJ
$= 513268.9$ kJ

The daily requirement of energy = 15000 kJ

∴ Cylinder will last $= \dfrac{513268.9}{15000} \simeq$ **34 days**

(b) Total loss of energy due to wastage $= \dfrac{513268.9 \times 70}{100}$ kJ is 30% and thus energy used for work

∴ Cylinder will last $= \dfrac{513268.9 \times 70}{100 \times 15000}$ = **24 days**

Solution 12. $KCl + aq. \longrightarrow KCl_{aq.}$; $\Delta H = ?$

∵ 3.725 g KCl on dissolution absorbed heat = X kJ

∴ 74.5 g KCl on dissolution absorbed heat $= \dfrac{X(74.5)}{3.725} = 20X$

∴ $KCl + aq. \longrightarrow KCl_{aq}$; $\mathbf{\Delta H = 20X}$

Solution 13. (a) ∵ 1 mole of HNO_3 and 1 mole of NaOH give heat = 57.0 kJ

∴ 0.3 mole of HNO_3 and 0.3 mole of NaOH give heat = 57 × 0.3
= **17.1 kJ**

Note : Both acid and base are monovalent and thus 1 mole = 1 equivalent
Also 0.2 mole of HNO_3 are left unreacted.

(b) Meq. of H_2SO_4 = 200 × 0.1 × 2 = 40;
Meq. of KOH = 150 × 0.2 × 1 = 30

∵ 1000 Meq. of H_2SO_4 and 1000 Meq. of KOH on mixing produce heat
= 57.0 kJ

∴ 30 Meq. of H_2SO_4 and 30 Meq. of KOH on mixing produce heat

$$= \frac{57 \times 30}{1000} = \mathbf{1.71\ kJ}$$

Note : 10 Meq. of H_2SO_4 is left unreacted.

Solution 14. Meq. of $H_2SO_4 = 200 \times 0.1 \times 2 = 40$ (H_2SO_4 is dibasic)

Meq. of KOH $= 200 \times 0.2 = 40$

∵ 40 Meq. of H_2SO_4 and 40 Meq. of KOH on mixing gives heat $= 2.3$ kJ

∴ 1000 Meq. of H_2SO_4 and 1000 Meq. of KOH on mixing gives heat

$$= \frac{2.3 \times 1000}{40} = \mathbf{57.5\ kJ}$$

Solution 15. *mM* of HCl $= 50 \times 1.0 = 50$; *mM* of NaOH $= 50 \times 1.0 = 50$

Heat changes during mixing $= m.s.\Delta T$

50 *mM* of HCl and 50 *mM* of NaOH $= (100 \times 1) \times 4.18 \times 6.5 = 2717$ J $= 2.72$ kJ

Further, on mixing 50 *mM* of HCl and 50 *mM* of NaOH produces heat $= 2.72$ kJ

∴ 1000 *mM* of HCl (or 1000 Meq.) and 1000 *mM* of NaOH produces

$$\text{heat} = \frac{2.72 \times 1000}{50} = \mathbf{54.4\ kJ}$$

(∵ acid and bases are monobasic and monoacidic, respectively).

Solution 16. (a) $q = m.s.\Delta T = 10 \times 0.45 \times (773 - 298)$ J $= \mathbf{2137.5\ J}$

(b) $q = m.s.\Delta T$ [Given $q = 2137.5$, $T = (773 - 298) = 475$; $s = 0.13$]

∴ $2137.5 = m \times 0.13 \times 475$

∴ $\mathbf{m = 34.61\ g}$

Solution 17. 100 g benzene contains $= \frac{100}{78}$ mole (mol.wt. of benzene, $C_6H_6 = 78$)

∴ Heat of vaporisation of $C_6H_6 = \frac{100}{78} \times 30.8$ kJ $= \frac{100 \times 10^3 \times 30.8}{78}$ J

Since, $\text{Power} = \frac{\text{energy}}{\text{time}}$ (1 *W* = 1J)

$$\therefore \quad 100 = \frac{100 \times 10^3 \times 30.8}{78 \times \text{time}}$$

$$\therefore \quad \text{time} = 394.87\ \text{sec.} = \frac{394.87}{60}\ \text{min.} = \mathbf{6.6\ min}$$

Solution 18. Enthalpy of neutralisation for HCl $= -57.3$ kJ mol^{-1}

Enthalpy of neutralisation for $CH_3COOH = -55.8$ kJ mol^{-1}

In case of neutralisation of CH_3COOH, the part of heat released

[– 57.3 – (– 55.8) = – 1.5 kJ] is used up in dissociation of acetic acid and thus heat given out is lesser than 57.3 kJ.

Solution 19. Molar heat capacity = at.wt. × specific heat.

Molar heat capacity (in J mol^{-1} K^{-1}) of :

$Li(s)$ = 3.57 × 6.94 = 24.78

$Na(s)$ = 1.23 × 22.99 = 28.28

$K(s)$ = 0.756 × 39.10 = 29.56

$Rb(s)$ = 0.363 × 85.47 = 31.03

$Cs(s)$ = 0.242 × 132.91 = 32.16

There is a trend plotting these values with atomic number, the extrapolation of graph gives the value of Fr(*s*) = **33.5 J mol^{-1} K^{-1}**

Solution 20.
$$\Delta H^\circ_{form}\ CH_4 = H^\circ_{CH_4} = -74.81\ \text{kJ mol}^{-1}$$

Also H° for $C_{graphite}$ and $H_2(g) = 0$ (standard state of elements)

$$\therefore\quad C_{graphite} + 2H_2(g) \longrightarrow CH_4(g);$$

$$\Delta H^\circ = \Delta H_{CH_4} - H_{C_{graphite}} - 2 \times H_{H_2} = -74.81$$

$$\therefore\quad \text{Also } \Delta S^\circ \text{ (for the reaction)} = S_{CH_4} - S_{C_{graphite}} - 2 \times S_{H_2}$$

$$= 186.3 - 5.70 - 130.7 \times 2$$

$$= -80.8\ \text{JK}^{-1}\ \text{mol}^{-1}$$

Using
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -74.81 - 298 \times [-80.8 \times 10^{-3}]$$

$$= -50.73\ \text{kJ}$$

Solution 21. Let *q* amount of heat is produced during the course of reaction when 0.562 g of graphite in a bomb calorimeter is burnt in excess of O_2. This is condition of constant volumve (volume of bomb calorimeter is constant) Thus **heat produced (q_v)** is :

Thus
$$q_V = -C_V \times \Delta T$$

Where C_V is heat capacity of calorimeter and its content, ΔT is change in temperature. The negative sign indicates for exothermic reaction.

$$q_V = -20.7 \times 10^3 \times 0.89$$

$$= -18.42 \times 10^3\ \text{J per 0.562 g carbon}$$

Amount of heat liberated during burning of 1 mole carbon

$$\frac{18.42 \times 10^3 \times 12}{0.562} = -3.93 \times 10^5\ \text{J}$$

Thus heat is used to change the internal energy *E* i.e., ΔE as the conditions are of constant volume.

Now
$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta n = 1 - 1 = 0 \quad \therefore \quad \Delta H = \Delta E = -3.93 \times 10^5\ \text{J}$$

Solution 22. $I_2 + Br_2 \longrightarrow 2HBr$

ΔH = Bond energy data for formation of bond + bond energy data for dissociation of bond

$$= -[2 \times e_{H-Br}] + [e_{H-H} + e_{Br-Br}]$$

$$= -2 \times 368 + 435 + 192 = \mathbf{-109\ kJ}$$

Solution 23. ΔH = [Bond energy for dissociation of bond] + [Bond energy for formation of bond]

$$= [4(C—H) + 1(Cl—Cl)] - [3(C—H) + 1(C—Cl) + 1(H—Cl)]$$

$\because$ Bond energy of formation is always –ve.

$$= e_{(C-H)} + e_{(Cl-Cl)} - e_{(C-Cl)} - e_{(H-Cl)} = 412 + 242 - 338 - 431$$

$$= \mathbf{-115\ kJ\ mol^{-1}}$$

Solution 24. $\because$ 280×10^3 J heat is given by combustion of CO = 1 mole

$$\therefore \quad 7 \text{ J heat is given by combustion of CO} = \frac{7}{280 \times 10^3}$$

$$= 2.5 \times 10^{-5} \text{ mole}$$

$$\text{Initial moles of air} = \frac{112}{22400} = 5 \times 10^{-4} \text{ mole}$$

$$\therefore \quad \% \text{ of CO initially in air} = \frac{2.5 \times 10^{-5}}{5 \times 10^{-4}} \times 100 = 5$$

Now in one inhaling by Sabu only half of the total air is taken out as during inhaling pressure drops to half because.

$$P \propto n \qquad (V \text{ and } T \text{ are constant})$$

$$P \propto n$$

$$\frac{P}{2} \propto (n - a)$$

where n moles of poisonous air are present in cave and a moles of poisonous air are inhaled by Sabu

$$\therefore \qquad a = \frac{n}{2};$$

(a) Thus half moles of poisonous air are given out and the pure air again makes the tatal mole n by diffusing in cave as pressure becomes 1 atm.

Thus % of CO in poisonous air is reduced by ½ in each inhaling or 50% CO is taken out in one inhaling. Thus to reduce CO from 5% to 0.001% 13 times inhaling is necessary by Sabu which gives 0.00061% CO in air.

(b) Sabu has only 10 minutes time *i.e.*, 600 sec in which he wastes 80 second in thinking thus he is left only 520 sec in which he has to inhail and exhail 13 times or he should go for 40 sec for one inhaling and exhaling.

Selected Problems with Solutions

➤ **Problem 1.** The heat of reaction for,

$$C_{10}H_{8(s)} + 12O_{2(g)} \longrightarrow 10CO_{2(g)} + 4H_2O_{(l)}$$

at constant volume is – 1228.2 kcal at 25°C. Calculate the heat of reaction at constant pressure at 25°C.

➤ **Problem 2.** The heat of reaction for $N_2 + 3H_2 \longrightarrow 2NH_3$ at 27°C is –91.94 kJ. What will be its value at 50°C? The molar heat capacities at constant P and 27°C for N_2, H_2 and NH_3 are 28.45, 28.32 and 37.07 joule respectively.

➤ **Problem 3.** The heat evolved in the conversion of 1 g-atom of β-sulphur into α-sulphur is 82 cal at 25°C. If the specific heats of α- and β-sulphur are 0.163 and 0.171 cal/g, calculate the heat of transition for β-sulphur into α-sulphur at 50°C.

➤ **Problem 4.** Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. In a recently reported data, the specific internal energy of combustion of crystalline C_{60} is found to be –36 kJ g^{-1} at 298 K. Compute the standard enthalpy of combustion and formation for the same. Standard enthalpy of combustion of graphite is –395 kJ. mol^{-1}. If the standard enthalpy of formation of diamond is +2 kJ per mol of C-atom, which is more stable: C_{60} or diamond?

➤ **Problem 5.** The heat evolved on combustion of 1 g starch $(C_6H_{10}O_5)_n$ into CO_2 and $H_2O_{(l)}$ is 17.49 kJ g^{-1}. Compute the enthalpy of formation of 1 g starch. Given ΔH_f of $H_2O_{(l)} = -285.85$ kJ mol^{-1}, ΔH_f of $CO_2 = -293.7$ kJ mol^{-1}.

➤ **Problem 6.** Given below are some standard heats of reaction;

(a) Heat of formation of water = –68.3 kcal
(b) Heat of combustion of acetylene = –310.6 kcal
(c) Heat of combustion of ethylene = –337.2 kcal

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume at 25°C.

➤ **Problem 7.** Calculate the heat of neutralization from the following data. 200 mL of 1 M HCl is mixed with 400 mL of 0.5 M NaOH. The temperature rise in colorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is 1 cal /mL /degree for solution.

➤ **Problem 8.** The enthalpies of neutralisation of a strong acid HA and weaker acid HB by NaOH are –13.7 and –12.7 kcal equivalent. When one equivalent of NaOH is added to a mixture containing 1 equivalent of HA and HB, the enthalpy change was –13.5 kcal. In what ratio is the base distributed between HA and HB.

➤ **Problem 9.** Two solutions initially at 25°C were mixed in an insulated bottle. One contains 400 mL of 0.2 *N* weak monoprotic acid solution. The other contains 100 mL of 0.8 *N* NaOH solution. After mixing the temperature rises to 26·17°C. Calculate the heat of neutralisation of weak acid with NaOH. Assume density of final solution 1.0 g cm^{-3} and specific heat of final solution 4.2 J g^{-1} K^{-1}.

➤ **Problem 10.** A monobasic acid is dissociated to 25% in 0.1 *N* solution. When 100 mL of the acid is neutralised by 0.1 *N* KOH solution, heat evolved was 120 cal. Calculate heat of dissociation per mol of acid.

➤ **Problem 11.** The dissolution of 1 mole of $NaOH_{(s)}$ in 100 mole of $H_2O_{(l)}$ give rise to evolution of heat as –42.34 kJ. However if 1 mole of $NaOH_{(s)}$ is dissolved in 1000 mole of $H_2O_{(l)}$ the heat given out is 42.76 kJ. What would be enthalpy change when 900 mole of $H_2O_{(l)}$ are added to a solution containing 1 mole of $NaOH_{(s)}$ in 100 mole of H_2O.

➤ **Problem 12.** The integral enthalpy of solution in kJ of one mole of H_2SO_4 dissolved in *n* mole of water is given by:

$$\Delta H_s = \frac{75.6 \times n}{n + 1.8}$$

Calculate ΔH for the following process:

(a) 1 mole of H_2SO_4 dissolved in 2 mole of H_2O.
(b) 1 mole of H_2SO_4 dissolved in 7 mole of H_2O.
(c) 1 mole of H_2SO_4 dissolved in 5 mole of H_2O.
(d) solution (a) dissolved in 5 mole of H_2O.
(e) 1 mole of H_2SO_4 dissolved in excess of H_2O.

➤ **Problem 13.** The heat of solution of NH_4NO_3 in water was determined by measuring the amount of electrical work needed to compensate for the cooling which would otherwise occur when the salt dissolves. After the NH_4NO_3 was added to the water, electrical energy was provided by passage of current through a resistance coil until the temperature of the solution reached the value it had prior to the addition of salt. In a typical experiment, 4.4 g of NH_4NO_3 was added to 200 g water. A current of 0.75 ampere was provided through the heater coil, and the voltage across the terminals was 6.0 V. The current was applied for 5.2 minute. Calculate ΔH for the solution of 1.0 mole NH_4NO_3 in enough water to give same concentration as was attained in the above experiment.

➤ **Problem 14.** An athelete takes 20 breaths per minute at room temperature. The air inhaled in each breath is 200 mL which contains 20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all the oxygen consumed if used for converting glucose into CO_2 and $H_2O_{(l)}$, how much glucose will be burnt in the body in one hour and what is the heat produced? (Room temperature = 27°C and enthalpy of combustion of glucose is – 2822.5 kJ mol^{-1} at 0°C).

➤ Problem 15. A slice of banana weighing 2.502 g was burnt in a bomb calorimeter producing a temperature rise of 3.05°C. The combustion of 0.316 g of benzoic acid in the same calorimeter produced a temperature rise of 3.24°C. The heat of combustion of benzoic acid at constant volume is $-3227\ \text{kJ mol}^{-1}$. If average banana weigh 125 g, how many calories can be obtained from one average banana.

➤ Problem 16. A person inhales 640 g of O_2 per day. If all the O_2 is used for converting sugar into CO_2 and H_2O, how much sucrose ($C_{12}H_{22}O_{11}$) is consumed in the body in one day and what is the heat evolved? $\Delta H_{\text{Combustion of sucrose}} = -5645\ \text{kJ mol}^{-1}$.

➤ Problem 17. The heat of formation of carbon dioxide from graphite at 15°C and constant volume is 97400 cal, and that of carbon monoxide under the same conditions is 25400 cal. What heat should be evolved when 100 litre of carbon monoxide measured at N.T.P. is burnt in an excess of oxygen, both reactants and products being at 15°C?

➤ Problem 18. When 12.0 g of carbon reacted with oxygen to form CO and CO_2 at 25°C and constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen which reacted. $\Delta H_f^\circ (CO_2) = -95\ \text{kcal mol}^{-1}$, $\Delta H_f^\circ (CO) = -24\ \text{kcal mol}^{-1}$.

➤ Problem 19. The heat of combustion of ethane gas is 368 kcal/mol. Assuming that 60% of the heat is useful, how many m^3 of ethane measured at STP must be burnt to supply enough heat to convert 50 kg of water at 10°C to steam at 100°C? Specific heat of water is 1 cal/g. Heat of vaporisation of H_2O is 540 cal/g.

➤ Problem 20. The commercial production of water gas utilizes the reaction under standard conditions: $C + H_2O(g) \rightarrow H_2 + CO$. The heat required for this endothermic reaction may be supplied by adding a limited amount of air and burning some carbon to CO_2. How many g of carbon must be burnt to CO_2 to provide enough heat for the water gas conversion of 100 g carbon? Neglect all heat losses to the environment. Also ΔH_f° of CO, $H_2O_{(g)}$ and CO_2 are −110.53, −241.81 and −393.51 kJ/mol respectively.

➤ Problem 21. From the following data of ΔH, of the following reactions,

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \qquad \Delta H = -110\ \text{kJ}$$

$$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}; \qquad \Delta H = 132\ \text{kJ}$$

Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping temperature constant.

➤ Problem 22. When 100 c.c. of a mixture of methane (CH_4) and ethylene (C_2H_4) was exploded with an excess of oxygen, the volume of carbon dioxide produced (measured at the same temperature and pressure) was 160 c.c. Calculate the heat evolved when 22.4 litre of the mixture of methane and ethylene (measured at N.T.P.) is completely oxidised to carbon dioxide and water at constant volume.

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 212000 \text{ cal.},$$
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O + 333000 \text{ cal.}$$

➤ **Problem 23.** 1.0 g magnesium atoms in vapour phase absorbs 50.0 kJ of energy to convert all Mg into Mg ions. The energy absorbed is needed for the following changes:

$$Mg_{(g)} \longrightarrow Mg^{+}_{(g)} + e \;; \qquad \Delta H = 740 \text{ kJ mol}^{-1}$$
$$Mg_{(g)} \longrightarrow Mg^{2+}_{(g)} + e \;; \qquad \Delta H = 1450 \text{ kJ mol}^{-1}$$

Find out the % of Mg^+ and Mg^{2+} in final mixture.

➤ **Problem 24.** Calculate the enthalpy change when 6.80 g of NH_3 is passed over heated CuO. The standard heat enthalpies of $NH_{3(g)}$, $CuO_{(s)}$ and $H_2O_{(l)}$ are –46.0, –155.0 and –285.0 kJ mol^{-1} respectively and the change is $NH_3 + \frac{3}{2}CuO \longrightarrow \frac{1}{2}N_{2(g)} + \frac{3}{2}H_2O_{(l)} + \frac{3}{2}Cu_{(s)}$.

