CHAPTER

11

The Liquids

KEY CONCEPTS AND EQUATIONS

INTERMOLECULAR FORCES IN LIQUIDS

In the liquid state the molecules are in contact with each other. The forces of attraction between the molecules are strong enough to hold them together. The intermolecular forces in liquids are collectively called **van der Waals'** forces. These are weak attractive forces in large number of substances like HCl, Cl_2 , Br_2 , etc. The strength of van der Waals' forces range from 0.1 to 10 kJ mol^{-1}. Hydrogen bonding occurs in substances having hydrogen covalently bonded to a highly electronegative atom.

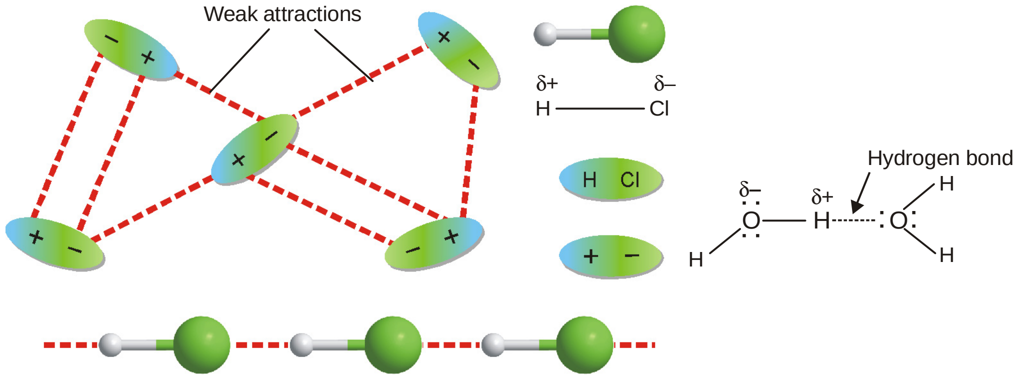


Figure 11.1
van der Waal's forces and hydrogen bonding.

The strength of hydrogen bond is of the order of 10 to 40 kJ mol^{-1}. It is about one-tenth as strong as covalent bond.

VAPOUR PRESSURE

The vapour pressure of a liquid is the partial pressure of the vapour over the liquid at equilibrium. The vapour pressure of different liquids depend upon their nature and the intermolecular forces. For example, ethyl alcohol has weaker hydrogen bonding than water and evaporates faster than water. With rise in temperature the vapour pressure increases.

BOILING POINT

When the vapour pressure becomes equal to the atmospheric pressure boiling occurs. **The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure is called the boiling point.** The graph between the vapour pressure and temperature for some liquids is shown in Fig.1.2 which shows that vapour pressure increases rapidly with temperature.

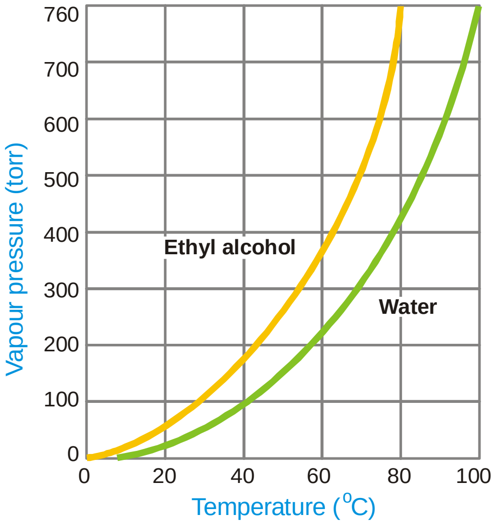


Figure 11.2
Variation of vapour pressure with temperature.

SURFACE TENSION

It is defined as the energy required to increase the surface area of a liquid by a unit amount. It is measured by dynes cm^{-1} (CGS unit) or in Newton per meter, Nm^{-1} (SI units) or Jm^{-2}.

DETERMINATION OF SURFACE TENSION

(i) Capillary rise method

The formula used for the determination of surface tension by capillary rise method is

$$\gamma = \frac{h\,r\,d\,g}{2}$$

where h is the height to which liquid rises in a capillary tube of radius r, d is density of the liquid and g the force of gravity.

(ii) Drop-weight method

The formula used in drop weight method is

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$$

where γ_1 and γ_2 are the surface tension of given liquid and water, m_1 and m_2 the masses of one drop of each liquid and water respectively. Knowing the surface tension of reference liquid γ_2, the surface tension of the liquid under study can be calculated.

(iii) Drop-number method

The formula used is

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2}{n_1} \times \frac{d_1}{d_2}$$

where γ_1 and γ_2 are the surface tension of given liquid and water respectively, n_1 & n_2 are the number of drops in a given volume, d_1 and d_2 are their densities.

VISCOSITY

Viscosity is the resistance to flow that is exhibited by all liquids. It may be defined as the force of resistance per unit area which will maintain unit velocity difference between two layers of a liquid at a unit distance from each other. It is denoted by η. Its units are mass $length^{-1}$ $time^{-1}$ *i.e.* kg m^{-1} sec^{-1} (SI units) or g cm^{-1} sec^{-1} (CGS units) and

$$1 \text{ poise} = 1 \text{ g cm}^{-1}\text{ sec}^{-1} = 0.1 \text{ kg m}^{-1}\text{ sec}^{-1}$$

DETERMINATION OF VISCOSITY

Ostwald's method

The formula used for the determination of viscosity by the Ostwald's method is

$$\eta = \frac{\pi P r^4 t}{8 l V}$$

where V is the volume of the liquid flowing through a capillary in time t, P is the pressure-head, r, the radius of the tube and l its length.

The relative viscosity is given by the relation

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

where t_1 and t_2 are times of flow of fixed volume (V) of two liquids with densities d_1 and d_2 respectively.

Knowing the value of η_2, η_1 can be calculated.

REFRACTIVE INDEX

The refractive index n of a substance is defined as the ratio of velocity of light in substance to that in air or vacuum.

$$n = \frac{\text{Velocity of light in substance}}{\text{Velocity of light in air}}$$

The refractive index of the liquid with respect to air is given by Snelle's law

$$n = \frac{\text{Sin } i}{\text{Sin } r}$$

where i is the angle of incidence and r, the angle of refraction.

SPECIFIC REFRACTION

It is given by the formula

$$R_S = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$$

where R_S is the specific refraction, d the density and n is the refractive index

MOLAR REFRACTION

It is the product of specific refraction and molecular mass

i.e.

$$R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

where M is the molecular mass of the substance.

OPTICAL ACTIVITY

A compound that can rotate the plane of polarised light is called optically active. This property of a compound is called optical activity.

SPECIFIC ROTATION

It is expressed as

$$[\alpha] = \frac{\alpha}{l \times c}$$

where $[\alpha]$ is the specific rotation in degrees

α, the observed angle of rotation in degrees

l, the length of the sample in decimeter

C, the concentration of the sample solution in g cm^{-3}.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A capillary tube of internal diameter 0.2 mm is dipped into water when water rises 15 cm. Calculate the surface tension of water.

SOLUTION :

Formula used

$$\gamma = \frac{(h + \frac{1}{3} r)\, r \rho g}{2}$$

Quantities given

$r = 0.1 \text{ mm} = 0.01 \text{ cm}$ $h = 15 \text{ cm}$ $\rho = 1 \text{ g cm}^{-3}$ $g = 980 \text{ cm sec}^{-2}$

Substitution of values

$$\gamma = \frac{(15 + \frac{1}{3} \times 0.01)\text{ cm} \times 0.01 \text{ cm} \times 980 \text{ cm sec}^{-2} \times 1 \text{g cm}^{-3}}{2}$$

$$= \mathbf{73.51 \text{ dyne cm}^{-1}}$$

SOLVED PROBLEM 2. In a measurement of viscosity by Ostwald's viscometer at 20.2 ºC, water takes 30 seconds to flow between the upper and lower marks while the flow of another liquid of density 1.5 g cm^{-3} takes 35 seconds. Taking density of water at 20.2 ºC to be 0.9982 g cm^{-3}, calculate the viscosity of the other liquid if the viscosity of water at this temperature is 10 centipoise.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

or

$$\eta_2 = \frac{\eta_1 d_2 t_2}{d_1 t_1}$$

Quantities given

$\eta_1 = 10$ centipoise $d_1 = 0.9982 \text{ g cm}^{-3}$ $t_1 = 30$ sec

$d_2 = 1.5 \text{ g cm}^{-3}$ $t_2 = 35$ sec

Substitution of values

$$\eta_2 = \frac{10 \text{ centipoise} \times 1.5 \text{ g cm}^{-3} \times 35 \text{ sec}}{0.9982 \text{ g cm}^{-3} \times 30 \text{ sec}}$$

$$= 17.53 \text{ centipoise}$$

$$= \mathbf{0.1753 \text{ poise}}$$

SOLVED PROBLEM 3. At 20 ºC, toluene rises 1.95 cm in a capillary tube of radius 0.3412 mm. Calculate the surface tension of toluene. The density of toluene at 20 ºC is 0.866 g cm^{-3}.

SOLUTION :

Formula used

$$\gamma = \frac{(h + \frac{1}{3} r)\, r \rho g}{2}$$

Quantities given

$h = 1.95 \text{ cm}$ $r = 0.3412 \text{ mm} = 0.03412 \text{ cm}$ $\rho = 0.866 \text{ g cm}^{-3}$ $g = 981 \text{ cm sec}^{-2}$

Substitution of values

$$\gamma = \frac{(1.95 + \frac{1}{3} \times 0.03412)\ \text{cm} \times 0.03412\ \text{cm} \times 0.866\ \text{g cm}^{-3} \times 981\ \text{cm sec}^{-2}}{2}$$

$$= \frac{1.961373 \times 0.03412 \times 0.866 \times 981}{2}\ \text{dynes cm}^{-1}$$

$$= \mathbf{28.42\ dynes\ cm^{-1}}$$

SOLVED PROBLEM 4. The density of a liquid at 25 ºC is 1.2 g ml^{-1}. Its refractive index n_D^{25} is 1.552. Calculate its molar refractivity. (Molecular mass of liquid = 123)

SOLUTION :

Formula used

$$R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Quantities given

$n = 1.552$ $d = 1.203$ g ml^{-1} $M = 123$

Substitution of values

$$R_M = \frac{(1.552)^2 - 1}{(1.552)^2 + 2} \times \frac{123}{1.203}$$

$$= \frac{1.4087}{4.4087} \times \frac{123}{1.203}$$

$$= \mathbf{32.66\ cm\ mol^{-1}}$$

SOLVED PROBLEM 5. In an Ostwald viscometer, the flow times for two liquids A and B are in the ratio 4:5. If the density of liquid B is twice as high as that of A, calculate the ratio of their viscosities.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1\ t_1}{d_2\ t_2}$$