➤ **Problem 25.** 1.00 litre sample of a mixture of $CH_{4(g)}$ and $O_{2(g)}$ measured at 25°C and 740 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1260 cal/K. The complete combustion of the methane to CO_2 and H_2O caused a temperature rise in the calorimeter of 0.667 K. What was the mole per cent of CH_4 in the original mixture? $\Delta H^{\circ}_{\text{comb}}$ $(CH_4) = -215$ kcal mol^{-1}.

➤ **Problem 26.** The standard enthalpy of formation of FeO and Fe_2O_3 is –65 kcal mol^{-1} and –197 kcal mol^{-1} respectively. A mixture of two oxides contains FeO and Fe_2O_3 in the mole ratio 2 : 1. If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mol of initial mixture.

➤ **Problem 27.** When 120 mg of naphthalene $C_{10}H_{8(s)}$ was burnt in a bomb calorimeter, the temperature rise was 3.05 K. Calculate the calorimeter constant and molar standard internal energy change of combustion. Also report by how much will the temperature rise when 100 mg of phenol, $[C_6H_5OH_{(s)}]$ is burnt in the same calorimeter under the same conditions, if heat liberated is 3962.85 J. ΔH°_{C} for $C_{10}H_8 = -5157$ kJ mol^{-1}.

➤ **Problem 28.** The heat of dissociation of H_2 is 435 kJ mol^{-1}. If $C_{(s)} \longrightarrow C_{(g)}$; $\Delta H = 720$ kJ mol^{-1}, calculate the bond energy per mol of the C—H bond in CH_4 molecule. ΔH_f for $CH_4 = -75$ kJ mol^{-1}.

➤ **Problem 29.** The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 and H_2O are 94.38 and 68.38 kcal respectively. Calculate C═C bond energy. Given that heat of atomisation of C and H are 150.0 and 51.5 kcal respectively and C — H bond energy is 93.64 kcal.

➤ **Problem 30.** Calculate the resonance energy of C_6H_6 using Kekule formula for C_6H_6 from the following data.

(i) ΔH_f° for $C_6H_6 = -358.5$ kJ mol^{-1}

(ii) Heat of atomisation of C = 716.8 kJ mol^{-1}

(iii) Bond energy of C—H, C—C, C═C and H—H are 490, 340, 620, 436.9 kJ mol^{-1} respectively.

➤ **Problem 31.** The specific heat at constant volume for a gas 0.075 cal/g and at constant pressure is 0.125 cal/g. Calculate:

(i) The molecular weight of gas,

(ii) Atomicity of gas,

(iii) No. of atoms of gas in its 1 mole.

Answers

1. −1229.392 kcal ; **2.** −92.843 kJ ;

3. 88.4 cal/g-atm ;

4. $\Delta H_f^\circ = +2220$, $\Delta H_C^\circ = -25.920$ MJ mol^{-1}, Diamond is more stable ;

5. −2.21 kJ ; **6.** −41.104 kcal ;

7. −13.464 kcal ; **8.** 4 : 1 ;

9. 30.71 kJ equivalent^{-1} ; **10.** 2266.6cal ;

11. −0.42 kJ ;

12. (a) 39.79 kJ, (b) 60.14 kJ, (c) 55.59 kJ,
(d) 20.35 kJ, (e) −75.60 kJ ;

13. 25.45×10^3 J ; **14.** 29.25 g, 458.66 kJ ;

15. 93.97 kcal ; **16.** 570 g, 9408.33 kJ ;

17. 321408 cal ; **18.** 27.49 g ;

19. 3.196 m^3 ; **20.** 33.36 g carbon ;

21. $\frac{0.6}{1}$; **22.** 284.60 kcal ;

23. $Mg^+ = 68.28\%$, $Mg^{2+} = 31.72\%$; **24.** −59.6 kJ ;

25. 9.75% ; **26.** −13.4 kcal mol^{-1} ;

27. $\Delta H = 1585.14$ JK^{-1}, $\Delta E = -5152.0$ kJ mol^{-1}, $\Delta T = 2.5$ K ;

28. 416.25 kJ mol^{-1} ; **29.** 160.86 kcal ;

30. −150.0 kJ mol^{-1} ;

31. (i) 40, (ii) Gas is monoatomic, (iii) 6.023×10^{23} atoms.

Problems for Self Assessment

1. The ΔH° for the mutarotation of glucose in aqueous solution,

$$\alpha\text{-D-glucose}_{(aq)} \longrightarrow \beta\text{-D-glucose}_{(aq)}$$

has been measured in a microcalorimeter and found to be –1.16 kJ mol^{-1}. The enthalpies of solution of the two forms of glucose have been determined to be,

$$\alpha\text{-D-glucose}_{(s)} \longrightarrow \alpha\text{-D-glucose}_{(aq)}\ ; \qquad \Delta H^\circ = 10.72 \text{ kJ mol}^{-1}$$

$$\beta\text{-D-glucose}_{(s)} \longrightarrow \beta\text{-D-glucose}_{(aq)}\ ; \qquad \Delta H^\circ = 4.68 \text{ kJ mol}^{-1}$$

Calculate ΔH° for the mutarotation of solid α-D-glucose to solid β-D-glucose.

2. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.0 kg of CCl_2F_2 needed. ΔH for vaporisation of SO_2 and CCl_2F_2 are 6.0 kcal mol^{-1} and 17.4 kJ mol^{-1} respectively. (At. wt. of F = 19)

3. One mole of water at 373 K is converted into steam at a pressure of one atm, 40.68 kJ of heat is absorbed. The molar volume of water and steam are 18 mL and 30600 mL. Calculate ΔE for process.

4. Both CH_4 and C_2H_6 can be used as fuels. Which of them is more efficient as a fuel? The heat of formation of $CH_{4(g)}$, $C_2H_{6(g)}$, $CO_{2(g)}$ and $H_2O_{(g)}$ are –17.9, –20.2, –94.0 and –57.8 kcal respectively. Also report the heat of combustion for both hydrocarbons.

5. The standard enthalpy of formation of fumarate ion is –777.4 kJ mol^{-1}. If the standard enthalpy change of the reaction given below is –131.4 kJ mol^{-1},

$$\text{Fumarate}^{2-}_{(aq)} + H_{2(g)} \longrightarrow \text{Succinate}^{2-}_{(aq)}$$

Calculate the standard enthalpy of formation of succinate ion.

6. Assume that a human requires 2.5×10^3 kcal of energy each day for metabolic activity. What mass of ethanol be needed to provide this energy if.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}; \qquad \Delta H = -1371 \text{ kJ}$$

If the human body is considered to be a closed system, what would be the temperature increase resulting from this energy intake? Assume a mass of 75 kg and specific heat of human body 4 JK^{-1} g^{-1}. If the body temperature is to be maintained at a constant value by the evaporation of water, what mass of water must evaporate? Assume heat of vaporisation of water is 44 kJ mol^{-1}.

7. A person working in laboratory, takes 400 g grapes equivalent to 8200 kJ energy. Laboratory is air conditioned. Energy is not stored in body. Calculate what mass of water is to be prespired if temperature of body is maintained constant? Heat of vaporisation of water is 44 kJ/mol.

8. A couple sitting in a warm room on a winter day takes 1/2 kg of cheese sandwitches (an energy intake of 8130 kJ for both). Supposing that none of the energy is stored in body, what mass of water would they need to perspire in order to maintain their original temperature? The enthalpy of vaporisation of water is 40.65 kJ mol^{-1}.

9. A cylinder of gas supplied by a company contains 14 kg of butane. The heat of combustion of butane is 2658 kJ mol^{-1}. A normal family requires 20 MJ of energy per day for cooking. If the cylinder lasts for 26 days, what percentage of gas is wasted due to insufficient combustion.

10. The following reactions might be used to power rockets,

(i) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)}$

(ii) $CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$

(iii) $H_{2(g)} + F_{2(g)} = 2HF_{(g)}$

Given, ΔH°_f for $H_2O_{(g)}$, $CH_3OH_{(l)}$, $CO_{2(g)}$ and $HF_{(g)}$ is –285.8, –238.7, –393.5 and –271.1 kJ mol^{-1} respectively.

(a) Calculate the enthalpy changes at 25°C for each of these reactions per kilogram of reactants.

(b) Since the thrust is greater when the molar mass of the exhaust gas is lower, divide the heat per kilogram by the molar mass of the product (or the average molar mass in the case of reaction 2) and arrange the above reactions in order of effectiveness on the basis of thrust.

11. Find out the heat change during the reaction:

$$CaCl_2 + 2Na \longrightarrow 2NaCl + Ca; \quad \Delta H = ?$$

Given heat of formation of $CaCl_2$ and NaCl are 191 and 97.7 calorie respectively.

12. Calculate the standard heat of formation of sodium ions in aqueous solution from the following data:

Heat of formation of $NaOH_{(aq)}$ at 25°C = –470.7 kJ

Heat of formation of $OH^-_{(aq)}$ at 25°C = –228.8 kJ.

13. The reaction of heated graphite with superheated steam is endothermic

$$C_{(graphite)} + H_2O_{(g)} = CO_{(g)} + H_{2(g)} \qquad \ldots(1)$$

The heat required for this reaction is provided by burning part of the graphite;

$$C_{(graphite)} + O_{2(g)} = CO_{2(g)};\ \Delta H^\circ\ (500\ K) = -393.7\ kJ\ mol^{-1} \qquad \ldots(2)$$

If 1.34 mole of graphite is required for the production of one mole of hydrogen at 500 K, what is ΔH° (500 K) for reaction (1)?

14. Oxidation of NH_3 to HNO_3 involves the initial step:

$$NH_{3(g)} + \frac{7}{4}O_{2(g)} \longrightarrow NO_{2(g)} + \frac{3}{2}H_2O_{(g)}$$

ΔH°_f NH_3 = –46.11 kJ mol^{-1}

ΔH°_f NO_2 = 33.18 kJ mol^{-1}

ΔH°_f $H_2O_{(g)}$ = –241.818 kJ mol^{-1}

Calculate the enthalpy change per g of NH_3 oxidised.

15. When 100 g of anhydrous $CuSO_4$ is dissolved in water, the heat evolved is 9.1 kcal. If the same amount of $CuSO_4{\cdot}5H_2O$ is dissolved in water, the amount of heat absorbed is 1.06 kcal. Calculate the heat of hydration of 1 mole $CuSO_4$ into $CuSO_4 \cdot 5H_2O$.

16. For dissolution of $NaOH_{(s)}$ in H_2O, the heat released are given as:

$$NaOH_{(s)} + nH_2O_{(l)} \longrightarrow NaOH_{(aq)} \quad ; \quad \Delta H = ?$$

(a) $n = 100$; $\Delta H = -42.34$ kJ

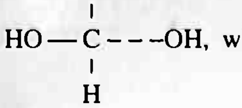
(b) $n = 1000$; $\Delta H = -42.76$ kJ

Calculate the enthalpy change when 900 mole of water is added to 1 mole NaOH solution in 100 mole H_2O solution.

17. A solution of 5 g of haemoglobin (Mol. wt. = 64000) in 100 cc of solution shows a temperature rise of 0.031°C for complete oxygenation. Each mole of haemoglobin binds 4 mole of oxygen. If the heat capacity of the solution is 4.18 JK^{-1} cm^{-3}, calculate ΔH per g mole of oxygen bound.

18. Calculate the H—F bond energy in HF at 25°C. Given that heat of formation of HF, H atoms and F atoms are –64.2, +52.1 and +18.9 kcal respectively.

19. The heat of formation of N and H atoms are 218 kJ mol^{-1} and 470.65 kJ mol^{-1}. Calculate bond energy of N—H bond if heat of formation of NH_3 is –46.0 kJ mol^{-1}.

20. In acid solution, the —CHO group undergoes hydration to form gemdiol  $HO—\overset{|}{\underset{\underset{H}{|}}{C}}---OH$, which is unstable and cannot be isolated. Given the bond energies > C ═ O : 749 kJ mol^{-1}, O — H : 464 kJ mol^{-1}, C — O : 360 kJ mol^{-1}, determine whether gemdiol formation is thermodynamically favoured.

21. Calculate the calorific value, expressed in therms per 1000 cubic feet, of a gaseous fuel of the percentage molar composition: H_2, 30; CO, 20 ; CH_4, 40 ; N_2, 10, using the following data:

$$H_2 + \frac{1}{2}O_2 = H_2O + 68400 \text{ cal.},$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 212000 \text{ cal.},$$

$$CO + \frac{1}{2}O_2 = CO_2 + 68000 \text{ cal.}$$

[1 cubic foot = 28.32 litres ; 1 therm = 2.52×10^7 cal.]

22. One litre sample of a mixture of methane gas and O_2 measured at 25°C and 740 torr, was allowed to react at constant pressure in a calorimeter which together with its content had a heat capacity of 1260 cal/degree. The complete combustion of methane to CO_2 and H_2O caused temperature rise in calorimeter of 0.667 K. What was the percentage of CH_4 in original mixture? Given $\Delta H_{Combustion}$ of CH_4 is –210.8 kcal mol^{-1}.

23. 3.5 g of a fuel (with molecular weight 28), was burnt in a calorimeter and raised the temperature of 1 g water from 25°C to 67.3°C. If all the heat generated was used in heating water, calculate heat of combustion of fuel.

24. Only gases remains alter 15.5 g of carbon is treated with 25.0 litre of air at 25°C and 5.50 atm pressure (Assume 19% by volume O_2, 80% N_2 and 1% CO_2). Determine the heat evolved under constant pressure if ΔH_f for CO and CO_2 are –26.41 and –94.05 kcal/mol.

25. Calculate resonance energy of benzene assuming Kekule formula from the following:

(a) ΔH°_f for $C_6H_6 = -85.77$ kcal

(b) Heat of atomization of carbon is 171.48 kcal mol^{-1}.

(c) Bond energy of C — H, C — C, C ═ C and H — H are 117.23, 81.34, 148.33 and 104.52 kcal mol^{-1} respectively.

26. From the following bond energy (e) and standard ΔH° values for the formation of elements in gaseous state, calculate the standard heat of formation of acetone:

$e_{C-C} = 334.7$ kJ ; ΔH° for $H_{(g)} = 217.9$ kJ
$e_{C-H} = 414.3$ kJ ; ΔH° for $O_{(g)} = 247.5$ kJ
$e_{C-O} = 338.9$ kJ ; ΔH° for $C_{(g)} = 718.3$ kJ

27. Calculate resonance energy for CO_2 from the following:

$e_{C=O}$ 339 kJ
e_{O-O} 498 kJ
$C_{(s)} \longrightarrow C_{(g)}$ 718 kJ

Heat of combustion of carbon = –393 kJ

28. For the reduction of ferric oxide by hydrogen,

$$Fe_2O_{3(s)} + 3H_{2(g)} \longrightarrow 2Fe_{(s)} + 3H_2O_{(l)} \;;\; \Delta H^\circ_{298} = -35.1 \text{ kJ}$$

The reaction was found to be too exothermic to be convenient. It is desirable that ΔH° should be at most –26 kJ. At what temperature it is possible.

$C_{p\,Fe_2O_3} = 104.5$, $C_{p\,Fe(s)} = 25.5$, $C_{p\,H_2O(l)} = 75.3$,

$C_{pH_{2(g)}} = 28.9$ (All in J/mol^{-1})

Answers

1. 4.88 kJ mol^{-1} ; 2. 366.95 g ;

3. 17.601 kJ ;

4. $\Delta H_{combustion}$ $CH_4 = -191.7$ kcal, $\Delta H_{combustion}$ $C_2H_6 = -341.2$ kcal, CH_4 is better fuel ;

5. –908.8 kJ mol^{-1} ; 6. 350 g, 0.03 K, 4275 g ;

7. 3.35 kg ; 8. 3.6 kg ;

9. 18.95% ;

10. (a) –13.4, –7.98, –13.6 MJ kg^{-1}, (b) (i) > (iii) > (ii) ;

11. 1.4 cal ; 12. –241.9 kJ ;

13. 133.86 kJ mol^{-1} ; 14. –16.672 kJ g^{-1} ;

15. –17.13 kcal ; 16. –0.42 kJ ;

17. –41.47 kJ ; 18. +135.2 kcal ;

19. 550.98 kJ ;

20. The reaction is endothermic to an extent of +29 kJ mol^{-1}, Not favoured ;

21. 5.965 therms per cubic foot ; 22. 10% ;

23. –338.4 cal ; 24. –91.2 kcal ;

25. –35.82 kcal mol^{-1} ; 26. 215.7 kJ ;

27. –931 kJ ; 28. 404.18 K.

14

Crystallography

Chapter at a Glance

1. Elements of symmetry in cubic crystals

Plane of symmetry = 3 + 6 = 9
Axis of symmetry = 3 + 4 + 6 = 13
Centre of symmetry = 1
Total elements of symmetry = 9 + 13 + 1 = 23

2. Atomic radius

(a) In s.c. structure, radius of atom = $a/2$
(b) In f.c.c. structure, radius of atom = $a/(2\sqrt{2})$
(c) In b.c.c. structure, radius of atom = $(\sqrt{3}a)/4$

3. Number of atoms per unit cell

(a) In s.c. structure : one atom per unit cell
(b) In f.c.c. structure : 3 face centred atom and one corner atom; In all four atoms per unit cell.
(c) In b.c.c. structure : 1 body centred atom and one corner atom; In all two atoms per unit cell.

4. Co-ordination number

(a) In s.c. structure : Co-ordination number is six.
(b) In f.c.c. structure : Co-ordination number is twelve.
(c) In b.c.c. structure : Co-ordination number is eight.

5. Density of lattice matter

$$\text{Density of lattice matter} = \frac{n \times \text{at. wt.}}{\text{Av. No.} \times \text{Volume of unit cell}}$$

(n is number of atoms per unit cell)

6. Packing density

$$\text{Packing density} = \frac{\text{Volume of atom in unit cell}}{\text{Volume of unit cell}}$$

(a) In s.c. structure : Packing density = 0.52
(b) In f.c.c. structure : Packing density = 0.74
(c) In b.c.c. structure : Packing density = 0.68

7. Dimensions of unit cell

(a) In s.c. structure : $a = \sqrt[3]{\dfrac{1 \times A}{\text{Av. No.} \times \rho}}$

(b) In f.c.c. structure : $a = \sqrt[3]{\dfrac{4 \times A}{\text{Av. No.} \times \rho}}$

(c) In b.c.c. structure : $a = \sqrt[3]{\dfrac{2 \times A}{\text{Av. No.} \times \rho}}$

where a is edge length of unit cell; A is at. wt. and ρ is density of unit cell.

8. Ionic radii

$r_c + r_a = a/2$ (for f.c.c. structure)

$r_c + r_a = (\sqrt{3a})/2$ (for b.c.c. structure)

The Basic Problems with Solution

➤ **Problem 1.** Calculate the number (n) of atoms contained within (a) cubic cell, (b) a body centred cubic cell, (c) a face centred cubic cell.

➤ **Problem 2.** A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. What is the formula of the compound?

➤ **Problem 3.** At room temperature, sodium crystallizes in a body centred cubic lattice with $a = 4.24$ Å. Calculate theoretical density of sodium (At. wt. of Na = 23).

➤ **Problem 4.** Sodium metal crystallizes in a body centred cubic lattice with the cell edge $a = 4.29$ Å. What is the radius of sodium atom?

➤ **Problem 5.** Silver crystallizes in f.c.c. lattice. If edge length of the cell is 4.077×10^{-8} cm and density is 10.5 g cm^{-1}, calculate the atomic mass of silver.

➤ **Problem 6.** Niobium crystallizes in body centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 92.90.

➤ **Problem 7.** Copper crystallizes into a f.c.c. lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

➤ **Problem 8.** Formula mass of NaCl is 58.45 g mol^{-1} and density of its pure form is 2.167 g cm^{-3}. The average distance between adjacent sodium and chloride ions in the crystal is 2.814×10^{-8} cm. Calculate Avogadro constant.

➤ **Problem 9.** Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?

➤ **Problem 10.** Aluminium crystallizes in a cubic close-packed structure. Its metallic radius is 125 pm.

(a) What is the length of the side of the unit cell?

(b) How many unit cells are there in 1.00 cm^3 of aluminium?

➤ **Problem 11.** Gold (atomic radius = 0.144 nm) crystallizes in a face centred unit cell. What is the length of a side of the cell?

➤ **Problem 12.** Thallium chloride, TlCl crystallizes in either a simple cubic lattice or a face centred cubic lattice of Cl^- ions with Tl^+ ions in the holes. If the density of the solid is 9.00 g cm^{-3} and edge of the unit cell is 3.85×10^{-8} cm, what is the unit cell geometry?

➤ **Problem 13.** A solid AB has the NaCl structure. If the radius of the cation is 100 pm, what is the radius of the anion B?

➤ **Problem 14.** The radius of Cs^+ ion in 160 pm while the radius of Cl^- ion is 181 pm. Suggest the co-ordination of cesium in CsCl.

▶ Problem 15. If the radius of the octahedral void is r and radius of the atoms in close packing is R, derive relation between r and R.

▶ Problem 16. The first order diffraction of X-rays from a certain set of crystal planes occurs at an angle of 11.8° from the planes. If the planes are 0.281 nm apart, what is the wavelength of X-rays?

▶ Problem 17. Under what conditions, the Bragg's equation will fail to define a crystal.

Answers

1. (a) 1, (b) 2, (c) 4 ;
2. AB_3 ;
3. 1.002 g cm^{-3} ;
4. 1.8574 Å ;
5. 107.15 ;
6. 1.43×10^{-8} cm ;
7. 8.97 g/cm^3 ;
8. 6.06×10^{23} ;
9. Ni^{2+} = 96%, Ni^{3+} = 4% ;
10. 2.25×10^{22} unit cell ;
11. 0.407 nm ;
12. Cubic cell ;
13. 241.55 to 136.61 pm ;
14. 8 ;
15. $r = 0.414 \times R$;
16. 0.1149 pm ;
17. See solution.

Solution

Solution 1. (a) The cubic unit cell has 8 atoms at eight corners. Each atom is shared by 8 unit cells.

$$\therefore \qquad n = 8 \times \frac{1}{8} = \mathbf{1}$$

(b) The body centred cubic cell consists of 8 atoms at the corners and one atom at centre.

$$n = \left(8 \times \frac{1}{8}\right) + 1 = \mathbf{2}$$

(c) The face centred cubic unit cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore \qquad n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = \mathbf{4}$$

Solution 2. A atoms are at eight corners of the cube.

Therefore, the number of A atoms in the unit cell = $\frac{8}{8} = \mathbf{1}$

B atoms are at the face centre of six faces

Therefore, its share in the unit cell = $\frac{6}{2} = \mathbf{3}$

The formula is $\boldsymbol{AB_3}$

Solution 3. A body centred cubic unit cell contains 8 atoms at the 8 corners and one in the centre.

$$\therefore \text{ Total number of atoms per unit cell } (n) = 8 \times \frac{1}{8} + 1 = 2$$

$$\because \qquad \text{Density} = \frac{n \times \text{at. wt.}}{\text{Av. No.} \times a^3}$$

$$= \frac{2 \times 23}{6.023 \times 10^{23} \times (4.24 \times 10^{-8})^3} = \mathbf{1.002\ g\ cm^{-3}}$$

Solution 4. Radius of Na (if b.c.c. lattice) = $\frac{\sqrt{3}a}{4}$

$$\therefore \qquad = \frac{\sqrt{3} \times 4.29}{4} = \mathbf{1.8574\ \text{Å}}$$

Solution 5. Edge length $(a) = 4.077 \times 10^{-8}$ cm

$\therefore$ Volume of unit cell $(a^3) = (4.077 \times 10^{-8})^3 = 67.77 \times 10^{-24}\ \text{cm}^3$

In a f.c.c. unit cell there are four atoms per unit cell (*i.e.*, $n = 4$)

$$\text{Atomic mass of Ag} = \frac{\text{Density} \times \text{Av.No.} \times \text{Volume of unit cell}}{n}$$

$$= \frac{10.5 \times 6.023 \times 10^{23} \times 67.77 \times 10^{-24}}{4}$$

$$= \mathbf{107.15}$$

Solution 6. $$\text{Atomic mass of Nb} = \frac{\text{Density} \times 6.023 \times 10^{23} \times \text{Volume}}{n}$$

For b.c.c., $n = 2$, Atomic mass of Nb = 92.90

$$\therefore \quad 92.90 = \frac{8.55 \times 6.023 \times 10^{23} \times V}{2}$$

$$\therefore \quad V = 3.6 \times 10^{-23}\ \text{cm}^3$$

Now, $V = a^3$

$$\therefore \quad a = \sqrt[3]{(3.6 \times 10^{-23})} = 3.3 \times 10^{-8}\ \text{cm}$$

For b.c.c. structure $r = \frac{\sqrt{3}}{4} a = \mathbf{1.43 \times 10^{-8}\ cm}$

Solution 7. $$\text{Atomic mass} = \frac{\text{Density} \times \text{Av.No.} \times \text{Volume of unit cell}}{n}$$

$n = 4$ (for f.c.c.)

$$\therefore \quad \text{Density} = \frac{63.55 \times 4}{6.023 \times 10^{23} \times (3.61 \times 10^{-8})^3} = \mathbf{8.97\ g/cm^3}$$

The calculated value 8.97 g/cm^3 is closer to given value 8.92 g/cm^3.

Solution 8. $$\text{Density} = \frac{\text{Formula mass} \times n}{\text{Av. No.} \times \text{Volume}}$$

$n = 4$ (for f.c.c.), $d = 2.167\ \text{g/cm}^3$, formula mass = 58.45 g/mol

For f.c.c. structure of NaCl, edge length $= 2(r^+ + r^-)$

$= 2 \times 2.814 \times 10^{-8} = 5.628 \times 10^{-8}$

$$\therefore \quad \text{Volume} = a^3 = (5.628 \times 10^{-8})^3 = 1.78 \times 10^{-22}\ \text{cm}^3$$

$$\therefore \quad 2.167 = \frac{58.45 \times 4}{\text{Av. No.} \times 1.78 \times 10^{-22}}$$

$$\therefore \quad \text{Av. No.} = \mathbf{6.06 \times 10^{23}}$$

Solution 9. $Ni_{0.98}O_{1.00}$

Let Ni^{2+} be a and Ni^{3+} be $(1-a)$, the average oxidation no. of Ni

$$a \times 2 + (1-a) \times 3 = \frac{2 \times 1.00}{0.98}$$

$$\therefore \quad a = 0.959$$

$$\therefore \quad Ni^{2+} = 0.959, \quad Ni^{3+} = 0.041$$

The percentage of Ni^{2+} is 95.9% ≈ **96%** and that of Ni^{3+} ≈ **4%**

Solution 10. For f.c.c. structure, radius of atom $= \frac{\text{edge length}}{2\sqrt{2}}$

$$\therefore \quad \text{edge length} = 125 \times 2\sqrt{2} = 354 \text{ pm}$$

$$\text{Volume of unit cell} = a^3 = (354 \times 10^{-12})^3 \text{m}^3$$

$$= 4.436 \times 10^{-29} \text{ m}^3$$

$$= 4.436 \times 10^{-23} \text{ cm}^3$$

$$\therefore \quad \text{No. of unit cell in 1 cm}^3 = \frac{1}{4.436 \times 10^{-23}}$$

$$= \mathbf{2.25 \times 10^{22}} \textbf{ unit cell}$$

Solution 11. For f.c.c. structure, radius of atom $= \frac{\text{edge length}}{2\sqrt{2}}$

$$\therefore \quad \text{edge length} = 2\sqrt{2} \times r = 2\sqrt{2} \times 0.144$$

$$= \mathbf{0.407 \text{ nm}}.$$

Solution 12.

$$\text{Density} = \frac{\text{Formula mass} \times n}{\text{Av. No.} \times \text{Volume}}$$

$$\therefore \quad 9 = \frac{240 \times n}{6.023 \times 10^{23} \times (3.85 \times 10^{-8})^3}$$

$$\therefore \quad n = 1.288$$

Thus, TlCl is a **cubic cell.**

Solution 13. NaCl has octahedral arrangement and thus $\frac{r^+}{r^-} = 0.414$ to 0.732

If $\quad r^+ = 100$ pm,

then $\quad r^- = \frac{100}{0.414 \text{ to } 0.732}$

$$= \mathbf{241.55 \text{ to } 136.61 \text{ pm}}$$

Solution 14.

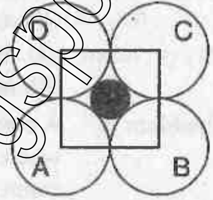
$$\text{Radius of } Cs^+ = 160 \text{ pm}$$

$$\text{Radius of } Cl^- = 181 \text{ pm}$$

$$\text{Radius ratio } \frac{r^+}{r^-} = \frac{160 \text{ pm}}{181 \text{ pm}} = 0.884$$

The radius ratio is greater than 0.732 and therefore the co-ordination number of cesium in CsCl is **8.**

Solution 15. Consider an octahedral void (fig.) represented by the shaded portion (the spheres present below and above the void are not shown). Now suppose the length of the each arm of the square will be $2R$ (R is radius of atom). Let r be the radius of void. For right angle triangle ABC.



$$AC = \sqrt{[(AB)^2 + (BC)^2]} = \sqrt{[(2R)^2 + (2R)^2]} = \sqrt{8}R$$

Also, $AC = R + R + 2r = 2r + 2R = 2(r + R)$

or $\sqrt{8}R = 2\sqrt{2}R = 2(r + R)$

or $r = \sqrt{2}R - R$

$$r = \left[\sqrt{2} - 1\right]R = \mathbf{0.414 \times R}$$

Solution 16.

$$n\lambda = 2d \sin\theta$$

Given : $n = 1$, $d = 0.281 \times 10^{-9}$ m, $\theta = 11.8°$

$$\therefore \quad \lambda = \frac{2 \times 0.281 \times 10^{-9} \times \sin\ 11.8}{1}$$

$$= 2 \times 0.281 \times 10^{-9} \times 0.2044 = \mathbf{0.1149\ nm}$$

Solution 17. According to Bragg's equation : $n\lambda = 2d \sin\theta$

$$\sin\theta = \frac{n\lambda}{2d}$$

Thus, if $2d < n\lambda$, **then** $\sin\theta > 1$ **which is not possible.**

Selected Problems with Solutions

➤ Problem 1. Calculate the number (n) of atoms contained with:
(a) cubic cell,
(b) a body-centred cubic cell,
(c) a face-centred cubic cell.

➤ Problem 2. A body centred cubic lattice is composed of anions Q and cations P, where ions Q occupy the corners and ions P occupy the centre.
(i) What is the formula of the compound?
(ii) What is the co-ordination number of P and Q?

➤ Problem 3. A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. What is the formula of the compound?

➤ Problem 4. Calculate the co-ordination number of an atom in,
(i) A primitive cubic unit cell,
(ii) A body-centred cubic unit cell,
(iii) A face-centred cubic unit cell.

➤ Problem 5. In a close packed structure of an ionic compound anions B form the close packed lattice and the cations A occupy octahedral voids. Predict the formula of the compound.

➤ Problem 6. In corrundum, oxide ions are arranged in h.c.p. array and the aluminium ions occupy two-thirds of octahedral voids. What is the formula of corrundum?

➤ Problem 7. A solid between A and B has the following arrangement of atoms:
(i) Atoms A are arranged in c.c.p. array.
(ii) Atoms B occupy all the octahedral voids and half the tetrahedral voids. What is the formula of the compound?

➤ Problem 8. In a close packed structure of mixed oxides, the lattice is composed of oxide ions, one eighth of tetrahedral voids are occupied by divalent cations while one half of octahedral voids are occupied by trivalent cations. What is the formula of the oxide?

➤ Problem 9. In a crystal of an ionic compound, the anions B form a close packed lattice and the cations A occupy one half of the tetrahedral voids. What is the formula of the compound?

➤ Problem 10. In a crystal of an ionic compound the ions B form the close packed lattice and the ions A occupy all the tetrahedral voids. What is the formula of the compound?

➤ Problem 11. A closed packed structure of uniform spheres has the cell edge $= 0.8$ mm. Calculate the radius of molecule if it has:
(a) simple cubic lattice,
(b) b.c.c. lattice,
(c) f.c.c. lattice.

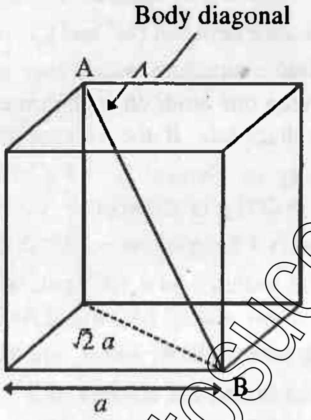
➤ Problem 12. An ionic solid A^+B^- crystallizes as a body centred cubic structure. The distance between cation and anion in the lattice is 338 pm. Calculate the edge length of the unit cell.

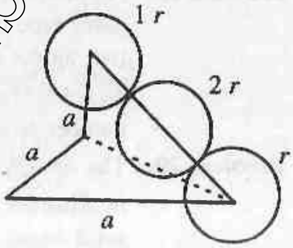
➤ Problem 13. The edge length of a body centred cubic unit cell is 390 pm. If the radius of the cation is 150 pm, what is the radius of the anion?

➤ Problem 14. The edge length of a face centred cubic unit cell is 508 pm. If the radius of the anion is 144 pm, what is the radius of the cation?

➤ Problem 15. The unit cell cube length for LiCl (NaCl structure) is 14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.

➤ Problem 16. The length of the unit cell edge of a body-centred cubic metal crystal is 352 pm. Calculate the radius of an atom of the metal.





➤ Problem 17. Cessium bromide crystallizes in the cubic system. Its unit cell has a Cs^+ ion at the body centre and a Br ion at each corner. Its density is 4.44 g cm^{-3}. Determine the length of the unit cell edge.

➤ Problem 18. Calculate the value of Avogadro number from the internuclear distance of adjacent ions in NaCl, 0.282 nm and the density of solid NaCl is 2.17×10^3 kg/m^3. A unit cell contains 4 NaCl formula units.

➤ Problem 19. Gold has a close-packed structure which can be viewed as spheres occupying 0.74 of the total volume. If the density of gold is 19.3 g/cc, calculate the apparent radius of a gold ion in the solid.

➤ Problem 20. Lithium borohydride crystallizes in an orthorhombic system with 4 molecule per unit cell. The unit cell dimensions are $a = 6.8$ Å, $b = 4.4$ Å and $c = 7.2$ Å. If the molar mass is 21.76, calculate density of crystal.

➤ Problem 21. An element crystallizes as body centred cubic lattice. Its density is 7.12 g cm^{-3} and the length of the side of the unit cell is 2.88 Å. Calculate the number of atoms present is 288 g of the element.

➤ Problem 22. A compound CuCl has face-centred cubic structure. Its density is 3.4 g cm^{-3}. What is the length of unit cell?

➤ Problem 23. The density of KCl is 1.9893 g cm^{-3} and the length of a side unit cell is 6.29082 Å as determined by X-ray diffraction. Calculate the value of Avogadro's number.

➤ Problem 24. A f.c.c. element (atomic mass = 60) has a cell edge of 400 pm. What is its density?

➤ Problem 25. Potassium fluoride (KF) has NaCl structure. Its density is 2.48 g cm^{-3} and its molar mass is 58 g mol^{-1}. Compute the distance between K^+ and F^- ions in KF.

➤ Problem 26. At room temperature, sodium crystallizes in a body centred cubic lattice with $a = 4.24$ Å. Calculate theoretical density of sodium (At wt. of Na = 23).

➤ Problem 27. Use the following data to calculate Avogadro's number (N). Density of NaCl = 2.165 g cm^{-3}. Distance between Na^+ and Cl^- in NaCl = 281 pm.

➤ Problem 28. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}. Calculate the number of atoms present in 200 g of element.

➤ Problem 29. The density of solid argon is 1.65 g/mL at − 233°C. If the argon atom is assumed to be sphere of radius 1.54×10^{-8} cm, what percentage of solid argon is apparently empty space? (At. wt. of Ar = 40).

➤ Problem 30. In a compound AB, the ionic radii A^+ and B^- are 88 pm and 200 pm respectively. What is the co-ordination number of A^+?

➤ Problem 31. Calculate the concentration of cation vacancies if NaCl is doped with 10^{-3} mole % of $SrCl_2$.

➤ Problem 32. In the cubic crystal of CsCl (d = 3.97 g cm^{-3}) the eight corners are occupied by Cl^- with a Cs^+ at the centre and vice-versa. Calculate the distance between the neighbouring Cs^+ and Cl^- ions. What is the radius ratio of the two ions? [At. wt. of Cs = 132.92 and Cl = 35.45]

➤ Problem 33. Calculate the wavelength of X-rays which produces a diffraction angle 2θ equal to 16.80° for a crystal. Assume first order diffraction with inter particle distance in crystal of 0.2 nm.

➤ Problem 34. The angle of diffraction 2θ for a first order nature was found to be 27°8′ using X rays of wavelength 2.29 Å. Calculate the distance between two diffracted planes.

Answers

1. (a) 1, (b) 2, (c) 4 ;

2. (i) PQ, (ii) $P = 8$, $Q = 8$;

3. AB_3 ;

4. (i) 6, (ii) 8, (iii) 12 ;

5. AB ;

6. Al_2O_3 ;

7. AB_2

8. AB_2O_4 ;

9. AB ;

10. A_2B ;

11. (a) 0.4 atm, (b) 0.3464 mm, (c) 0.2828 mm ;

12. 390.3 pm ;

13. 187.7 pm ;

14. 110 pm ;

15. 1.815 Å ;

16. 152.4 pm ;

17. 4.30 Å ;

18. 6.01×10^{23} ;

19. 1.439×10^{-8} cm ;

20. 0.6709 g cm^{-3} ;

21. 3.39×10^{24} ;

22. 5.783 Å ;

23. 6.017×10^{23} ;

24. 6.23 g cm^{-3} ;

25. 268.7 ;

26. 1.002 g cm^{-3} ;

27. 6.089×10^{23} mol^{-1} ;

28. 3.4722×10^{24} atoms ;

29. 62% ;

30. Six ;

31. 6.02×10^{18} ;

32. 0.73 ;

33. 5.84×10^{-11} m ;

34. 4.88×10^{-10} m.