Quantities given

Density of liquid A, $d_1 = d_1$ time for liquid A = 4 t sec

Density of liquid B, $d_2 = 2 \times d_1$ time for liquid B = 5 t sec

Substitution of values

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \times 4\,t}{2\,d_1 \times 5\,t} = \frac{2}{5}$$

or $$\boldsymbol{\eta_1 : \eta_2 = 2 : 5}$$

SOLVED PROBLEM 6. Time taken for the same volume of water and benzene to flow in viscometer at 20º C have been found to be 120 seconds and 88 seconds respectively. The density of benzene at this temperature is 0.879 g cm^{-3}. If the absolute viscosity of water at 20 ºC is 10.05×10^{-3} poise, calculate the specific viscosity of benzene at this temperature.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1\ t_1}{d_2\ t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1\ d_2\ t_2}{d_1\ t_1}$$

Quantities given

$\eta_1 = 10.05 \times 10^{-3}$ poise

$d_1 = 1.0$ g cm^{-3}

$d_2 = 0.879$ g cm^{-3}

$t_1 = 120$ sec

$t_2 = 88$ sec

Substitution of values

$$\eta_2 = \frac{10.05 \times 10^{-3} \text{ poise} \times 0.879 \text{ g cm}^{-3} \times 88 \text{ sec}}{1.0 \text{ g cm}^{-3} \times 120 \text{ sec}}$$

$$= \mathbf{6.4782 \times 10^{-3}\ \text{poise}}$$

SOLVED PROBLEM 7. It takes 100 sec for water to flow through a capillary tube at fixed pressure. How long will it take toluene to do so under similar conditions? Given that :

density of water = 0.998 g cm^{-3}

absolute viscosity of water = 0.01 dyne sec cm^{2}

density of toluene = 0.866 g cm^{-3}

viscosity = 0.006 dyne sec cm^{-2}.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1\ t_1}{d_2\ t_2} \quad \text{or} \quad t_2 = \frac{\eta_2\ d_1\ t_1}{\eta_1\ d_2}$$

Quantities given

$\eta_1 = 0.01$ dyne sec cm^{-2}

$\eta_2 = 0.006$ dyne sec cm^{-2}

$d_1 = 0.998$ g cm^{-3}

$d_2 = 0.866$ g cm^{-3}

$t_1 = 100$ sec

Substitution of values

$$t_2 = \frac{0.006 \text{ dyne sec cm}^{-2} \times 0.998 \text{ g cm}^{-3} \times 100 \text{ sec}}{0.01 \text{ dyne sec cm}^{-2} \times 0.866 \text{ g cm}^{-3}}$$

$$= \mathbf{69.15\ \text{sec}}$$

SOLVED PROBLEM 8. At 20 °C, pure water required 102.2 sec to flow the capillary of an Ostwald viscometer while toluene at 20 °C required 68.9 sec. Calculate the relative viscosity of toluene. Densities of water and toluene are 0.998 and 0.866 g cm^{-3}.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1\ t_1}{d_2\ t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1\ d_2\ t_2}{d_1\ t_1}$$

Quantities given

$\eta_1 = 1$ poise

$d_1 = 0.998$ g cm^{-3}

$d_2 = 0.866$ g cm^{-3}

$t_1 = 102.2$ sec

$t_2 = 68.9$ sec

Substitution of values

$$\eta_2 = \frac{1 \text{ poise} \times 0.866 \text{ g cm}^{-3} \times 68.9 \text{ sec}}{0.998 \text{ g cm}^{-3} \times 102.2 \text{ sec}}$$

$$= \mathbf{0.5850\ \text{poise}}$$

SOLVED PROBLEM 9. The rise of water level in a capillary of radius 0.2 mm at 20 ºC is 7.4 cm. Calculate the surface tension of water taking its density as 1 g cm^{-3} at 20 ºC.

SOLUTION :

Formula used

$$\gamma = \frac{(h + \frac{1}{3} r)\, r \rho g}{2}$$

Quantities given

$h = 7.4$ cm $\quad r = 0.2$ mm $= 0.02$ cm $\quad \rho = 1$ g cm^{-3} $\quad g = 980$ dynes sec^{-1}

Substitution of values

$$\gamma = \frac{(7.4 \times \frac{1}{3} \times 0.02)\text{cm} \times 0.02\text{cm} \times 980 \text{ dynes sec}^{-1}}{2}$$

$$= \mathbf{72.65 \text{ dynes cm}^{-1}}$$

SOLVED PROBLEM 10. At 20 °C flow times of water and another liquid in a viscometer are 2 min 24 sec and 1 min respectively. Take density of water = 1g cm^{-3} ; density of liquid = 0.8 g cm^{-3} ; viscosity coefficient of water = 1 centipoise (all at 20 °C). Calculate the viscosity coefficient for the liquid at 20 °C.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \; t_1}{d_2 \; t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1 \; d_2 \; t_2}{d_1 \; t_1}$$

Quantities given

$d_1 = 1$ g cm^{-3} $\quad t_1 = 144$ sec $\quad \eta_1 = 1$ centipoise

$d_2 = 0.8$ g cm^{-3} $\quad t_2 = 60$ sec

Substitutions of values

$$\eta_2 = \frac{1 \text{ centipoise} \times 0.8 \text{ g cm}^{-3} \times 60 \text{ sec}}{1.0 \text{ g cm}^{-3} \times 144 \text{ sec}}$$

$$= \mathbf{0.33 \text{ centipoise}}$$

SOLVED PROBLEM 11. How long a machine oil take to pass through a viscometer if water under the same conditions takes one minute ? Density of water = 1.0×10^3 kg m^{-3} ; $\eta = 0.00101$ Nm^{-2} sec; Density of oil = 0.97×10^3 kg m^{-3} ; $\eta = 0.060$ Nm^{-2} sec.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \; t_1}{d_2 \; t_2} \quad \text{or} \quad t_2 = \frac{\eta_2 \; d_1 \; t_1}{n_1 \; d_2}$$