Problems for Self Assessment

1. A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre. What is the formula of compound?
2. A compound alloy of gold and copper crystallizes in a cubic lattice in which the gold atom occupy the lattice points at the corners of a cube and the copper atoms occupy the centres of each of the cube faces. What is the formula of this compound?
3. Calculate the density of diamond from the fact that it has face-centred cubic structure with two atoms per lattice point and a unit cell of edge of 3.569 Å.
4. A compound formed by element X and Y crystallizes in the cubic structure where X is at the corners of a cube and Y are at the face centre. What is the formula of compound? If side length is 5 Å, estimate the density of the solid assuming at. wt. of X and Y as 60 and 90 respectively.
5. If the density of crystalline CsCl is 3.988 g/cm^3, calculate the volume effectively occupied by a single CsCl ion pair in the crystal.
6. A solid AB has the NaCl structure. If the radius of the cation A^+ is 120 pm, calculate the maximum possible value of the radius of the anion B^-.
7. Tungsten has a body-centred cubic lattice and each lattice point is occupied by one atom. Calculate the radius of metallic tungsten if density of tungsten is 19.30 g cm^{-3} and at. wt. is 183.9.
8. The density of CaF_2 is 3.18 g cm^{-3} at 20°C. Calculate the dimensions of a unit cube of the substance containing four Ca^{2+} and eight F^- ions.
9. Sodium crystallizes in b.c.c. lattice of side length 4.30 Å. How many atoms are present in a unit lattice? What is density of the metal? At. wt. of Na = 23.
10. The diffraction of barium with X-ray of wavelength 2.29 Å gives a first order diffraction at 30°. Calculate the distance between diffracted planes.

Answers

1. AB ;
2. $AuCu_3$;
3. 3.509 g cm^{-3} ;
4. XY_3, 4.38 g cm^{-3} ;
5. 7.014×10^{-23} cm^3 ;
6. 290 pm ;
7. 1.37 Å ;
8. 5.46 Å ;
9. 2, 0.96 g cm^{-3} ;
10. 4.42 Å.

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Conductances of Solution

Chapter at a Glance

Resistance (R) :

$$R = \frac{V}{C}; \qquad R \text{ is expressed in ohm}$$

Conductance of Solution (C) :

$$C = \frac{1}{R}; \qquad C \text{ is expressed in ohm}^{-1}\text{, Mho, In SI unit Siemens (S)}$$

Cell Constant :

$$\text{Cell constant} = \frac{l}{a};$$

l is distance of separation of electrodes in cm or m

a is area of cross-section of electrodes in cm^2 or m^2 unit of cell constant is cm^{-1} or m^{-1}

Conductivity of Solution (κ) :

$$\kappa = C \times \frac{l}{a}$$

Equivalent Conductivity (λ) :

$$\lambda = \kappa \times \frac{1000}{N} \qquad (\kappa \text{ is S cm}^{-1}\text{. } N \text{ in eq. / litre})$$

$$\lambda = \kappa \times \frac{1}{N} \qquad (\kappa \text{ in S m}^{-1}\text{, } N \text{ in eq./m}^3)$$

λ is expressed in S cm^2 eq^{-1} or S m^2 eq^{-1}

Molar Conductivity (Λ) :

$$\Lambda = \kappa \times \frac{1000}{M} \qquad (\kappa \text{ in S cm}^{-1}\text{, } M \text{ is mole/litre})$$

$$\Lambda = \kappa \times \frac{1}{M} \qquad (\kappa \text{ in S m}^{-1}\text{, } M \text{ is mole/}m^3)$$

Λ is expressed in S cm^2 $mole^{-1}$ or Sm^2 $mole^{-1}$

Important Conversion :

$1 \text{ S m}^2 \text{ mole}^{-1} = 10^4 \text{ S cm}^2 \text{ mole}^{-1}$

$1 \text{ S cm}^2 \text{ mole}^{-1} = 10^{-4} \text{ S m}^2 \text{ mole}^{-1}$

$1 \text{ S cm}^{-1} = 10^2 \text{ S m}^{-1}$

$1 \text{ S m}^{-1} = 10^{-2} \text{ S cm}^{-1}$

Infinite dilution :

All electrolytes are 100% ionised at infinite dilution.

For weak electrolytes :

Degree of dissociation $\alpha = \dfrac{\lambda_v}{\lambda_\infty}$

Where λ_v and λ_∞ are equivalent conductivities at dilution v and ∞ respectively

Also $\lambda_v = \Lambda_v$ (For monovalent electrolyte)

$\therefore$ $\lambda_v = \Lambda_\infty$ (at infinite dilution)

Thus $\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$

Λ_∞ may also be represented as Λ^0 where zero signifies for zero concentration *i.e.*, infinite dilution.

The dissociation of weak electrolytes is given by :

$$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_v^2}{\left[1 - \dfrac{\Lambda_v}{\Lambda_\infty}\right]\Lambda_\infty^2} = \frac{c\Lambda_v^2}{\Lambda_\infty\left[\Lambda_\infty - \Lambda_v\right]}$$

Where K is dissociation constant and α is degree of dissociation at conc. c.

Kohlrausch law :

$$\lambda^0_{\text{electrolyte}} = \lambda^0_{\text{cation}} + \lambda^0_{\text{anion}}$$

Where λ_c^0 and λ_a^0 are ionic equivalent conducatances of cation and anion at infinite dilution respectively at infinite dilution expressed in $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$.

Thus,

$$\lambda^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$$

$$\lambda^0_{BaCl_2} = \frac{1}{2}\lambda^0_{Ba^{2+}} + \frac{1}{1}\lambda^0_{Cl^-}$$

$$\lambda^0_{AlCl_3} = \frac{1}{3}\lambda^0_{Al^{3+}} + \frac{1}{1}\lambda^0_{Cl^-}$$

$$\lambda^0_{Al_2(SO_4)_3} = \frac{1}{3}\lambda^0_{Al^{3+}} + \frac{1}{2}\lambda^0_{SO_4^{2-}}$$

Thus, in general $\lambda^0 = \dfrac{1}{n^+}\cdot\lambda^0_+ + \dfrac{1}{n^-}\cdot\lambda^0_-$

Where n^+ and n^- are charge on each ion furnished by electrolyte

For molar conducatance (Λ) at infinite dilution

$$\Lambda^0_{BaCl_2} = \lambda^0_{Ba^{2+}} + 2\lambda^0_{Cl^-}$$

$$\Lambda^0_m = r^+\cdot\lambda^0_+ + r^-\lambda^0_-$$

Where r^+ and r^- are the numbers of +ve and –ve ions furnished by one molecule of electrolyte.

$$\lambda^0_+ = u^0_+ \times \text{Faraday}$$

$$\lambda^0_- = u^0_- \times \text{Faraday}$$

Where u^0_+ and u^0_- are ionic mobilities of cations and anions respectively.

Transport no. of cations and anions in an electrolyte :

$$t_{\text{ion}} = \frac{\text{Current carried by an ion}}{\text{Total current carried by both the ions}}$$

or $$t_{\text{cation}} = \frac{\text{Current carried by cation}}{\text{Current carried by anion and cation both}}$$

$$t_{\text{anion}} = \frac{\text{Current carried by anion}}{\text{Current carried by anion and cation both}}$$

$$\therefore \quad t_{\text{cation}} + t_{\text{anion}} = 1$$

$\therefore$ Current carried by an ion $\propto$ speed or ionic mobility of that ion

$$\propto \mu$$

$$\therefore \quad t_c = \frac{u_c}{u_c + u_a}$$

and $$t_a = \frac{u_a}{u_c + u_a}$$

At infinite dilution

Also $$t_c^0 = \frac{u_c^0}{u_c^0 + u_a^0}$$

$$t_a^0 = \frac{u_a^0}{u_c^0 + u_a^0}$$

Also $$t_c^0 \times \lambda_{\text{electrolyte}}^0 = \lambda_c^0$$

and $$t_a^0 \times \lambda_{\text{electrolyte}}^0 = \lambda_a^0$$

The Basic Problems with Solution

➤ **Problem 1.** The conductivity of 0.02N solution of a cell of KCl at 25°C is $2.765 \times 10^{-3}\ S\ cm^{-1}$. If the resistance of a cell containing this solution is 400 ohm, find out cell constant.

➤ **Problem 2.** The resistance of a decinormal solution of a salt occupying a volume between two Platinum electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 30 ohm. Calculate the conductivity and equivalent conductivity of solution.

➤ **Problem 3.** The resistance of a 0.02 N solution of an electrolyte $MgCl_2$ was found to be 210 ohm at 298 K using a conductivity cell with a cell constant of $0.88\ cm^{-1}$. Calculate conductivity and equivalent conductivity and molecular conductivity of solution.

➤ **Problem 4.** The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^{3} ohm. Calculate its conductance, resistivity, conductivity and molar conductivity.

➤ **Problem 5.** Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 Ω. Calculate the conductivity and molar conductivity of 0.02 M KCl solution. [Given conductivity of 0.1M KCl is $1.29\ Sm^{-1}$]

➤ **Problem 6.** The resistance of a solution '*A*' is 50 ohm and that of solution '*B*' is 150 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solution *A* and *B* are mixed, what will be the resistance of the mixture using the same cell? (Assume that there is no increase in the degree of dissociation of *A* and *B* on mixing).

➤ **Problem 7.** Λ^0 for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 $S\ cm^2\ mol^{-1}$ respectively. Calculate Λ^0 for HAc.

➤ **Problem 8.** Calculate equivalent and molar conductivities at infinite dilute for $CaCl_2$ using the data given below :

Λ^0 for $Ca^{2+} = 119.0\ S\ cm^2\ mol^{-1}$ and Λ^0 for $Cl^- = 76.3\ S\ cm^2\ mol^{-1}$

➤ **Problem 9.** The conductivity of 0.001028 M acetic acid is $4.95 \times 10^{-5}\ S\ cm^{-1}$. Calculate its dissociation constant if Λ^0 for acetic acid is $390.5\ S\ cm^2\ mol^{-1}$.

➤ **Problem 10.** How much charge is required for the reduction of

(a) 1 mole of Al^{3+} to Al

(b) 1 mole of Cu^{2+} to Cu

(c) 1 mole of MnO_4^{4-} to Mn^{2+}

(d) 1 mole of $Cr_2O_7^{2-}$ to Cr^{3+}

➤ **Problem 11.** Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity and if $\Lambda^0_{CH_3COOH}$ is 390.5 S cm^2 mol^{-1}, calculate its degree of dissociation and dissociation constant.

Answers

1. 1.106 cm^{-1} ;
2. 1.11 S m^{-1}
3. 4.19×10^{-3} S cm^{-1}, 209.5 S cm^2 eq^{-1}, 419 S cm^2 mole^{-1}
4. 181.82 ohm^{-1}, 87.135 ohm cm, 0.01148 ohm^{-1} cm^{-1}, 229.6 ohm^{-1} cm^2 mol^{-1}
5. 2.48×10^{-3} S cm^{-1}, 111×10^4 S m^2 eq^{-1}
6. 75 ohm
7. 390.5 S cm^2 mol^{-1}
8. 135.8 S cm^2 eq^{-1}, 271.6 S cm^2 mol^{-1}
9. 1.78×10^{-5}
10. (a) 3F, (b) 2F, (c) 5F, (d) 6F
11. 32.76, 0.01%, 2.43×10^{-7}

Solutions

Solution 1. Given for 0.02 *N* solution

$$\kappa = 0.002765 \text{ S cm}^{-1}, \quad R = 400 \text{ ohm}$$

$\because$ $$\kappa = \frac{1}{R} \times \frac{l}{a}$$

$$2.765 \times 10^{-3} = \frac{1}{400} \times \text{cell constant}$$

$\therefore$ $$\text{Cell constant} = \mathbf{1.106\ cm^{-1}}$$

Solution 2. Given, $R = 30$ ohm, $l = 1.80$ cm, $a = 5.4 \text{ cm}^2$

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = \frac{1}{30} \times \frac{1.8}{5.4} = 0.011 \text{ S cm}^{-1}$$

$$= \mathbf{1.11\ S\ m^{-1}}$$

Solution 3. Given for 0.02 N solution.

$$R = 210 \text{ ohm}, \quad \frac{l}{a} = 0.88 \text{ cm}^{-1}$$

$\therefore$ $$\kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = \frac{1}{210} \times 0.88 = \mathbf{4.19 \times 10^{-3}\ S\ cm^{-1}}$$

Also $$\lambda = \kappa \times \frac{1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.02}$$

$$= \mathbf{209.5\ S\ cm^2\ eq^{-1}}$$

[$\because$ $M \times$ Valence factor $= N$ and valence factor for $MgCl_2 = 2$]

Also $$\Lambda_M = \frac{\kappa \times 1000}{M} = \frac{4.19 \times 10^{-3} \times 1000}{0.01}$$

$$= \mathbf{419\ S\ cm^2\ mole^{-1}}$$

Solution 4. Given, [NaOH] = 0.05 M, $l = 50$ cm, diameter of column = 1 cm.

$R = 5.5 \times 10^3$ ohm

$\therefore$ Area of circular column $= \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \text{ cm}^2$

$$\text{Cell constant} = \frac{l}{a} = \frac{50}{0.785} \text{ cm}^{-1}$$

Now $$\text{Conductance} = \frac{1}{R} = \frac{1}{5.55 \times 10^3} \text{ ohm}^{-1}$$

$$= \mathbf{181.82\ ohm^{-1}}$$

$$\text{Resistivity} = R \times \frac{a}{l} = 5.55 \times 10^3 \times \frac{0.785}{50}$$

$$= \mathbf{87.135\ ohm\ cm}$$

$$\text{Conductivity} = \frac{1}{\text{Resistivity}} = \frac{1}{87.135}$$

$$= \mathbf{0.01148\ ohm^{-1}\ cm^{-1}}$$

$$\text{Molar conductivity} = \frac{\text{Conductivity} \times 1000}{M} = \frac{0.01148 \times 1000}{0.05}$$

$$= \mathbf{229.6\ ohm^{-1}\ cm^2\ mol^{-1}}$$

Solution 5. For 0.01 M KCl :

$$\text{Cell constant} = \text{conductivity} \times \text{resistance}$$

$$= 1.29 \times 100 = 129\ \text{m}^{-1}$$

For 0.02 M KCl :

$$\text{Cell constant} = \text{conductivity} \times \text{resistance}$$

$$129 = \text{conductivity} \times 520$$

$$\therefore \quad \text{Conductivity} = 0.248\ \text{S m}^{-1}$$

$$= \mathbf{2.48 \times 10^{-3}\ S\ cm^{-1}}$$

$$\text{Also Molar conductivity} = \text{conductivity} \times \frac{1000}{M_{(\text{mole/l})}}$$

$$= \frac{2.48 \times 10^{-3} \times 1000}{0.02} = 124\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\text{or} \quad \text{Molar conductivity} = \text{Conductivity}\ (\text{S m}^{-1}) \times \frac{1}{\text{M (mole/m}^3)}$$

$$= \frac{0.248 \times 1}{0.02 \times 10^3} = 12.4 \times 10^{-3} = 124 \times 10^{-4}\ \text{S m}^2\ \text{mole}^{-1}$$

$$\left[M = 0.02 \frac{\text{mole}}{\text{litre}} = 0.02 \frac{\text{mole}}{\text{dm}^3} = 0.02 \frac{\text{mole}}{10^{-3}\ \text{m}^3} = 0.02 \times 10^3 \frac{\text{mole}}{\text{m}^3} \right]$$

$$\lambda = \frac{\kappa \times 1000}{N} = \frac{1.11 \times 10^{-2} \times 1000}{0.1}$$

$$= 111\ \text{S cm}^2\ \text{eq}^{-1} = \mathbf{111 \times 10^{-4}\ S\ m^2\ eq^{-1}}$$

$$\text{or} \quad \lambda = \frac{\kappa_{(\text{S m}^{-1})}}{N_{(\text{eq/m}^3)}} = \frac{1.11}{0.1 \times 10^3}$$

$$= \mathbf{111 \times 10^{-4}\ S\ m^2\ eq^{-1}}$$

Solution 6. Let K_1 and K_2 be the conductivity of the solutions A and B respectively and the constant of the cell be x.

$\therefore$ **For solution A :** Conductivity = Conductance × Cell constant

$$K_1 = \frac{1}{50} \times x \qquad \ldots (1)$$

For solution B : Conductivity $K_2 = \frac{1}{150} \times x$ . . . (2)

When equal volumes of A and B are mixed, both the solutions get doulby diluted, hence their individual contribution towards the conductivity of the mixture will be $\frac{K_1}{2}$ and $\frac{K_2}{2}$ respectively and the conductivity of the mixture will be $\frac{1}{2}(K_1 + K_2)$.

$$\therefore \quad \text{For the mixture :} \quad \frac{1}{2}(K_1 + K_2) = \frac{1}{R} \times x \qquad \ldots (3)$$

(R is the resitance of mixture)

From eqs. (1), (2) and (3),

$$R = \mathbf{75\ ohm}$$

Solution 7. Given ,

$$\Lambda^0_{NaCl} = \Lambda^0_{Na^+} + \Lambda^0_{Cl^-} = 126.4 \qquad \ldots (i)$$
$$\Lambda^0_{HCl} = \Lambda^0_{H^+} + \Lambda^0_{Cl^-} = 425.9 \qquad \ldots (ii)$$
$$\Lambda^0_{NaAc} = \Lambda^0_{Na^+} + \Lambda^0_{Ac^-} = 91.0 \qquad \ldots (iii)$$

Adding (ii) and (iii) and then subtracting (i)

$$\Lambda^0_{HAc} = \Lambda^0_{H^+} + \Lambda^0_{Ac^-} = 425.9 + 91.0 - 126.4$$
$$= \mathbf{390.5\ S\ cm^2\ mol^{-1}}$$

Solution 8.

$$\lambda^0_{CaCl_2} = \frac{1}{2}\lambda^0_{Ca^{2+}} + \frac{1}{1}\lambda^0_{Cl^-}$$
$$= \frac{1}{2} \times 119.0 + 76.3$$
$$= \mathbf{135.8\ S\ cm^2\ eq^{-1}}$$
$$\Lambda^0_{CaCl_2} = \Lambda^0_{Ca^{2+}} + 2\,\Lambda^0_{Cl^-}$$
$$= 119.0 + 2 \times 76.3$$
$$= \mathbf{271.6\ S\ cm^2\ mol^{-1}}$$

Solution 9. For acitic acid, $\kappa = 4.95 \times 10^{-5}\ S\ cm^{-1}$

$$\therefore \quad \Lambda_v \text{ of } CH_3COOH = \kappa \times \frac{1000}{M} = 4.95 \times 10^{-5} \times \frac{1000}{0.001028}$$
$$= 48.15\ S\ cm^2\ mol^{-1}$$

Also Λ° of $CH_3COOH = 390.5\ S\ cm^2\ mol^{-1}$

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{48.15}{390.5} = 0.1233$$

Now

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \times (0.1233)^2}{(1-0.1233)}$$
$$= \mathbf{1.78 \times 10^{-5}}$$

Solution 10. Change required to reduce 1 mole

$= \text{no. of electrons} \times \text{Av. No.} \times \text{charge of electron}$

$= n \times F \qquad (F = 6.023 \times 10^{23} \times 1.602 \times 10^{-19})$

(a) $Al^{3+} + 3e \longrightarrow Al \qquad \therefore$ charge needed = **3F**

(b) $Cu^{2+} + 2e \longrightarrow Cu \qquad \therefore$ charge needed = **2F**

(c) $Mn^{7+} + 5e \longrightarrow Mn^{2+} \qquad \therefore$ charge needed = **5F**

(d) $Cr_2^{6+} + 6e \longrightarrow 2Cr^{3+} \qquad \therefore$ charge needed = **6F**

Solution 11.

$$\Lambda_v = \kappa \times \frac{1000}{M}$$

$$= \frac{7.896 \times 10^{-5} \times 1000}{0.00241} = \mathbf{32.76}$$

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{32.76}{390.5} = 0.1 \times 10^{-3} = \mathbf{0.01\%}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$= \frac{0.00241 \times (0.01)^2}{0.99} = \mathbf{2.43 \times 10^{-7}}$$

Selected Problems with Solutions

➤ **Problem 1.** The equivalent conductance of 0.20 N solution of $MgCl_2$ is 97.1 $S\ cm^2\ eq.^{-1}$ at 25°C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when the potential difference between the electrodes is 5 volt?

➤ **Problem 2.** The equivalent conductivity of acetic acid at infinite dilution is 387 $S\ cm^2\ eq.^{-1}$. At the same temperature, 0.001 *M* solution of acetic acid, it is 55 $S\ cm^2\ eq.^{-1}$. What is the degree of dissociation of 0.1 *N* acetic acid? Assume $1 - \alpha \approx 1$

➤ **Problem 3.** A big irregular shaped vessel contained water, the sp. conductance of which was $2.56 \times 10^{-5}\ S\ cm^{-1}$. 500 g of NaCl was then added to the water and the conductivity after the addition of NaCl, was found to be $3.10 \times 10^{-5}\ S\ cm^{-1}$. Find the capacity of the vessel if it is fulfilled with water (λ^{∞} NaCl = 149.9).

➤ **Problem 4.** At 18°C the conductance of H^+ and CH_3COO^- at infinite dilution are 315 and 35 $S\ cm^2\ eq^{-1}$, respectively. The conductivity of 0.001 *N* solution of acetic acid is $4.1 \times 10^{-4}\ S\ cm^{-1}$ at the same temperature. What is the degree of dissociation of acetic acid?

➤ **Problem 5.** Ionic conductances at infinite dilution of Al^{3+} and SO_4^{2-} ions are 189 $S\ cm^2\ eq.^{-1}$ and 160 $S\ cm^2\ eq.^{-1}$ respectively. Calculate the equivalent and molar conductances of $Al_2(SO_4)_3$ at infinite dilution.

➤ **Problem 6.** The molar conductances at infinite dilution of $AgNO_3$, NaCl and $NaNO_3$ are 116.5, 110.3 and 105.2 $S\ cm^2\ mol^{-1}$ respectively. The electrolytic conductance of AgCl in water is $2.40 \times 10^{-6}\ S\ cm^{-1}$ and of water used is $1.16 \times 10^{-6}\ S\ cm^{-1}$. Find the solubility of AgCl in g $litre^{-1}$.

➤ **Problem 7.** The equivalent conductances of CH_3COONa, HCl and NaCl at infinite dilution are 91.6, 425.0 and 128.1 $S\ cm^2\ eq.^{-1}$ respectively. Calculate equivalent conductance of acetic acid at infinite dilution. Also if degree of dissociation of 0.1 *N* acetic acid is 0.001, find the equivalent conductance at this concentration of acetic acid.

➤ **Problem 8.** Calculate the dissociation constant of water at 25°C from the following data:

Conductivity of $H_2O = 5.8 \times 10^{-8}\ S\ cm^{-1}$, $\lambda^{\infty}_{H^+} = 350.0$ and

$\lambda^{\infty}_{OH^-} = 198.0\ S\ cm^2\ eq.^{-1}$

➤ **Problem 9.** The equivalent conductivity of KCl at infinite dilution is 130 S cm^2 eq^{-1}. The transport no. of Cl^- ion in KCl at the same temperature is 0.505. What is the limiting ionic mobility and ionic conductance of K^+. ion?

➤ **Problem 10.** At a certain temperature, the saturated solution of metal chloride *M*Cl has electrolytic conductivity of 1.12×10^{-6} S cm^{-1}. The ionic conductances of M^+ and Cl^- ions at infinite dilution are 54.3 and 65.5 S cm^2 eq^{-1}t same temperature. Find the solubility of *M*Cl at this temperature. Mol wt. of *M*Cl is 143.5.

➤ **Problem 11.** A dilute solution of KCl was placed between two Pt electrodes 10.0 cm apart, across which a potential difference of 6.0 volt was applied. How far would K^+ ions move in 3 hours at 27°C ? Ionic conductance of K^+ at infinite dilution is 73.52 S cm^2 eq^{-1} at 27°C.

➤ **Problem 12.** At 298 K, the conductivity of pure water is 5.51×10^{-8} mho cm^{-1}. The ionic conductances of H^+ and OH^- at this temperature are 349.8 and 198.5 S cm^2 eq^{-1} respectively. Calculate the ionic product of water.

➤ **Problem 13.** A decinormal solution of MNO_3 was electrolysed between Pt electrodes. After passing a small current for two hours, a fall of concentration of 0.0005124 equivalent occurred in anodic solution. The weight of copper deposited in copper coulometer placed in series was found to be 0.03879 g. Find the transport no. of M^+ and NO_3^- in MNO_3.

➤ **Problem 14.** A solution of $AgNO_3$ was electrolysed between silver electrodes. Before electrolysis, 10 g of solution contained 0.01788 g of $AgNO_3$. After the experiment, 20.09 g of the anodic solution contained 0.06227 g of $AgNO_3$. At the same time, 0.009479 g of Cu was deposited in the copper coulometer placed in series. Calculate transport no. of Ag^+ and NO_3^-.

➤ **Problem 15.** Calculate the transport no. of H^+ and Cl^- ions from the following data obtained by moving boundary method using $CdCl_2$ as the indicator electrolyte :

Concentration of HCl solution : 0.1 *N*
Wt. of Ag deposited in coulometer = 0.1209 g
Movement of boundary = 7.50 cm
Cross-section of tube = 1.24 cm^2

Answers

1. 2.913 ampere ;
2. 1.5% ;
3. 2372.5×10^2 litre ;
4. 11.7% ;
5. 143 S cm^2 eq^{-1}, 858 S cm^2 mol^{-1} ;
6. 1.463×10^{-3} g $litre^{-1}$;
7. 388.5 S cm^2 $eq.^{-1}$, 0.3885 S cm^2 $eq.^{-1}$;
8. 2×10^{-16} mol $litre^{-1}$;
9. 6.67×10^{-2} cm^2 sec^{-1} $volt^{-1}$;
10. 1.34×10^{-3} g $litre^{-1}$;
11. 4.938 cm ;
12. 1.01×10^{-14} ;
13. 0.4303, 0.5697 ;
14. 0.4792, 0.5208 ;
15. 0.8308, 0.1692

Problems for Self Assessment

1. When a certain conductance cell was filled with 0.02 M KCl solution (sp. conductivity 0.002768 S cm^{-1}), it had a resistance of 82.4 ohm at 298 K. When filled with 0.005 N K_2SO_4, it had a resistance of 324 ohm. Calculate:
   - (i) Cell constant.
   - (ii) Conductance of 0.005 N K_2SO_4 solution.
   - (iii) Conductivity of 0.005 N K_2SO_4 solution.
   - (iv) Equivalent conductance of 0.005 N K_2SO_4 solution.
   - (v) Molecular conductance of 0.005 N K_2SO_4 solution.
2. The equivalent conductivity of 0.05 N solution of a monobasic acid is 15.8 S cm^2 $eq.^{-1}$. If equivalent conductivity of the acid at infinite dilution is 350 S cm^2 $eq.^{-1}$, calculate the
   - (i) Degree of dissociation of acid.
   - (ii) Dissociation constant of acid.
3. Calculate molar conductance for NH_4OH, given that molar conductances for $Ba(OH)_2$, $BaCl_2$, and NH_4Cl are 523.28, 280.0 and 129.8 S cm^2 mol^{-1} res pectively.
4. A particular cell when filled with 0.05 M solution of NaCl gave a resistance of 140 ohm at 20°C, while with 0.05 M solution of HCl^- gave a resistance of 75 ohm. Calculate the equivalent conductance of HCl solution. Given conductivity of 0.05 M NaCl is 0.00141 S cm^{-1}.
5. Calculate the equivalent conductivity of a salt solution of 0.75 N which in a conductance cell, whose electrodes are 2 cm apart and 6.6 cm^2 in area, was found to offer a resistance of 50 ohm.
6. 0.1 N solution of NaCl at 18°C has a conductivity of 0.039 S cm^{-1}. Its equivalent conductivity at infinite dilution is recorded to be 450 S cm^2 $eq.^{-1}$. Calculate the degree of dissociation of NaCl in solution.
7. Calculate the equivalent conductance at infinte dilution of the salt $NaKC_2O_4$. Given ionic equivalent conductance of oxalate, Na^+ and K^+ ions are 74.1, 50.1 and 73.5 S cm^2 $eq.^{-1}$.
8. The absolute velocity of Ag^+ is 5.7×10^{-4} cm sec^{-1} and of NO_3^- is 6.9×10^{-4} cm sec^{-1}. Assuming complete dissociation, calculate the equivalent conductivity of 0.01 M $AgNO_3$ at infinite dilution.
9. At 291 K, the equivalent conductivity of Ag^+ and NO_3^- are 54.14 and 61.27 at infinite dilution. Calculate the ionic mobilities and transport no. of Ag^+ and NO_3^- at infinite dilution.

10. At 291 K, the conductivity of saturated solution of CaF_2 is 3.86×10^{-5} S cm^{-1} and that of water used for solution is 0.15×10^{-5}. The ionic conductances of Ca^{2+} and F^- at infinite dilution are 51.0 and 47.0 S cm^2 $eq.^{-1}$ respectively. Calculate the solubility of CaF_2 in solution.

11. At 20°C, the equivalent conductivity of $LiNO_3$ at infinite dilution is 100.0 and in 0.2 N solution 79.0 S cm^2 eq^{-1}. Determine concentration of Li^+ in solution.

12. The transport no. of Ag^+ ion in $AgNO_3$ is 0.48. The equivalent conductance of $AgNO_3$ at infinite dilution is 120. Calculate the ionic conductance and ionic mobilities at infinite dilution.

13. A solution of $AgNO_3$ was electrolysed between Pt electrodes for sometime. The concentration of Ag^+ in the anodic solution before and after the electrolysis was x and y equivalents respectively. If the amount of Cu deposited in coulometer connected in series for the same time was Z equivalents, calculate the transport number of Ag^+. What will be transport number of Ag^+ if electrodes used are of Ag?

14. In an electrolysis of $CuSO_4$ solution, between two Cu electrodes the total mass of Cu deposited at the cathode was 0.2295 g. Masses of Cu in the anode liquid before and after electrolysis were 1.1860 g and 1.1365 g respectively in same amount of water. Calculate transport number of Cu^{2+} and SO_4^{2-}.

15. In determining the transport number of Ag^+ and NO_3^- ions, following results were obtained. Before experiment 1 g of anode solution contained 0.001788 g of $AgNO_3$. After the experiment 20g anode solution contained 0.06227 g $AgNO_3$. In a voltmeter placed in series, 0.0322 g of Ag was deposited. Calculate transport number of Ag^+ and NO_3^- ions.

16. Calculate the equivalent conductance at infinite dilution of the salt $NaKC_2O_4$. Given ionic equivalent conductance of oxalate, Na^+ and K^+ ions are 74.1, 50.1 and 73.5 S cm^2 $eq.^{-1}$.

17. The resistance of 0.02 *M* KCl solution was 225 ohm. The specific conductivity of 0.02 *M* KCl solution was 0.0027 S cm^{-1}. The resistance of 0.1 *M* $CuSO_4$ solution was found to be 37.5 ohm using the same cell. Find the equivalent and molar conductances of $CuSO_4$ solution.

18. The conductivity of a saturated solution of AgCl at 25°C after subtracting the conductivity of water is 2.28×10^{-6} S cm^{-1}. Calculate the solubility of AgCl in water at this temperature. Given $\Lambda^{\infty}_{AgCl} = 138.3$ S cm^2 $eq.^{-1}$.

Answers

1. (i) 3.086×10^{-3} mho, (ii) 7.04×10^{-4} S cm^{-1},
(iii) 14.80 S cm^2 eq.$^{-1}$, (iv) 281.6 mho cm^2 mol^{-1} ;

2. (i) 0.04514 , (ii) 1.019×10^{-4}

3. 251.44 S cm^2 mol^{-1}

4. 52.64 S cm^2 eq.$^{-1}$

5. 8.08 S cm^2 eq.$^{-1}$

6. 86.66%

7. 98.85 S cm^2 eq.$^{-1}$

8. 121.59 S cm^2 eq.$^{-1}$

9. $t_{Ag^+} = 0.47$, $t_{NO_3^-} = 0.53$, $u_{Ag^+} = 5.6 \times 10^{-4}$, $u_{NO_3^-} = 6.35 \times 10^{-4}$

10. 1.99×10^{-2} g litre^{-1}

11. 1.106 g litre^{-1}

12. $\lambda_{Ag^+} = 57.6$; $\lambda_{NO_3^-} = 62.4$ S cm^2 eq.$^{-1}$;

$u_{Ag^+} = 5.97 \times 10^{-4}$; $u_{NO_3^-} = 6.47 \times 10^{-4}$ cm^2 sec^{-1} v^{-1}

13. $t_{Ag^+_I} = \dfrac{x-y}{Z}$; $t_{Ag^+_{II}} = \dfrac{Z-(y-x)}{Z}$

14. 0.2157. 0.7843

15. 0.477. 0.523

16. 98.55 S cm^2 eq^{-1} ;

17. 81 S cm^2 eq^{-1}. 162.0 S cm^2 mol^{-1} ;

18. 2.365×10^{-3} g litre^{-1}.

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Miscellaneous Problems

Selected Problems with Solutions

➤ **Problem 1.** Calculate the enthalpy change for the reaction,

$$XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$$

The average Xe — F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/ mol and bond dissociation energy of F_2 is 38 kcal/mol.

➤ **Problem 2.** (i) Calculate the ionization energy for the process,

$$Mg_{(g)} \longrightarrow Mg^{2+}_{(g)} + 2e^-$$ from the following:

$$\begin{tikzcd}
Mg_{(s)} \arrow[dd, "133.2"'] & + \ 1/8S_{8(s)} \arrow[r] \arrow[d, "36.5"] & MgS_{(s)} \ ; \quad \Delta H_f \\
 & S_{(g)} \arrow[r, "-72.4"] & S^{2-}_{(g)} \arrow[u, "-700.2"'] \\
Mg_{(g)} \arrow[rr, "IP_1 + IP_2"] & & Mg^{2+}_{(g)}
\end{tikzcd}$$

All the numerical data are in kcal/mol. ΔH_f is the enthalpy of formation of $MgS_{(s)}$, IP_1 and IP_2 are the first and second ionization energies. Given: $3(IP_1 + IP_2) = -19\Delta H_f$.

(ii) In the preceding problem if $\left[\frac{IP_1}{(IP_1 + IP_2)}\right] = 0.337$, calculate the individual values of IP_1 and IP_2 in electron volts, $1\ eV = 1.6 \times 10^{-19}$ J.

➤ **Problem 3.** In a sample containing fluorine and chlorine atoms, removal of one electron from each atom of the sample involves a total energy expenditure of 300 kJ. Adding one electron to each atom releases a total of 70 kJ. Ionization potentials of F and Cl atoms are 17.422 and 12.967 eV. Electron affinities are 3.45 and 3.61 eV. Calculate the number of fluorine and chlorine atoms in the sample.

➤ **Problem 4.** The first IP of lithium is 5.41 eV and electron affinity of Cl is −3.61 eV. Calculate ΔH in kJ mol^{-1} for the reaction:

$$Li_{(g)} + Cl_{(g)} \longrightarrow Li^+_{(g)} + Cl^-_{(g)}$$

➤ Problem 5. You are given Avogadro's no. of 'X' atoms. If half of the atoms of X transfer one electron to the other half of 'X' atoms, 409 kJ must be added. If these X^- ions are subsequently converted to X^+, an additional 733 kJ must be added. Calculate IP and EA of X in eV. Use (1 eV = 1.602×10^{-19} J and $N = 6.023 \times 10^{23}$).

➤ Problem 6. Helium can be excited to the $1s^1 2p^1$ configuration by light of 58.44 nm. The lowest excited singlet state, with the configuration $1s^1, 2s^1$ lies 4857 cm^{-1} below the $1s^1 2p^1$ state. What would the average He — H bond energy have to be in order that HeH_2 could form non-endothermically from He and H_2? Assume that the compound would form from the lowest excited singlet state of helium. Neglect any differences between ΔE and ΔH. Take ΔH_f (H) = 218.0 kJ/mol.

➤ Problem 7. Calculate the electronegativity of fluorine from the following data:

$$E_{H—H} = 104.2 \text{ kcal mol}^{-1}$$

$$E_{F—F} = 36.6 \text{ kcal mol}^{-1}$$

$$E_{H—F} = 134.6 \text{ kcal mol}^{-1}$$

➤ Problem 8. 1 g of Mg atoms in the vapour phase absorbs 50.0 kJ of energy. Find the composition of Mg^+ and Mg^{2+} formed as a result of absorption of energy. IE_1 and IE_2 for Mg are 740 and 1450 kJ mol^{-1} respectively.

➤ Problem 9. A mixture contains atoms of fluorine and chlorine. The removal of an electron from each atom of sample absorbs 284 kJ while the addition of an electron to each atom of mixture releases 68.8 kJ. Determine the percentage composition of mixture. Given IE_1 for F and Cl are 27.91×10^{-22} and 20.77×10^{-22} kJ/atom respectively and EA_1 for F and Cl are -5.53×10^{-22} and -5.78×10^{-22} kJ/atom respectively.

➤ Problem 10. The boiling point of krypton (Kr) and radon (Rn) are −152°C and −62°C respectively. Calculate the approximate boiling point of xenon.

➤ Problem 11. Calculate the % ionic character in HCl molecule. Given bond length of HCl is 1.275 Å and $\mu_{HCl} = 1.03$ debye.