Quantities given

$\eta_1 = 0.00101$ Nm^{-2} sec $\quad d_1 = 1 \times 10^3$ kg m^{-3} $\quad t_1 = 60$ sec

$\eta_2 = 0.060$ Nm^{-2} sec $\quad d_2 = 0.97 \times 10^3$ kg m^{-3}

Substitution of values

$$t_2 = \frac{0.060 \text{ Nm}^{-2} \text{ sec} \times 1 \times 10^3 \text{ kg m}^{-3} \times 60 \text{ sec}}{0.00101 \text{ Nm}^{-2} \text{ sec} \times 0.97 \times 10^3 \text{ kg m}^{-3}}$$

$$= \mathbf{3674.59 \text{ sec}}$$

SOLVED PROBLEM 12. Some volume of benzene takes 46 sec to flow through an Ostwald viscometer while an equal volume of water takes 68 sec at the same temperature. Their respective densities are 0.800 g cm^{-3} and 0.998 g cm^{-3}. Coefficient of viscosity of water under the conditions is 1.008 centipoise. Calculate the coefficient of viscosity of benzene.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1\, t_1}{d_2\, t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1\, d_2\, t_2}{d_1\, t_1}$$

Quantities given

η_1 = 1.008 centipoise

d_1 = 0.998 g cm^{-3}

d_2 = 0.800 g cm^{-3}

t_1 = 68 sec

t_2 = 46 sec

Substitution of values

$$\eta_2 = \frac{1.008 \text{ centipoise} \times 0.800 \text{ g cm}^{-3} \times 46 \text{ sec}}{0.998 \text{ g cm}^{-3} \times 68 \text{ sec}}$$

$$= \mathbf{0.05466 \text{ centipoise}}$$

SOLVED PROBLEM 13. When 12.0 cc of water is allowed to flow through a stalgamometer, 50.0 drops of water were obtained and when the same volume of liquid is allowed to flow, the number of drops formed was 35. If the density of the liquid is 1.2 g per cc and the surface tension of water is 72 dynes cm^{-1}, calculate the surface tension of the liquid.

SOLUTION :

Formula used

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2\, d_1}{n_1\, d_2} \quad \text{or} \quad \gamma_2 = \frac{\gamma_1\, n_1\, d_1}{n_2\, d_2}$$

Quantities given

n_1 = 35

n_2 = 50

d_1 = 1.0 g cm^{-3}

d_2 = 1.2 g cm^{-3}

γ_1 = 72 dynes cm^{-1}

Substitution of values

$$\gamma_2 = \frac{72 \text{ dynes cm}^{-1} \times 50 \times 1.2 \text{ g cm}^{-3}}{35 \times 1.0 \text{ g cm}^{-3}}$$

$$= \mathbf{123.428 \text{ dyne cm}^{-1}}$$

SOLVED PROBLEM 14. In an experiment at 293 K, water rose in a capillary of diameter 0.078 cm to a height of 3.96 cm. Calculate the surface tension of water if the density of water at this temperature is 0.998 g cm^{-3} and g = 980 cm sec^{-2}.

SOLUTION :

Formula used

$$\gamma = \frac{h\, r\, d\, g}{2}$$

Quantities given

$$h = 3.96 \text{ cm} \qquad r = \frac{0.078}{2} = 0.039 \text{ cm}$$

$$d = 0.998 \text{ g cm}^{-3} \qquad g = 980 \text{ cm sec}^{-2}$$

Substitution of values

$$\gamma = \frac{0.039 \text{cm} \times 3.96 \text{ cm} \times 0.998 \text{ g cm}^{-3} \times 980 \text{ cm sec}^{-2}}{2}$$

$$= \frac{151.048}{2} \text{ dynes cm}^{-1} \qquad [\because 1 \text{ dyne} = 1 \text{ g cm sec}^{-2}]$$

$$= \mathbf{75.524 \text{ dynes cm}^{-1}}$$

SOLVED PROBLEM 15. Fifty drops of water weigh 3.75 g and that of a liquid 0.850 g. Calculate the surface tension of the liquid if the surface tension of water is 72.7 dynes cm^{-1}.

SOLUTION :

Formula used

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$$

Quantities given

$$\gamma_1 = 72.7 \text{ dynes cm}^{-1} \qquad m_1 = \frac{3.75}{50} \text{ g} \qquad m_2 = \frac{0.850}{50} \text{ g}$$

Substitution of values

$$\frac{72.7 \text{ dynes cm}^{-1}}{\gamma_2} = \frac{3.75}{50} \times \frac{50}{0.850}$$

or

$$\gamma_2 = \frac{72.7 \times 0.850}{3.75} \text{ dynes cm}^{-1}$$

$$= \mathbf{16.479 \text{ dynes cm}^{-1}}$$

SOLVED PROBLEM 16. The number of drops of water counted in a stalgamometer at 298 K is 300 whereas the number of drops for ethyl alcohol is 320. Calculate the surface tension of ethyl alcohol given that the density of water = 0.998 g cm^{-3}, density of ethyl alcohol = 0.9614 g cm^{-3} surface tension of water = 72.75 dynes cm^{-1}.