➤ Problem 12. The dipole moment of LiH is 1.964×10^{-29} Cm and the intermolecular distance between Li and H in this molecule is 1.596 Å. What is per cent ionic character in molecule?

➤ Problem 13. The experimental dipole moment of water molecule is 1.84 D. Calculate the bond angle H—O—H in water molecule, if dipole moment of OH bond is 1.5 D.

➤ Problem 14. The H—O—H bond angle in the water molecule is 105°, the H—O bond distance being 0.94 Å. The dipole moment for the molecule is 1.85 D. Calculate the charge on the oxygen atom.

➤ **Problem 15.** Assuming that all the four valency of carbon atom in propane pointing towards the corners of a regular tetrahedron, calculate the distance between the terminal carbon atoms in propane. Given, C—C single bond length is 1.54 Å.

➤ **Problem 16.** Calculate the molecular weight of HF if density of HF gas is 3.17 g/L at 300 K and 1.0 atm. Comment on the result.

➤ **Problem 17.** Assuming covalent radii to be additive property; calculate the iodine-iodine distances in *o*-, *m*-, *p*-di-iodobenzene. The benzene ring is regular hexagon and each C—I bond lies on a line passing through the centre of hexagon. The C—C bond length in C_6H_6 are 1.40 Å and covalent radius of iodine and carbon atom are 1.33 Å and 0.77 Å. Also neglect different overlapping effect.

➤ **Problem 18.** A solution containing 2.665 g of $CrCl_3{\cdot}6H_2O$ is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 2.87 g of AgCl. Deduce the structure of compound.

➤ **Problem 19.** 1 g of the complex $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ was passed through a cation exchanger to produce HCl. The acid liberated was diluted to 1 litre. What is normality of this acid solution?

➤ **Problem 20.** A solution containing 0.319 g of complex $CrCl_3{\cdot}6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 mL of 0.125 *M* NaOH. What is the correct formula of complex?

➤ **Problem 21.** Metal carbonyls having formula $M(CO)_x$, where x is the number of carbonyl units co-ordinated to metal *M* are formed by Fe, Cr and Ni. If effective atomic number of each metal is 36, what are the formula of metal carbonyls?

➤ **Problem 22.** Calculate the electronegativity X of silicon using Allred-Rochow equation: $X = \frac{0.359\,Z'}{r^2_{(\text{Å})}} + 0.744$ where Z' is $Z_{\text{effective}}$ calculated on the basis of Slater's rule taking all the electrons. Covalent radius of Si = 1.175 Å.

➤ **Problem 23.** 100 mL of 1×10^{-2} *M* aqueous solution of an organic compound were shaken with 50 mL of an organic solvent till equilibrium is attained. Calculate the concentration of organic compound in organic solvent. Given that distribution coefficient of organic compound for the given solvent is 50 in favour of organic solvent.

➤ **Problem 24.** Distribution coefficient of an organic acid between water and benzene is 4.1 is favour of C_6H_6. If 5 g of the acid is distributed in between 50 mL of benzene and 100 mL of water, calculate the concentration of the acid in two solvents.

➤ **Problem 25.** 10 g of iodine is allowed to distribute between H_2O and CCl_4. If the partition coefficient is 85 in favour of CCl_4, find the ratio between volumes of H_2O and CCl_4 such that 5 g of iodine will be present in aqueous layer.

➤ **Problem 26.** Prove that succinic acid forms a dimer in C_6H_6 from the following data:

Grams of acid per 100 mL H_2O	0.2	0.4	0.6
Grams of acid per 100 mL C_6H_6	0.64	2.55	5.78

➤ **Problem 27.** 50 mL of a saturated solution of iodine in water is shaken with 5 mL $CHCl_3$ to attain equilibrium. If partition coefficient of I_2 in favour of $CHCl_3$ is 90, calculate the amount of I_2 in $CHCl_3$. The solubility of I_2 in water is 0.7 g litre^{-1}.

➤ **Problem 28.** An organic acid is three times more soluble in water than hexane. When 14.5 g of the acid is mixed with 100 mL of water and 100 mL of hexane, 1.6 g of acid was found to be present in 50 mL of hexane. Calculate degree of dissociation of acid in water.

➤ **Problem 29.** A solution of H_2O_2 in amyl alcohol containing 20 g of H_2O_2 in 200 cm^3 is to be extracted out with 200 cm^3 of water when used in:

(a) One lot,

(b) Two lots of 100 cm^3 each.

Calculate the amount of H_2O_2 extracted in each case. The partition coefficient of H_2O_2 between amyl alcohol and water is 1 : 7.

➤ **Problem 30.** An organic substance has a normal molecular weight in water but gives a higher value in C_6H_6. The following data were obtained during a distribution experiment.

Conc. of substance in water (gL^{-1})	0.01	0.12	0.24
Conc. of substance in C_6H_6 (gL^{-1})	1.848×10^{-5}	2.661×10^{-3}	1.089×10^{-2}

Find the degree of complexity of the substance in C_6H_6.

➤ **Problem 31.** Iodine was permitted to distribute between water and CCl_4. When 50 mL of aqueous layer was treated with 1 *M* $Na_2S_2O_3$ solution, 5 mL of $Na_2S_2O_3$ were used up. 1 mL of CCl_4 layer consumed 17 mL of 0.5*M* $Na_2S_2O_3$ solution. Calculate the partition coefficient of I_2 in between CCl_4 and H_2O.

Answers

1. 292 kcal mol^{-1} ;

2. (i) 548.27 kcal, (ii) $IP_1 = 184.77$ kcal mol^{-1}, (iii) $IP_2 = 363.50$ kcal mol^{-1} ;

3. $n_1 = 6.35 \times 10^{22}$ atoms, $n_2 = 6.023 \times 10^{22}$ atoms ;

4. 173.7 kJ ; **5.** IP = 11.835 eV, EA = 3.358 eV ;

6. 1211.8 kJ mol^{-1} ; **7.** 3.88 ;

8. $Mg^+ = 68.28\%$, $Mg^{2+} = 31.72$; **9.** F = 37.76%, Cl = 64.24% ;

10. −107°C ; **11.** 16.82% ;

12. 76.82% ; **13.** 104°20′ ;

14. 3.23×10^{-10} esu cm ; **15.** 2.514 Å ;

16. 78.08 ;

17. (a) 3.50 Å, (b) 6.06 Å, (c) 7.0 Å ;

18. See solution ; **19.** 0.0075 ;

20. $[Cr(H_2O)_6]Cl_3$;

21. $Fe(CO)_5$, $Cr(CO)_6$, $Ni(CO)_4$; **22.** 1.73

23. 9.62×10^{-4} mol per 50 mL ;

24. $C_6H_6 = 67.22$ g/litre, $H_2O = 16.39$ g/litre ;

25. 85 : 1 ; **26.** See solution ;

27. 0.0315 g in 5 mL of $CHCl_3$; **28.** 15.04% ;

29. (a) 17.5 g, (b) 19.01 g ; **30.** See solution (dimer in C_6H_6) ;

31. 85 ;

Solutions

Solution 1.

$$XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$$

$$e_{Xe—F} = 34 \text{ kcal mol}^{-1} \quad ; \quad e_{F—F} = 38 \text{ kcal mol}^{-1}$$

$$\therefore \quad F + F \longrightarrow F_2 \text{ or } e_{F_2} = -38 \text{ kcal mol}^{-1}$$

$$IE_1 \text{ of Xe} = 279 \text{ kcal mol}^{-1} \quad ; \quad EA_1 \text{ of F} = -85 \text{ kcal mol}^{-1}$$

$$\Delta H \text{ for change} = IE_1 \text{ of Xe} + EA_1 \text{ of } F^- + e_{F_2} + 4e_{Xe—F}$$

$$= 279 - 85 - 38 + 4 \times 34$$

$$= \mathbf{292 \text{ kcal mol}^{-1}}$$

Solution 2. (i) Given, $3[IP_1 + IP_2] = -19 \quad \Delta H_f$

Also from Born-Haber cycle of MgS

$$\Delta H_f = H{\cdot}S_{Mg} + IP_1 + IP_2 + \frac{1}{8} H{\cdot}S_S + (EA_1 + EA_2)_S + E_L$$

From the chart using the values

$$\Delta H_f = 133.2 + IP_1 + IP_2 + \frac{1}{8} \times 36.5 + (-72.4) - 700.2$$

$$\Delta H_f = 133.2 + \left(\frac{-19}{3} \Delta H_f\right) + \frac{36.5}{8} - 72.4 - 700.2$$

$$\therefore \quad \Delta H_f + \frac{19}{3} \Delta H_f = -634.84$$

$$\therefore \quad \Delta H_f = -86.6 \text{ kcal}$$

$$\therefore \quad IP_1 + IP_2 = \frac{-19 \times (-86.6)}{3} = \mathbf{548.27 \text{ kcal}}$$

(ii) $IP_1 + IP_2 = 548.27$

Also $\dfrac{IP_1 + IP_2}{IP_1} = \dfrac{1}{0.337}$

$$\therefore \quad \frac{548.27}{IP_1} = \frac{1}{0.337}$$

$$\therefore \quad IP_1 = \mathbf{184.77 \text{ kcal mol}^{-1}} \text{ and } IP_2 = \mathbf{363.50 \text{ kcal mol}^{-1}}$$

Solution 3.

$$F \longrightarrow F^+ + e \quad ; \quad IP_1 = 17.422 \text{ eV}$$

$$Cl \longrightarrow Cl^+ + e \quad ; \quad IP_2 = 12.967 \text{ eV}$$

$$F + e \longrightarrow F^- \quad ; \quad EA_1 = 3.45 \text{ eV}$$

$$Cl + e \longrightarrow Cl^- \quad ; \quad EA_2 = 3.61 \text{ eV}$$

Let n_1 atoms of F and n_2 atoms of Cl are present

$$n_1 \times 17.422 + n_2 \times 12.967 = \frac{300 \times 10^{+3}}{1.602 \times 10^{-19}} \text{ eV} \qquad (\because \ 1.602 \times 10^{-19} \text{ J} = 1 \text{ eV})$$

or $$17.422\, n_1 + 12.967\, n_2 = 187.27 \times 10^{22} \qquad (1)$$

and $$n_1 \times (-3.45) + n_2 \times (-3.61) = -\frac{70 \times 10^3}{1.602 \times 10^{-19}}\ \text{eV}$$

or $$3.45n_1 + 3.61n_2 = 43.70 \times 10^{22} \qquad \ldots(2)$$

By (1) and (2),

$$\mathbf{n_1 = 6.35 \times 10^{22}\ \text{atoms}}$$

$$\mathbf{n_2 = 6.023 \times 10^{22}\ \text{atoms}}$$

Solution 4. $$\Delta H/\text{molecule of } Li^+ \text{ and } Cl^- = \underset{Li}{IP_1} + \underset{Cl}{EA}$$

$$= 5.41 - 3.61 = 1.80\ \text{eV}$$

$\because$ $$Li \longrightarrow Li^+ + e \qquad IP_1 = +\text{ve}$$

and $$Cl + e \longrightarrow Cl^- \qquad EA = -\text{ve}$$

$\therefore$ $$\Delta H/\text{mol} = 1.8 \times 6.023 \times 10^{23}\ \text{eV}$$

$$= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\ \text{J}$$

$$= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \times 10^{-3}\ \text{kJ} = \mathbf{173.7\ kJ}$$

Solution 5. Assume that,

$$X \longrightarrow X^+ + e; \qquad \Delta H = IP_1 = a\ \text{eV}$$

$$X + e \longrightarrow X^-; \qquad \Delta H = -EA_1 = -b\ \text{eV}$$

if $N/2$ atoms of X lose electrons which are taken up by remaining $N/2$ of X to give X^-, then

$$a \times \frac{N}{2} - b \times \frac{N}{2} = \frac{409 \times 10^3}{1.602 \times 10^{-19}}\ \text{eV}$$

or $$a - b = \frac{409 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$\therefore$ $$a - b = 8.477$$

Now, $N/2$ of X^- lose two electrons to give X^+

$$X^- \longrightarrow X + e; \qquad \Delta H = +EA_1 = +b$$

$$X \longrightarrow X^+ + e; \qquad \Delta H = +IP_1 = +a$$

$\therefore$ $$a \times \frac{N}{2} + b \times \frac{N}{2} = \frac{733 \times 10^3}{1.602 \times 10^{-19}}\ \text{eV}$$

or $$a + b = \frac{733 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$$a + b = 15.194$$

$\therefore$ $$\mathbf{a = 11.835\ eV}$$

and $$\mathbf{b = 3.358\ eV}$$

Solution 6. Formation of HeH_2 requires energy equal to sum of

(i) energy for excitation from $1s^2$ to $1s^1 2s^1$ to form He singlet is equal to : [Energy needed for excitation from $1s^2$ to $1s^1 2p^1$ – energy level difference in between $1s^1 2s^1$ and $1s^1 2p^1$]

Thus, $$E_{He}\text{ singlet} = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = 3.40 \times 10^{-18} - 9.66 \times 10^{-20}\text{ J}$$
$$= 3.30 \times 10^{-18}\text{ J/molecule}$$

where $\lambda_1 = 58.44 \times 10^{-9}$ m and $\frac{1}{\lambda_2} = 4857\text{ cm}^{-1}$

(ii) energy to produce two mole of H, *i.e.*, 2 × 218.0 = 436 kJ/mol

Thus, E for 2 mole bonds of He — H
$$= [3.30 \times 10^{-18} \times 6.023 \times 10^{23} + 436 \times 10^3]\text{ J/mol}$$
$$= 2423.5\text{ kJ mol}^{-1}$$
$$\therefore \quad E_{He—H} = \mathbf{1211.8\ kJ\ mol^{-1}}$$

Solution 7. Let X_H and X_F be the electronegativity of H and F, then
$$X_H \sim X_F = 0.208\,[E_{H—F} - (E_{H—H} \times E_{F—F})^{1/2}]^{1/2}$$
$$X_H \sim X_F = 0.208[134.6 - (104.2 \times 36.6)^{1/2}]^{1/2}$$
$$X_H \sim X_F = 1.78 \quad \text{and} \quad X_H < X_F$$

Since, $X_H = 2.1$ (although this value is not given in problem)
$$X_F = 2.1 + 1.78 = \mathbf{3.88}$$

Solution 8. Given,
$$\text{Mole of Hg} = \frac{1}{24}$$

These mole of Mg will be converted to Mg^+ and Mg^{2+}. Let a mole of Mg^+ are formed, then
$$a \times 740 + \left(\frac{1}{24} - a\right) \times 2190 = 50$$
$$\therefore \quad a = 0.02845$$
$$\therefore \quad \%\text{ of }Mg^+ = \frac{0.02845}{1/24} \times 100 = \mathbf{68.28\%}$$
$$\%\text{ of }Mg^{2+} = \mathbf{31.72\%}$$

Solution 9. Let the mixture contains a, b atoms of F and Cl respectively.

Thus, total energy absorbed is:
$$284 = a \times 27.91 \times 10^{-22} + b \times 20.77 \times 10^{-22} \quad \ldots(1)$$

Also total energy released is:

$$-68.8 = a \times (-5.53 \times 10^{-22}) + b \times (-5.78 \times 10^{-22})$$

or $$68.8 = 5.53 \times 10^{-22} \times a + 5.78 \times 10^{-22} \times b \quad \ldots(2)$$

By Eqs. (1) and (2),

$$\therefore \quad a = 4.57 \times 10^{22}$$

$$b = 7.53 \times 10^{22}$$

$$\therefore \quad \% \text{ of F} = \left[\frac{4.57 \times 10^{22}}{4.57 \times 10^{22} + 7.53 \times 10^{22}}\right] \times 100 = \mathbf{37.76\%}$$

$$\% \text{ of Cl} = \mathbf{62.24\%}$$

Solution 10. The zero gp. members are He, Ne, Kr, Xe, Rn. Law of triad suggests that property of a middle element in a group of three is average of its two adjacent elements.

$$\therefore \quad \text{B. pt. of Xe} = \frac{\text{b. pt. of Kr} + \text{b. pt. of Rn}}{2} = \frac{-152 + (-62)}{2}$$

$$= -\frac{214}{2} = -\mathbf{107°C}$$

Solution 11. Dipole moment of HCl (μ_{HCl}) is given by,

$$\mu_{HCl} = \delta \times d$$

$$\because \quad \mu = 1.03 \text{ D} = 1.03 \times 10^{-18} \text{ esu cm}$$

and $$d = 1.275 \text{ Å} = 1.275 \times 10^{-8} \text{ cm}$$

$$\therefore \quad 1.03 \times 10^{-18} = \delta \times 1.275 \times 10^{-8}$$

$$\therefore \quad \delta = 0.808 \times 10^{-10} \text{ esu}$$

$\because$ 4.803×10^{-10} esu charge, % ionic nature of HCl = 100

$\therefore$ 0.808×10^{-10} esu charge, % ionic nature of HCl

$$= \frac{100 \times 0.808 \times 10^{-10}}{4.803 \times 10^{-10}} = \mathbf{16.82\%}$$

Solution 12. $$\mu_{\text{molecule}} - \delta \times d$$

$$\therefore \quad 1.964 \times 10^{-29} = \delta \times 1.596 \times 10^{-10}$$

$$\therefore \quad \delta = 1.2306 \times 10^{-19} \text{ coulomb}$$

$$\therefore \quad \% \text{ ionic nature} = \frac{1.2306 \times 10^{-19}}{1.602 \times 10^{-19}} \times 100 = \mathbf{76.82\%}$$

Solution 13.

$$\mu = \sqrt{\mu_1^2 + \mu_1^2 + 2\mu_1\mu_1 \cos\alpha}$$

In H_2O only two dipoles equal to μ_1 are operating due to two O—H bonds.