SOLUTION :

Formula used

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1}{n_2} \times \frac{d_1}{d_2}$$

Quantities given

$$\gamma_1 = 72.75 \text{ dynes cm}^{-1} \qquad n_1 = 300 \qquad d_1 = 0.998 \text{ g cm}^{-3}$$

$$n_2 = 320 \qquad d_2 = 0.9614 \text{ g cm}^{-3}$$

Substitution of values

$$\frac{72.75 \text{ dynes cm}^{-1}}{\gamma_2} = \frac{300 \times 0.998 \text{ g cm}^{-3}}{320 \times 0.9614 \text{ g cm}^{-3}}$$

or

$$\gamma_2 = \frac{72.75 \times 320}{300} \times \frac{0.9614}{0.998}$$

$$= \mathbf{77.75 \text{ dynes cm}^{-1}}$$

SOLVED PROBLEM 17. The times of flow for the same volume of water and carbon tetrachloride, through an Ostwald's viscometer are 400 and 300 secs respectively. The densities of water and carbon tetracholoride are 0.998 and 1.542 g cm^{-3} respectively. Calculate the viscosity coefficient of carbon tetrachloride if the value for water is 0.01002 poise.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \times \frac{d_1}{d_2}$$

Quantities given

$\eta_1 = 0.01002$ P $\quad t_1 = 400$ sec $\quad d_1 = 0.998$ g cm^{-3}

$t_2 = 300$ sec $\quad d_2 = 1.542$ g cm^{-3}

Substitution of values

$$\frac{0.01002\text{ P}}{\eta_2} = \frac{400\text{ sec} \times 0.988\text{ g cm}^{-3}}{300\text{ sec} \times 1.542\text{ g cm}^{-3}}$$

or

$$= \frac{0.01002 \times 300 \times 1.542}{400 \times 0.998}\text{ poise}$$

$$= \mathbf{0.01161\ poise}$$

SOLVED PROBLEM 18. In a measurement of viscosity with Ostwald's viscometer, water takes 580 sec to flow through a given volume, while an organic liquid takes 395 sec. Calculate the viscosity of organic liquid. Density of organic liquid and water are 0.7807 and 0.9984 g cm^{-3} respectively. Viscosity of water is 1.01 centipoise.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1\ t_1}{d_2\ t_2}$$

Quantities given

$\eta_1 = 1.01$ centipoise $\quad d_1 = 0.9984$ g cm^{-3} $\quad t_1 = 580$ sec

$d_2 = 0.7867$ g cm^{-3} $\quad t_2 = 395$ sec

Substitution of values

$$\frac{1.01\ \text{centipoise}}{\eta_2} = \frac{0.9984\text{ g cm}^{-3} \times 580\text{ sec}}{0.7867\text{ g cm}^{-3} \times 395\text{ sec}}$$

or

$$\eta_2 = \frac{1.01 \times 0.7867 \times 395}{0.9984 \times 580}\text{ centipoise}$$

$$= \mathbf{0.542\ centipoise}$$

SOLVED PROBLEM 19. The refractive index of carbon tetrachloride is 1.4573 and its density is 1.5952 g cm^{-3}. Calculate its molar refraction.

SOLUTION :

Formula used

$$R_m = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Quantities given

$n = 1.4573$ $\quad d = 1.5952$ g cm^{-3} $\quad M = 12 + 4 \times 35.5 = 154$ g mol^{-1}

Substitution of values

$$R_m = \frac{(1.4573)^2 - 1}{(1.4573)^2 + 2} \times \frac{154}{1.5952}$$

$$= \frac{1.1237}{4.1237} \times \frac{154}{1.5952}$$

$$= \mathbf{26.30\ cm^3\ mol^{-1}}$$

SOLVED PROBLEM 20. A solution of a certain optically active substance in water containing 5.2 g in 30 ml is introduced in a 20 cm long polarimeter tube. It rotated plane polarised light by 6.2º. Calculate the specific rotation.

SOLUTION :

Formula used

$$[\alpha] = \frac{\alpha}{l \times c}$$

Quantities given

$\alpha = 6.2^o$ $\qquad l = 20\ \text{cm} = 2\ \text{dm}$ $\qquad c = \frac{5.2}{30}\ \text{g ml}^{-1}$

$$[\alpha] = \frac{6.2^o \times 30}{2 \times 5.2} = \mathbf{17.88^o}$$

ADDITIONAL PRACTICE PROBLEMS

1. The surface tension of water at 20 ºC is 72.75×10^{-3} Nm^{-1}. A 33.24 vol% solution of ethyl alcohol has $\gamma = 33.24 \times 10^{-3}$ Nm^{-1} at this temperature. If $d = 0.9614 \times 10^3$ kg m^{-3} for the solution and 0.9982×10^3 kg m^{-3} for water, how much less in the same capillary tube will ethyl alcohol solution rise ?

   Answer. 47.4%

2. The surface tension of a liquid at 300 K is 27.1 dyne cm^{-1} and its density at this temperature is 0.9880 g cm^{-3}. What is the radius of the largest capillary that will allow the liquid to rise 2.0 cm ? (Assume the angle of contact to be zero and $g = 981$ cm sec^{-2})

   Answer. 0.028 cm

3. The surface tension of water at 293 K is 72.73×10^{-3} Nm^{-2}. How high will water rise in a capillary of diameter 0.01 cm?

   Answer. 29.7 cm

4. Compare the time of flow of the same volume of 20% wt. sucrose solution (density = 1.0794×10^3 kg m^{-3} and η = 1.695 centipoise) and 30% wt. sucrose solution (density 1.1252×103 kg m^{-3} and η = 2.735 centipoise)

   Answer. time 20% wt = time 30% wt × 0.65

5. If light machinery oil has η = 50 centipoise and density = 0.97×10^3 kg m^{-3} at 298 K, how long will it take for a sample to pass through a viscometer if water under the same conditions takes 1 minute (density of water = 1.00×10^3 kg m^{-3} and viscosity = 0.89 centipoise).

   Answer. 57.9 minutes

6. The refractive index of a liquid at 25 ºC is 1.6 and its density is 0.87 g cm^{-3}. Find the molar refraction. (Molar mass of the liquid is 78)

Answer. 26.36 cm^3 mol^{-1}

7. The molar refraction of a liquid is 12.95 cm^3 mol^{-1} and its density is 1.046 g cm^3. Calculate the refractive index (molar mass of liquid is 60 g mol^{-1})

Answer. 1.369

8. Calculate the optical rotation when sodium D light passes through a solution of a compound in chloroform, containing 25 g per 100 ml, placed in a cell of 20 cm. [α] for the compound in chloroform is 37.5º.

Answer. 18.75º

9. The refractive index of a liquid of molar mass 72 is 1.34 and its density is 0.98 g cm^{-3}. Find its molar refraction.

Answer. 15.40 cm^3 mol^{-1}

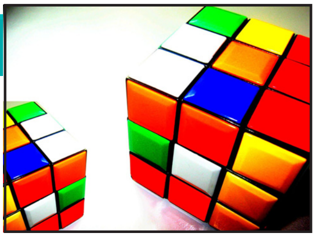
10. A glass capillary of diameter 0.1 cm is dipped into water. Calculate the level of the water that rises in the capillary if surface tension of water = 72.75 dyne cm^{-1} density = 0.9984 g cm^{-3} and contact angle for water = 10º.

Answer. 2.93 cm

12

The Solid State

CHAPTER



KEY CONCEPTS AND EQUATIONS

TYPE OF SOLIDS

In the solid state the matter is incompressible. That is why it has well defined shape. The units atom or molecules or ions in solid state are in close contact and have fixed position or sites. We can classify the solids into four types on the basis of Intermolecular forces holding the structural units together.

A MOLECULAR SOLID

It consists of atoms or molecules held together by intermolecular forces. Examples are solid neon, Ice, dry ice (solid carbon dioxide), etc.

AN IONIC SOLID

It consists of cations and anions held together by the electrical attraction of oppositely charged ions (Ionic bond). Examples are CsCl, NaCl, etc.

A COVALENT NETWORK SOLID

It consists of atoms held together in large network or chains of covalent bonds. Examples are diamond, graphite, etc.

A METALLIC SOLID

It consists of positive cores of atoms held together in a "sea" of electrons (metallic bonding). Examples are – copper, iron, silver, etc.

CRYSTALLINE AND AMORPHOUS SOLIDS

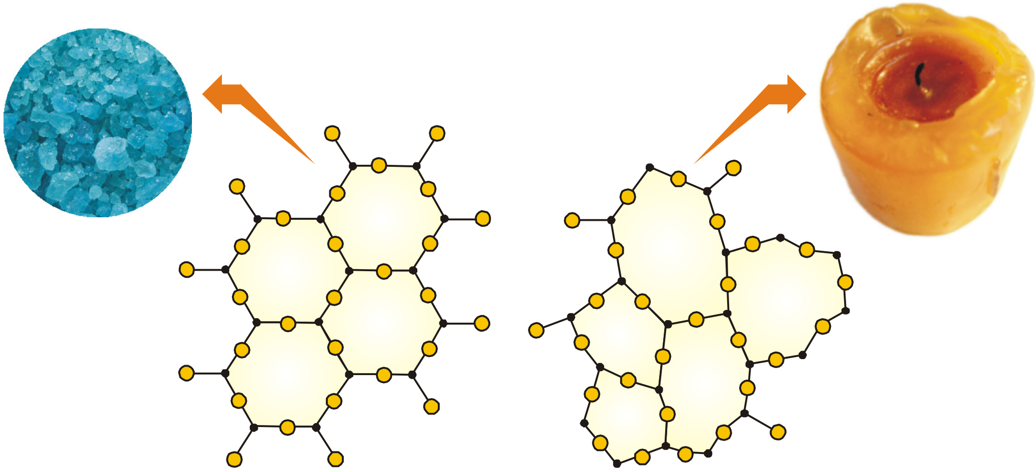
Solids may be crystalline or amorphous depending upon the arrangement of constituent units – atoms or molecules or ions.

A CRYSTALLINE SOLID

It is made up of one or more crystals and each crystal has a well-defined ordered three dimensional structure. Examples are NaCl, Sugar, etc.

AN AMORPHOUS SOLID

It has a disordered structure *i.e.* the constituent atoms, molecules or ions are arranged at random. Examples are rubber, plastic, glass, etc.



Crystalline solid

Amorphous solid

Figure 12.1

Two-dimensional representation of crystalline solid and an amorphous solid. Each substance has the formula A_2O_3. *A* is shown by ● and *O* is shown by ○.

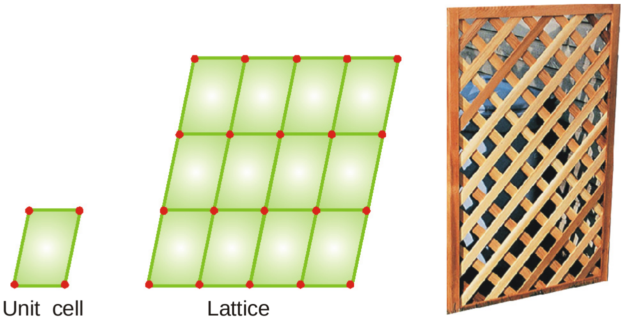
ISOTROPY AND ANISOTROPY

Amorphous substances are said to be isotropic because they exhibit the same value of any property in all directions. The refractive index, thermal and electrical conductivities, etc. are independent of the direction along which they are measured.

Crystalline substances are said to be anisotropic because the magnitude of a physical property varies with direction. For example, in a crystal of Ag I the coefficient of thermal expansion is positive in one direction and negative in the other.