Thus, $$1.84 = \sqrt{(1.5)^2 + (1.5)^2 + 2 \times (1.5) \times (1.5) \cos\alpha}$$

∴ $$\cos\alpha = -0.2476$$

∴ $$\alpha = \mathbf{104°20'}$$

Solution 14.

$$\therefore \mu_{H_2O} = \sqrt{\mu_{OH}^2 + \mu_{OH}^2 + 2\mu^2 \cos(105)}$$

Since H_2O has two vectors of O—H bond acting at 105°. Let dipole moment of O—H bond be '*a*'

∴ $$1.85 = \sqrt{2a^2(1 + \cos 105)}$$

or $$a, \ i.e., \ \mu_{O—H} = 1.52 \text{ debye} = 1.52 \times 10^{-18} \text{ esu cm}$$

Now $$M_{O—H} = \delta \times d \qquad \text{where, } \delta \text{ is charge on either end}$$

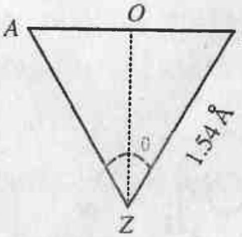
∴ $$1.52 \times 10^{-18} = \delta \times 0.94 \times 10^{-8}$$

∴ $$\delta = 1.617 \times 10^{-10} \text{ esu}$$

Since O acquires 2δ charge, one δ charge from each bond and thus,

Charge on O atom $= 2\delta = 2 \times 1.617 \times 10^{-10} = \mathbf{3.23 \times 10^{-10}}$ **esu cm**

Solution 15. Propane has three carbon atoms. Let *A* and *B* be the terminal carbon atoms and *Z* be the middle carbon. Then,



The angle θ = 109°28′ and $ZB = AZ = 1.54$ Å

Now, $$\frac{AO}{AZ} = \sin\left(\frac{\theta}{2}\right) = \sin\left(\frac{109°28'}{2}\right)$$

$$= \sin 54°44' = \sin 54.73°$$

or $$AO = 0.816 \times AZ = 0.816 \times 1.54 = 1.257 \text{ Å}$$

∴ $$AB = 2 \times AO = 1.257 \times 2 \text{ Å} = \mathbf{2.514 \text{ Å}}$$

Solution 16.

$$\because \qquad PV = \frac{w}{m} RT$$

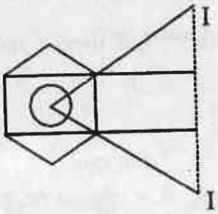
or
$$P = \frac{w}{V \cdot m} RT$$

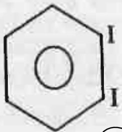
or
$$m = \frac{dRT}{P} = \frac{3.17 \times 0.0821 \times 300}{1} = \mathbf{78.08}$$

Molecular weight of HF in gaseous state is 78.08, whereas its normal molecular weight is 1 + 18 = 19.

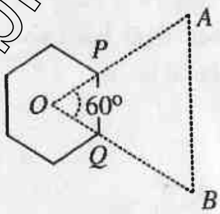
Thus, HF in gaseous state from a tetramer due to strong H-bonding.

Solution 17. **(a) *o*-di-iodobenzene:**





or

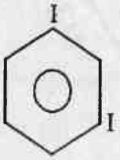


The distance between two I atoms $AB = AO = OB$, because ΔAOB is equilateral triangle.

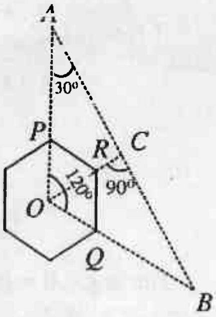
$$\therefore \qquad AB = OP + PA$$

$$\therefore \qquad AB = OP + \text{covalent radius of C} + \text{covalent radius of I}$$
$$= OP + 1.33 + 0.77$$
$$= 1.40 + 1.33 + 0.77$$
$$AB = \mathbf{3.50\ Å}$$
($OP = OQ = PQ$, because ΔOPQ is also equilateral triangle and PQ = C—C bond length)

(b) *m*-di-iodobenzene:



or

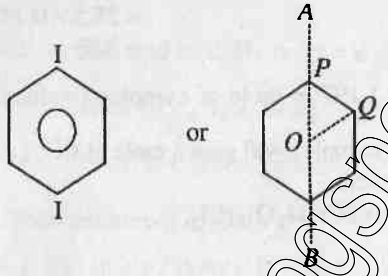


The distance between two I atoms is

$$AB = AC + BC = 2AC \qquad (\because AC = BC)$$
$$= 2AO \cos 30° = 2(AP + OP) \cos 30°.$$
$$= 2(AP + PR) \cos 30° \qquad (OP = PR \because \Delta POR \text{ is equilateral})$$
$$= 2(2.10 + 1.40) \times 0.866$$
$$= 6.06\ Å$$

[$\because$ AP = covalent radius of C + covalent radius of I = 0.77 + 1.33 = 2.10 Å and PR = covalent bond length of C—C = 1.40]

(c) *p*-di-iodobenzene:



$$\therefore \quad AB = OA + OB = 2OA$$
$$= 2(OP + PA)$$
$$= 2 \times (PQ + PA) \qquad (\because OP = PQ; \Delta OPQ \text{ is equilateral})$$
$$= 2\,(PQ + \text{ covalent radius of C + covalent radius of I})$$
$$= 2 \times (1.40 + 0.77 + 1.33) = \mathbf{7.0\ Å}$$

Solution 18. Moles of AgCl obtained

$$= \text{mole of } Cl^- \text{ ions ionised from } \frac{2.665}{266.5} \text{ moles of } CrCl_3\,6H_2O$$
$$= 0.01 \text{ (mol. wt. of } CrCl_3{\cdot}6H_2O = 266.5)$$

$$\therefore \quad \text{Moles of } Cl^- \text{ ionised} = \frac{2.87}{143.5} = 0.02$$

Thus, 0.01 mole of complex $CrCl_3{\cdot}6H_2O$ gives 0.02 moles of Cl^- on ionisation.

Now, since co-ordination number of Cr is six and only one Cl ion is attached to Cr by co-ordinate bond or secondary valency and therefore, complex is $[CrCl\,(H_2O)_5]Cl_2\,H_2O$.

$$[CrCl{\cdot}(H_2O)_5]Cl_2{\cdot}H_2O \longrightarrow [CrCl(H_2O)_5]^{2+} + 2Cl^- + H_2O$$
$$2Cl^- + 2AgNO_3 \longrightarrow 2AgCl + 2NO_3^-$$

Solution 19. Mol. wt. of $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O = 266.5$

$$\therefore \quad \text{Moles of complex} = \frac{1}{266.5}$$

Note: 1 mole of $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ will give 2 mole of Cl^- ions or 2 mole of HCl

$$\text{Thus,} \quad \text{mole of HCl formed} = \frac{2 \times 1}{266.5}$$

$$\therefore \quad N_{HCl} = \frac{2 \times 1}{266.5 \times 1} = \mathbf{0.0075}$$

Solution 20. The Cl atoms outside the co-ordination sphere will be ionised to produce acid HCl.

Thus, Meq. of Cl^- ions outside = Meq. of HCl formed

= Meq. of NaOH used

$= 28.5 \times 0.125$

$= 3.56$

$\frac{0.319}{266.5}$ mole or 1.197 *m* mole of complex produce 3.56 Meq. or millimole small of Cl^-. Thus 1 mole of complex will give 3 mole of Cl^-, *i.e.*, all the three Cl atoms are outside the co-ordination sphere.

Thus, complex is $\mathbf{[Cr(H_2O)_6]Cl_3}$.

Solution 21. $M(CO)_x$

In $Fe(CO)_x$: EAN = At. no. of Fe + 2 × No. of ligands, *i.e.*, CO

$\therefore \quad 36 = 26 + 2 \cdot x$

$\therefore \quad x = 5$

$\therefore$ Formula of iron carbonyl is $\mathbf{Fe(CO)_5}$

Similarly, $\mathbf{Cr(CO)_6}$ and $\mathbf{Ni(CO)_4}$

Solution 22. Electronic configuration of Si : $1s^2, 2s^22p^6, 3s^23p^2$

$Z_{effective} = Z - \sigma$ (where σ is screening constant and

$\sigma = [ns \text{ and } np \text{ electrons}] \times 0.35 + (n-1) \text{ electrons} \times 0.85 + (n-2) \text{ electrons} \times 1.0$ (Note—if $n = 1$ then for 1*s* electron the value = 1*s* electrons × 3.0)

$Z = 14 - 4 \times 0.35 + 8 \times 0.85 + 2 \times 1.0 = 3.80.$

$$\therefore \quad X = \frac{0.359 \times 3.8}{(1.175)^2} + 0.744 = \mathbf{1.73}$$

Solution 23. Distribution coefficient of system = 50 in favour of organic solvent

$$[\text{O.C.}] \text{ in water} = 1 \times 10^{-2}\, M$$

$$\therefore \quad [\text{O.C.}] \text{ in 100 mL water} = \frac{10^{-2} \times 100}{1000} = 10^{-3} \text{ mole}$$

Let *a* mole of organic compound be extracted out by 50 mL organic solvent.

At equilibrium,

$$\therefore \quad [\text{O.C.}] \text{ in 50 mL organic solvent} = \frac{a}{50}$$

$$[\text{O.C.}] \text{ in 100 mL } H_2O = \frac{(10^{-3} - a)}{100}$$

Now
$$K = \frac{[\text{O.C.}] \text{ in organic solvent}}{[\text{O.C.}] \text{ in } H_2O}$$

$$50 = \frac{a}{50} \times \frac{100}{(10^{-3} - a)}$$

$$a = \mathbf{9.62 \times 10^{-4}\ mol\ \ per\ 50\ mL}$$

Solution 24. Let the amount of organic acid in C_6H_6 layer = *a* g

∴ Volume of C_6H_6 = 50 mL

∴ Conc. of acid in $C_6H_6 = \frac{a}{50}$ g mL^{-1}

∵ Total amount of acid = 5 g

∴ Amount of acid in H_2O layer = (5 – *a*) g

and Volume of H_2O = 100 mL

∴ Conc. of acid in $H_2O = \frac{5-a}{100}$ g mL^{-1}

Now
$$K = \frac{\text{Conc. of acid in } C_6H_6}{\text{Conc. of acid in } H_2O} = \frac{a}{50} \times \frac{100}{(5-a)}$$

$$4.1 = \frac{a}{50} \times \frac{100}{(5-a)}$$

∴ $a = 3.361$ g

∴ Amount of acid in 50 mL C_6H_6 = **3.361 g**

∴ Acid concentration in $C_6H_6 = \frac{3.361}{50} \times 1000$

$= \mathbf{67.22\ g\ litre^{-1}}$

Also, Amount of acid in 100 mL H_2O = **1.639 g**

∴ Acid concentration in $H_2O = \frac{1.639}{100} \times 1000$

$= \mathbf{16.39\ g\ litre^{-1}}$

Solution 25. Let *x* and *y* litres be volumes of H_2O and CCl_4 respectively.

Total amount of I_2 shaken = 10 g

Amount of I_2 in water layer = 5 g

∴ $[I_2]$ in water $= \frac{5}{x}$ g litre^{-1}

Amount of I_2 in CCl_4 layer = 10 – 5 = 5 g

∴ $[I_2]$ in $CCl_4 = \frac{5}{y}$ g litre^{-1}

Now
$$K = \frac{[I_2] \text{ in } CCl_4}{[I_2] \text{ in water}}$$

$$85 = \frac{5/y}{5/x}$$

i.e., Ratio between volumes of H_2O and CCl_4 = **85 : 1**

Solution 26. Let C_1 and C_2 be the concentrations of acid in water and C_6H_6 respectively.

If succinic acid forms dimer in C_6H_6 then

$$K = \frac{C_1}{\sqrt{C_2}} \qquad \ldots(1)$$

Using Eq. (1) for the given data

$$K_1 = \frac{0.2}{\sqrt{(0.64)}} = 0.25$$

$$K_2 = \frac{0.4}{\sqrt{(2.55)}} = 0.2505$$

$$K_3 = \frac{0.6}{\sqrt{(5.78)}} = 0.2496$$

Since all the values of K are same and thus, succinic acid forms a **dimer in C_6H_6**.

Solution 27. Solubility of I_2 in water = 0.7 g litre^{-1}

$$\therefore \quad \text{Iodine in 50 mL water} = \frac{0.7 \times 50}{1000} = 0.035 \text{ g}$$

Let a g I_2 be extracted out from water layer at equilibrium

$\therefore$ At equilibrium,

$$\text{Amount of } I_2 \text{ in 50 mL } H_2O = (0.035 - a) \text{ g}$$

$$\therefore \quad \text{Concentration of } I_2 \text{ in } H_2O = \frac{(0.035 - a)}{50} \text{ g mL}^{-1}$$

$$\text{Amount of } I_2 \text{ in 5 mL } CHCl_3 = a \text{ g}$$

$$\therefore \quad \text{Concentration of } I_2 \text{ in } CHCl_3 = \frac{a}{5} \text{ g mL}^{-1}$$

Now

$$K = \frac{\text{Conc. of } I_2 \text{ in } CHCl_3 \text{ layer}}{\text{Conc. of } I_2 \text{ in } H_2O \text{ layer}}$$

$$90 = \frac{a/5}{(0.035 - a)/50}$$

$$\therefore \quad \mathbf{a = 0.0315 \text{ g in 5 mL of } CHCl_3}$$

Solution 28. We know,

$$\text{Partition coefficient} = \frac{\text{Solubility in water}}{\text{Solubility in hexane}} = \frac{3}{1}$$

$$\therefore \quad K = 3$$

Let α be the degree of dissociation of substance in water

$$\text{Acid present in 50 mL hexane} = 1.6 \text{ g}$$

$$\therefore \quad \text{Acid present in 100 mL hexane} = 1.6 \times 2 = 3.2 \text{ g}$$

$$\text{Total acid} = 14.5 \text{ g}$$

$$\therefore \quad \text{Acid present in 100 mL } H_2O = 14.5 - 3.2 = 11.3 \text{ g}$$

$$\therefore \quad [\text{Acid}] \text{ in water} = \frac{11.3}{M \times 100} \text{ mol mL}^{-1}$$

$$[\text{Acid}] \text{ in hexane} = \frac{3.2}{M \times 100} \text{ mol mL}^{-1}$$

where M is mol. wt. of acid

Now $$K = \frac{[\text{Acid}] \text{ in water} \times (1 - \alpha)}{[\text{Acid}] \text{ in hexane}}$$

$$3 = \frac{\dfrac{11.3(1-\alpha)}{M \times 100}}{\dfrac{3.2}{M \times 100}}$$

∴ $$\alpha = 0.1504 = \mathbf{15.04\%}$$

Solution 29. Wt. of H_2O_2 = 20 g

Volume of H_2O = 200 cm^3

Volume of amyl alcohol = 200 cm^3

Suppose w g of H_2O_2 exist in water at equilibrium

∴ Wt. of H_2O_2 in amyl alcohol = $(20 - w)$ g

(a) If single operation is made by amyl alcohol using 200 cm^3 in one lot

$$K = \frac{\text{Conc. of } H_2O_2 \text{ in amyl alcohol}}{\text{Conc. of } H_2O_2 \text{ in water}}$$

$$\frac{1}{7} = \frac{(20 - w)/200}{\dfrac{w}{200}}$$

∴ $$w = \mathbf{17.5\ g}$$

Alternate for (a)

Part (a) may also be solved as:

$$w_n = \left[\frac{KV}{v + KV}\right]^n \cdot W$$

Given, $V = 200\ cm^3$; $v = 200\ cm^3$; $n = 1$

$K = 1/7$ $W = 20$ g

∴ $$w_n = \left[\frac{(1/7) \times 200}{200 + (1/7) \times 200}\right]^1 \times 20$$

∴ $$w_n = \mathbf{2.5\ g}$$

i.e., Amount left unextracted in amyl alcohol = 2.5g

Amount extracted by water = 20 – 2.5

= **17.5 g**

(b) $W = 20$ g, $K = 1/7$, $V = 200\ cm^3$, $v = 100\ cm^3$, $n = 2$

∴ $$w_n = \left[\frac{(1/7) \times 200}{100 + (200 \times 1/7)}\right]^2 \cdot 20$$

$$= 0.99 \text{ g}$$

i.e., Amount left unextracted in amyl alcohol = 0.99 g

∴ Amount extracted by water in two operations of 100 cm^3 each

$$= 20 - 0.99 = \mathbf{19.01\ g}$$

Solution 30. Let n be the complexity of acid in C_6H_6 and C_1, C_2 are concentrations of acid in water and C_6H_6.

Then
$$K = \frac{C_1}{\sqrt[n]{(C_2)}}$$

Taking log,

$$\log K = \log C_1 - \frac{1}{n}\log C_2 \qquad \ldots(1)$$

Using data in Eq. (1),

$$\log K = \log 0.01 - \frac{1}{n}\log 1.848 \times 10^{-5} \qquad \ldots(2)$$

$$\log K = \log 0.12 - \frac{1}{n}\log 2.661 \times 10^{-3} \qquad \ldots(3)$$

$$\log K = \log 0.24 - \frac{1}{n}\log 1.089 \times 10^{-2} \qquad \ldots(4)$$

Solving Eqs. (1) and (3), $n = 1.999$

Solving Eqs. (3) and (4), $n = 2.033$

The value of n is almost 2 in above experiment which shows that organic substance forms **dimer in C_6H_6.**

Solution 31. The given redox change is,

∵ $$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

∵ Mole ratio of I_2 : $Na_2S_2O_3$: : 1 : 2

$$\text{mM of } I_2 \text{ in aqueous layer of 50 mL} = \frac{1}{2} \times \text{mM of } Na_2S_2O_3$$

$$= \frac{1}{2} \times 1 \times 5 = 5/2$$

∴ $$\text{mM of } I_2 \text{ in } CCl_4 \text{ layer of 1 mL} = \frac{1}{2} \times \text{mM of } Na_2S_2O_3$$

$$= \frac{1}{2} \times 17 \times 0.5 = 8.5/2$$

∴ $$\text{mM of } I_2 \text{ in 50 mL } CCl_4 \text{ layer} = \frac{8.5}{2} \times 50 = 425/2$$

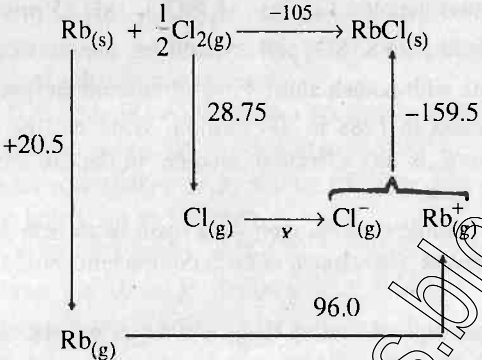
Now
$$K = \frac{\text{Conc. of } I_2 \text{ in } CCl_4 \text{ layer}}{\text{Conc. of } I_2 \text{ in } H_2O \text{ layer}}$$

$$K = \frac{\text{mM of } I_2 \text{ in 50 mL } CCl_4}{\text{mM of } I_2 \text{ in 50 mL } H_2O}$$

$$K = \frac{425/2}{5/2} = \mathbf{85}$$

Problems for Self Assessment

1. The Born-Haber's cycle for rubidium chloride (RbCl) is given below, (the energies are in kcal mol^{-1}).



Find out the electron affinity of chlorine in kJ mol^{-1}.

2. The heat of formation of $BaBr_{2(s)}$ is −764 kJ mol^{-1}. The first and second ionisation energies of Ba are 502 and 965 kJ mol^{-1} respectively. The heat of sublimation of Ba is 176 kJ mol^{-1}. The bond energy of Br_2 is 193 kJ mol^{-1}. Heat of vaporization of $Br_{(l)}$ is 31 kJ mol^{-1}. The electron affinity of bromine is 325 kJ mol^{-1}. Draw the Born-Haber cycle and calculate the lattice energy of $BaBr_{2(s)}$.

3. Cesium chloride is formed according to the following equation,

$$Cs_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow CsCl_{(s)}$$

The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and −348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is −388.6 kJ mol^{-1}. Calculate the lattice energy of CsCl.

4. By using the following data draw an appropriate energy cycle and calculate the enthalpy change of hydration of:
   (i) The chloride ion,
   (ii) The iodide ion.