CRYSTAL LATTICE

A crystal is a three dimensional ordered repeating arrangement of constituent unit atoms, molecules or ions. **A crystal lattice may be defined as the geometric arrangement of atoms or ions in space.** The position occupied by atoms or ions in the crystal lattice are called lattice sites.



Unit cell

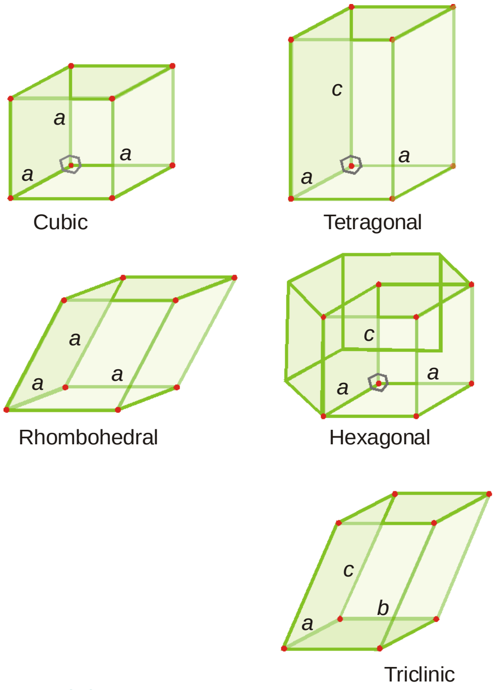
Lattice

Figure 12.2

Two-dimensional illustration of unit cell and crystal lattice.

UNIT CELL

It is smallest repeating box-like unit in space lattice which when repeated over and over results in the crystal of the substance in three dimensions. It is characterised by three axes *a*,*b* and *c* and three angles between axes α, β and γ. Depending upon the relationship between edge lengths and angles we have seven basic shapes possible for unit cells. These are given in Table 12.1 and shown in Fig.12.3.



Cubic Tetragonal Orthorhombic

Rhombohedral Hexagonal Monoclinic

Triclinic

Figure 12.3

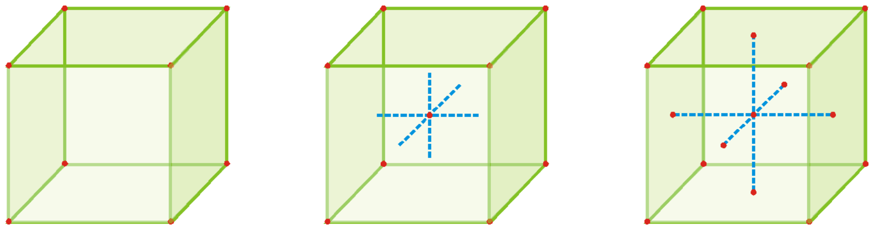
The primitive unit cells for the seven crystal systems. Where two or more of the axes are equal, the same letter is shown in each. Right angles (90^o) are shown as 7. The heavy line indicates the hexagonal unit cell.

TABLE 12.1. THE SEVEN CRYSTAL SYSTEMS

Crystal	Relative Edge Length	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	Cu, NaCl, etc.
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	Sn, TiO_2, etc.
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^o ; \gamma \neq 90^o$	Borax, $PbCrO_4$, etc.
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	$BaSO_4$, $CaCO_3$, etc.
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o ; \gamma = 120^o$	Zinc Oxide, Graphite, etc.
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$	Calcite, HgS, etc.
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	$K_2Cr_2O_7$, $CuSO_4 5H_2O$, etc.

CUBIC UNIT CELLS

There are three types of cubic unit cells. These are (i) Simple cubic unit cell (ii) A body centred cubic unit cell and (iii) A face centred cubic unit cell. These are shown in Fig.12.4.



Simple cube Body-centred cube Face-centred cube

Figure 12.4

Three cubic unit cells.

SIMPLE CUBIC UNIT CELL

It is the one in which the constituent units occupy only corners of a cube.

BODY CENTRED CUBIC UNIT CELL

It is the one in which there is one constituent unit at the centre of the cube in addition to the particles at the corners.

FACE CENTRED CUBIC UNIT CELL

It is the one in which there are constituent units, one each, at the six faces of the cube apart from the particles at the corners.

HOW TO DETERMINE THE NUMBER OF ATOMS IN A UNIT CELL

(i) Simple cube : Eight unit cells share each corner atom

∴ At each corner we have = 1/8 atom
and at 8 corners we have = 1/8 atom × 8
= 1 atom

(ii) Face centred cubic unit cell : Each face centred atom is shared by two units cells

∴ At each face we have = ½ atom
and at six faces we have = ½ atom × 6 = 3 atoms
at 8 corners we have = 1/8 atom × 8 = 1 atom
Thus the total number of atoms in face centred unit cell = 4 atoms

(iii) Body centred cubic unit cell : Each unit cell has one atom in the body

∴ No. of central atom = 1 atom
and at each corner we have = 1/8 atom
at 8 corners we have = 1/8 atom × 8 = 1 atom
Thus the total number of atom in body centred unit cell = 2 atoms

HOW TO DETERMINE MASS OF THE UNIT CELL

$$\text{Mass of the unit cell} = \text{No. of atoms in unit cell} \times \text{Mass of one atom}$$

$$= \text{No. of atoms in unit cell} \times \frac{\text{Molar mass of substance}}{\text{Avogadro's number}}$$

CO-ORDINATION NUMBER OF A CRYSTAL LATTICE

The co-ordination number of a crystal lattice is the number of particles (ions, atoms or molecules) immediately adjacent to each particle in the lattice. It is the characterstic of a given space lattice. The co-ordination numbers in different types of crystal lattice are as follows :