Enthalpy change of solution of $NaCl_{(s)}$ = −2 kJ mol^{-1}
Enthalpy change of solution of $NaI_{(s)}$ = +2 kJ mol^{-1}
Enthalpy change of hydration of $Na^+_{(g)}$ = -390 kJ mol^{-1}
Lattice energy of NaCl = −772 kJ mol^{-1}
Lattice energy of NaI = −699 kJ mol^{-1}

5. Calculate the electron affinity of fluorine atom using the following data. Make Born-Haber's cycle. All the values are in kJ mol^{-1} at 25°C. $\Delta H_{\text{diss}}(F_2) = 160$, $\Delta H_f^\circ = [NaF_{(s)}] = -571$, I.E. $[Na_{(g)}] = 494$, $\Delta H_{\text{vap}}[Na_{(s)}] = 101$, Lattice energy of $NaF_{(s)} = -894$.
6. 0.7160 g of a hydrated metallic sulphate $M_x(SO_4)_y \cdot 18H_2O$ precipitated 0.7002 g of $BaSO_4$. When mixed with K_2SO_4 and crystallised, the metallic sulphate yielded an alum isomorphous with potash alum. Find the atomic weight of metal.
7. The population of India in 1988 is 800 million. What will be the population in 2000 and 2100 if there is no effective change in the present growth which is 25 per thousand per year.
8. To make a benzene soluble cement, melt 49 g rosin in an iron pass, and add 28 g each shellac and beeswax. How much of each component should be taken to make 75 kg cement?
9. The molar heat capacities of water, $H_{2(g)}$ and $O_{2(g)}$ are 18, 6.76 and 6.62 cal respectively. The heat of formation of water at 25°C is –68.4 kcal. Calculate its heat of formation at 90°C.
10. From the following data on distribution of succinic acid between water and C_6H_6, what conclusions you draw?

Concentration in water	1.25	2.5	5.0
Concentration in C_6H_6	4.339	17.36	69.44

11. An organic acid is distributed between 500 mL each of a solvent *A* and water. In water it is dissociated. The amount of the acid in aqueous layer was 6.0 g and in the solvent layer 0.72 g. If the partition coefficient of the acid between solvent *A* and water is 0.16 in favour of *A*, calculate the degree of dissociation of acid in water.
12. Benzoic acid distributes itself between water and benzene in such a way that in definite volume of water there are 1.50 g, 1.95 g and 2.97 g of benzoic acid, while in same volumes of C_6H_6, there are 24.2 g, 41.2 g and 97.0 g of benzoic acid respectively. What conclusion you draw from these results about molecular state of benzoic acid in benzene?
13. An aqueous solution of succinic acid at 288 K containing 0.70 g in 10 cm^3 is in equilibrium with etheral solution containing 0.13 g in 10 cm^3. What will be the concentration of an etheral solution which is in equilibrium with an aqueous solution containing 0.024 g in 10 cm^3? Assume same molecular state of succinic acid in both solvent.
14. A substance is twice soluble in ether as it is in water. The molecular weight being the same in both the solvents. Calculate the quantities extracted from v cm^3 of aqueous solution by using v cm^3 of ether?
    (a) in single operation,
    (b) in two successive operations.

15. At 298 K, an aqueous solution of iodine containing 0.0516 g per litre is in equilibrium with CCl_4 solution containing 4.412 g of iodine per litre. If the solubility of I_2 in water is 0.340 g per litre at 298 K, what will be its solubility in CCl_4?

16. The solubility of a substance is three times as great in ether as in water. Calculate the quantities extracted from 100 mL of aqueous solution by using,

(a) 100 mL of ether is one operation.
(b) 100 mL of ether in two successive operations, *i.e.*, 50 mL in each.
(c) what fraction is left unextracted in each case?

17. Succinic acid was shaken in a mixture of water and ether. The concentration of acid in two layers are as follows:

C_1 (water layer per 10 mL)	0.024 g	0.071	0.121
C_2 (ether layer per 10 mL)	0.004 g	0.013	0.022

(i) What is partition coefficient for system in favour of water.
(ii) If succinic acid has molecular weight 118 in water, find its molecular weight in ether.

18. Benzoic acid is distributed between water and benzene according to the following data:

Concentration in water	0.013	0.021	0.032
Concentration in C_6H_6	0.1818	0.4742	1.101

Find out molecular weight of benzoic acid in benzene.

Answers

1. -90.75 kcal mol^{-1} ; **2.** -1981 kJ mol^{-1} ;

3. -618.7 kJ mol^{-1} ;

4. For $Cl^- = -384$ kJ mol^{-1}, $I^- = -307$ kJ mol^{-1} ;

5. EA = 352 kJ mol^{-1} ; **6.** 51.38 ;

7. 1040 million, 3040 million ;

8. 35 kg rosin, 20 kg each of shellac and beeswax ;

9. -67.88 kcal ;

10. Succinic acid forms dimer in C_6H_6 ;

11. 25% ; **12.** Dimer formation in C_6H_6 ;

13. 4.46×10^{-4} g in 10 cm^3 ; **14.** (a) 2/3 W, (b) 3/4 W ;

15. 29.07 g litre^{-1} ;

16. (a) 3/4 W, (b) $\frac{3W}{5} + \frac{6W}{25} = \frac{21}{25} W$, (c) (a) 25%, (b) 16% ;

17. (i) 5.65, (ii) 118 ; **18.** $n = 2$, molecular weight = 244

SOME IMPORTANT TABLES

Table-1
Physical Quantities, Symbols and Units

S.No.	Physical Quantities	Symbols	SI Units	Symbol of Units
1.	Area	*A*	Square meter	m^2
2.	Volume	*V*	Cubic meter	m^3
3.	Density	*d*	kilogram meter^{-3}	$kg\ m^{-3}$
4.	Velocity	*u*	meter per sec	$m\ s^{-1}$
5.	Acceleration	*g*	meter per sec^2	$m\ s^{-2}$
6.	Energy	*E*	joule	J ($kg\ m^2 s^{-2}$)
7.	Force	*F*	newton	N ($kg\ ms^{-2}$)
8.	Power	—	Watt	W ($kg\ m^2 s^{-3}$ or Js^{-1})
9.	Pressure	*P*	pascal	Pa ($N\ m^{-2}$)
10.	Frequency	*v*	Hertz	Hz (s^{-1})
11.	Electric charge	*Q*	Coulomb	C (Ampere second)
12.	Electric potential difference	*V*	Volt	V ($kg\ m^2 s^{-3}\ A^{-1}$)
13.	Electrical resistance	*R*	Ohm	∩ ($kg\ m^2 s^{-3}\ A^{-2}$)
14.	Electrical conductance	*S*	Siemens	S ($\cap^{-1}$)
15.	Amount	mole	mole	mole $\left(\frac{\text{Weight}}{\text{Mol. wt.}}\right)$

Table-2
Quantities with Traditional Units, SI and CGS. Values

S.No.	Quantity	Traditional Units	SI and CGS Value
1.	Mass	amu	1.6605×10^{-27} kg $= 1.6605 \times 10^{-24}$ g = 1 amu
2.	Length	Å	10^{-10} meter = 10^{-8} cm = 1 Å
3.	Volume	litre	10^{-3} m^3 = 10^3 cm^3 = 1 litre
4.	Force	dyne	10^{-5} Newton = 1 dyne
5.	Energy	erg	10^{-7} joule = 1 erg
		cal	4.184 joule = 1 cal
		electron volt	1.602×10^{-19} joule = 1 eV
		kilo watt hour	3.6×10^6 joule = 1 KWh
		horse power	2.6845×10^6 joule = 1 hp
6.	Pressure	atmosphere	101325 N m^{-2} or pascal = 1 atm
		cm	1333.2237 N m^{-2} = 1 cm
		mm or torr	133.32237 N m^{-2} = 1 mm
		bar	101325 N m^{-2} = 1 bar
7.	Temperature	centigrade	273.15 K = 0°C
8.	Electric charge	esu	3.3356×10^{-10} C = 1 esu
9.	Work	litre atm	101.3 J = 1 litre atm
10.	Radioactivity	Curie or Ci	3.7×10^{10} dps or Bq = 1 curie
		Rutherford	10^6 dps = 10^6 Bq = 1 rd

Table-3 Some direct Conversion factors

1 erg $= 10^{-7}$ Joule
$= 2389 \times 10^{-8}$ cal
$= 6.242 \times 10^{11}$ eV
1 calorie $= 4.184 \times 10^{7}$ erg
$= 4.184$ Joule
$= 2.613 \times 10^{19}$ eV
1 electron volt $= 1.6021 \times 10^{-12}$ erg
$= 1.6021 \times 10^{-19}$ Joule
$= 3.827 \times 10^{-20}$ calorie
1 litre $= 1000$ mL or cm^3
$= 10^{-3}\ m^3$
1 angstrom $= 10^{-8}$ cm
$= 10^{-10}$ m
1 nanometer $= 10^{-9}$ m
$= 10^{-7}$ cm
1 coulomb $= 2.9979 \times 10^{9}$ esu
1 faraday $= 9.6487 \times 10^{4}$ coulomb
1 curie $= 3.7 \times 10^{10}$ disintegration sec^{-1}
1 rutherford $= 10^{6}$ dps

Table-4 Wave Lengths and Frequencies of Electromagnetic Radiations

S.No.	Radiations	Wavelength λ (in Å)	Frequency (γ) (in Hz or sec^{-1})
1.	Radio wave	3×10^{9} to 3×10^{13}	1×10^{5} to 1×10^{9}
2.	Micro wave	6×10^{6} to 3×10^{9}	1×10^{9} to 5×10^{11}
3.	Infra red	3×10^{9} to 7.6×10^{3}	1×10^{11} to 3.95×10^{14}
4.	Visible rays	3800 to 7600	3.95×10^{14} to 7.9×10^{14}
5.	Ultra violet rays	150 to 3800	7.9×10^{14} to $2 \times 2 \times 10^{16}$
6.	X-rays	0.1 to 150	2×10^{16} to 3×10^{19}
7.	Gamma rays (γ)	0.01 to 0.1	3×10^{19} to 3×10^{20}
8.	Cosmic rays	0.00 to 0.001	3×10^{21} to infinite

Table-5
Physical Constants and their Values

S.No.	Name	Symbol	CGS Value	SI Unit Value
1.	Universal gas constant	(R)	8.314×10^7 erg K^{-1}	8.314 J K^{-1} mol^{-1}
2.	Boltzmann constant	(K)	1.380×10^{-16} erg K^{-1}	1.380×10^{-23} JK^{-1}
3.	Planck's constant	(h)	6.626×10^{-27} erg sec	6.626×10^{-34} J sec
4.	Speed of light	C	2.9979×10^{10} cm sec^{-1}	2.9979×10^8 m sec^{-1}
5.	Molar volume at STP	$\bar{v}$	22414 cm^3	0.0224 m^3
6.	Avogadro's No.	N	6.022169×10^{23} mol^{-1}	6.022169×10^{23} mol^{-1}
7.	Charge on electron	e	4.80291×10^{-10} esu	1.60210×10^{19} C
8.	Atomic mass unit	amu	1.660531×10^{-24} g	1.660531×10^{-27} kg
9.	Mass of electron in rest	m_e	9.109558×10^{-28} g	9.109558×10^{-31} kg
10.	Mass of proton	m_p	1.67261×10^{-24} g	1.67261×10^{-27} kg
11.	Mass of neutron	m_n	1.67492×10^{-24} g	1.67492×10^{-27} kg
12.	Rydberg constant	R_H	1.097373×10^5 cm^{-1}	1.097373×10^7 m^{-1}
13.	Faraday	(F)	2.89461×10^{14}	9.6487×10^7 C/kg
14.	Accelaration due to gravity	(g)	980.665 cm sec^{-2}	9.80665 m sec^{-2}
15.	I Bohr's radius (for H)	r_{1H}	0.529×10^{-8} cm	0.529×10^{-10} m
16.	Atmospheric pressure	(P)	1.013250×10^6 dyne cm^{-2}	1.013250×10^5 N m^{-2}
17.	Specific charge of electron	(e/m)	5.2764×10^{17} esu/g	1.75880×10^{11} C kg^{-1}
18.	Ice point	(m.pt.)	273.150 K	273.150 K
19.	Triple point of H_2O		273.16 K	273.16 K

Table-6
Elements, their Symbols, Atomic No., Atomic mass and Isotopes

Element	Symbol	Atomic number	Atomic mass	*Known Isotopes
Actinium	Ac	89	(227)	—
Aluminium	Al	13	25.9815	1
Amercium	Am	95	(243)	—
Antimony	Sb	51	121.75	2
Argon	Ar	18	39.948	3
Arsenic	As	33	74.9216	1
Astatine	At	85	(210)	—
Barium	Ba	56	137.4	7
Berkelium	Bk	97	(247)	—
Beryllium	Be	4	9.0122	2
Bismuth	Bi	83	208.980	14
Boron	B	5	10.820	14
Bromine	Br	35	79.904	2
Cadmium	Cd	48	112.40	9
Calcium	Ca	20	40.08	6
Californium	Cf	98	(251)	—
Carbon	C	6	12.01	2
Cerium	Ce	58	140.12	4
Cesium	Cs	55	132.905	5
Chlorine	Cl	17	35.453	3
Chromium	Cr	24	51.996	4
Cobalt	Co	27	58.9332	2
Copper	Cu	29	63.546	2
Curium	Cm	96	(247)	—
Dysprosium	Dy	66	162.50	4
Einsteinium	Es	99	(294)	—
Erbium	Er	68	167.26	4
Europium	Eu	63	152.00	2
Fermium	Fm	100	(253)	—
Fluorine	F	9	19.0	1
Francium	Fr	87	(223)	—

(contd.)

*values in parentheses are mass numbers of the most stable or the best known isotopes.

Gadolinium	Gd	64	157.25	5
Gallium	Ga	31	69.72	2
Germanium	Ge	32	72.60	5
Gold	Au	79	196.67	—
Hafnium	Hf	72	178.49	5
Helium	He	2	4.0026	2
Holmium	Ho	67	164.930	1
Hydrogen	H	1	1.00797	3
Indium	In	49	114.81	2
Iodine	I	53	126.9044	1
Iridium	Ir	77	192.2	2
Iron	Fe	26	55.847	4
Krypton	Kr	36	83.80	6
Kurchatovium	Ku	104	(260)	—
Lanthanum	La	57	183.91	1
Lawrenchium	Lw	103	(257)	—
Lead	Pb	82	207.19	16
Lithium	Li	3	6.94	2
Lutetium	Lu	71	174.97	1
Magnesium	Mg	12	24.312	3
Manganese	Mn	25	54.9380	7
Mendelevium	Md	101	(256)	—
Mercury	Hg	80	200.59	8
Molybdenum	Mo	42	95.94	8
Neodymium	Nd	60	144.24	5
Neon	Ne	10	20.183	3
Neptunium	Np	93	(237)	—
Nickel	Ni	28	58.71	5
Niobium	Nb	41	92.906	1
Nitrogen	N	7	14.0067	2
Nobelium	No	102	(254)	—
Osmium	Os	76	190.2	6
Oxygen	O	8	15.9994	3
Palladium	Pd	46	106.4	6
Phosphorus	P	15	30.9738	1
Platinum	Pt	78	195.09	5
Plutonium	Pu	94	(242)	—
Polonium	Po	84	(210)	—

(*contd.*)

Potassium	K	19	39.102	3
Prascodymium	Pr	59	140.007	1
Promethium	Pm	61	(147)	—
Protactinium	Pa	91	(231)	—
Radium	Ra	88	(226)	4
Radon	Rn	86	(222)	—
Rhenium	Re	75	186.2	2
Rhodium	Rh	45	102.905	2
Rubidium	Rb	37	85.47	2
Ruthenium	Ru	44	101.07	7
Samarium	Sm	62	150.35	7
Scandium	Sc	21	44.956	1
Selenium	Se	34	78.96	6
Silicon	Si	14	28.086	3
Silver	Ag	47	107.868	2
Sodium	Na	11	22.9898	3
Strontium	Sr	38	87.62	4
Sulphur	S	16	32.064	1
Tantalum	Ta	73	180.948	1
Technetium	Tc	43	(99)	—
Tellurium	Te	52	127.60	8
Terbium	Tb	65	158.924	1
Thallium	Tl	81	204.37	8
Thorium	Th	90	232.038	8
Thulium	Tm	69	168.934	1
Tin	Sn	50	118.69	10
Titanium	Ti	22	47.90	5
Tungusten	W	74	183.85	4
Uranium	U	92	238.03	8
Vanadium	V	23	50.942	1
Xenon	Xe	54	131.30	9
Ytterbium	Yb	70	173.40	5
Yttrium	Y	39	88.905	1
Zinc	Zn	30	65.37	5
Zirconium	Zr	40	91.22	5

Table-7
Electrochemical Series

Half reactions	Standard reduction potential at 25°C (in volts)
$Li^+ + e \longrightarrow Li$	–3.04
$K^+ + e \longrightarrow K$	–2.92
$Ba^{2+} + 2e \longrightarrow Ba$	–2.90
$Sr^{2+} + 2e \longrightarrow Sr$	–2.89
$Ca^{2+} + 2e \longrightarrow Ca$	–2.87
$Na^+ + e \longrightarrow Na$	–2.71
$Mg^{2+} + 2e \longrightarrow Mg$	–2.37
$Al^{3+} + 3e \longrightarrow Al$	–1.66
$Mn^{2+} + 2e \longrightarrow Mn$	–1.18
$Zn^{2+} + 2e \longrightarrow Zn$	–0.76
$Cr^{3+} + 3e \longrightarrow Cr$	–0.74
$Fe^{2+} + 2e \longrightarrow Fe$	–0.44
$Cd^{2+} + 2e \longrightarrow Cd$	–0.40
$Co^{2+} + 2e \longrightarrow Co$	–0.27
$Ni^{2+} + 2e \longrightarrow Ni$	–0.25
$Sn^{2+} + 2e \longrightarrow Sn$	–0.13
$Pb^{2+} + 2e \longrightarrow Pb$	–0.12
$2H^+ + 2e \longrightarrow H_2$	0.00
$Sn^{4+} + 2e \longrightarrow Sn^{2+}$	+0.15
$Cu^{2+} + 2e \longrightarrow Cu$	+0.34
$Fe^{3+} + e \longrightarrow Fe^{2+}$	+0.77
$Hg_2^{2+} + 2e \longrightarrow 2Hg$	+0.79
$Ag^+ + e \longrightarrow Ag$	+0.80
$Hg^{2+} + 2e \longrightarrow Hg$	+0.85
$Pt^{2+} + 2e \longrightarrow Pt$	+1.20
$Cl_2 + 2e \longrightarrow 2Cl^-$	+1.36
$Au^{3+} + 3e \longrightarrow Au$	+1.50
$Co^{3+} + 1e \longrightarrow Co^{2+}$	+1.84
$F_2 + 2e \longrightarrow 2F^-$	+2.87

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4256	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20