Type of crystal lattice	**Co-ordination number**
Simple cube	6
Body centred cube	8
Face centred cube	12

RADIUS RATIO AND ITS RELATION WITH CO-ORDINATION NUMBER

It is defined as the ratio of cation radius to that of the anion radius. It is denoted by r_+ / r_-. It is related to the co-ordination number in the following manner

Radius ratio	**Co-ordination Number**
between 0.225 – 0.414	4
between 0.414 – 0.732	6
between 0.732 –1	8

BRAGG'S EQUATION

When X-rays of wavelength λ strike the first plane at an angle θ, following equation is applicable

$$n\,\lambda = 2\,d\sin\theta$$

where d is the distance between two successive planes, n is the orientation of reflection.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Aluminium forms face-centred cubic crystals. The density of Al is 2.70 g cm^{-3}. Calculate the length of the side of the unit cell of Al (Atomic mass of Al = 27).

SOLUTION :

Number of Al atoms in unit cell $= 4$ [$\because$ f c c structure]

Avogadro's number $= 6.02 \times 10^{23}\ \text{mol}^{-1}$

$\therefore$ Mass of one Al atom $= \dfrac{\text{Atomic mass}}{\text{Avogadro's number}}$

$= \dfrac{27\ \text{g mol}^{-1}}{6.02 \times 10^{23}\ \text{mol}^{-1}}$

$= 4.485 \times 10^{-23}$

and Mass of one unit cell $= 4 \times 4.485 \times 10^{-23}\ \text{g}$

$= 17.940 \times 10^{-23}\ \text{g}$

Let the length of side of unit cell be $= a$

$\therefore$ volume of the unit cell $= a^3$

and density of unit cell $= \dfrac{\text{Mass}}{\text{Volume}} = 2.70\ \text{g cm}^{-3}$ (given)

Substitution of values

$2.70\ \text{g cm}^{-3} = \dfrac{17.940 \times 10^{-23}\ \text{g}}{a^3}$

or $a^3 = \dfrac{17.940 \times 10^{-23}\ \text{g}}{270\ \text{g cm}^{-3}}$

$a^3 = 66.444 \times 10^{-24}\ \text{cm}^3$

or $a = \sqrt[3]{66.444 \times 10^{-24}\ \text{cm}^3}$

$= \mathbf{4.0503 \times 10^{-8}\ cm}$

SOLVED PROBLEM 2. Gold has face-centred cubic structure with a unit length 4.07Å, a density of 19.3 g cm^{-3}. Calculate the Avogadro's number from the data (Atomic mass of Au = 197)

SOLUTION :

Number of atoms in Gold unit cell $= 4$ [$\because$ f c c structure]

Let Avogadro's number be $= N_0\ \text{mol}^{-1}$

Mass of gold atom $= \dfrac{\text{Atomic mass}}{\text{Avogadro's number}}$

$= \dfrac{197\ \text{g mol}^{-1}}{N_o}$

and Mass of one gold unit cell $= \dfrac{4 \times 197\ \text{g mol}^{-1}}{N_o\ \text{mol}^{-1}} = \dfrac{788}{N_o}\ \text{g}$

Edge length of gold unit cell, a $= 4.07$ Å (given)

$a = 4.07 \times 10^{-8}\ \text{cm}$

Volume of one gold unit cell, $a^3 = (4.07 \times 10^{-8}\text{ cm})^3$

$$\therefore \quad \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\frac{788}{N_o}}{(4.07 \times 10^{-8}\text{ cm})^3} = 19.3\text{ g cm}^{-3} \quad \text{(given)}$$

Substitution of values

$$\frac{788\text{ g}}{N_o \times (4.07 \times 10^{-8})^3\text{ cm}^3} = 19.3\text{ g cm}^{-3}$$

or

$$N_o = \frac{788\text{ g}}{(4.07 \times 10^{-8})^3 \times 19.3}$$

$$= 0.6056 \times 10^{24}$$

$$= \mathbf{6.056 \times 10^{23}}$$

SOLVED PROBLEM 3. Polonium crystallises in a simple cubic unit cell. It has an atomic mass = 209 and density = 91.5 kg m^{-3}. What is the edge length of its unit cell ?

SOLUTION :

Number of atoms of Po in unit cell = 1 [∵ Simple cube]

$$\text{Mass of one Po atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}}$$

$$= \frac{209\text{ g mol}^{-1}}{6.02 \times 10^{23}\text{ mol}^{-1}}$$

$$= 34.7176 \times 10^{-23}\text{ g}$$

Mass of one Po unit cell = $1 \times 34.7176 \times 10^{-23}$ g [∵ Simple Cube =1 atom]

Let the length of the unit cell be = a

Volume of the unit cell = a^3

And $\text{Density} = \dfrac{\text{Mass}}{\text{Volume}} = 91.5\text{ kg m}^{-3}$ (given)

$= 0.0915\text{ g m}^{-3}$

Substitution of values

$$0.0915\text{ g cm}^{-3} = \frac{34.7176 \times 10^{-23}\text{ g}}{a^3}$$

or

$$a^3 = \frac{34.7176 \times 10^{-23}\text{ g}}{0.0915\text{ g cm}^{-3}}$$

$$= 379.427 \times 10^{-23}\text{ cm}^3$$

$$= 3794.27 \times 10^{-24}\text{ cm}^3$$

or

$$a^3 = \sqrt[3]{3794.27 \times 10^{-24}\text{ cm}^3}$$

$$= \mathbf{15.597 \times 10^{-8}\text{ cm}}$$

SOLVED PROBLEM 4. Calculate the angle at which first order diffraction will occur in an X-ray diffractometer when X-rays of wavelength 1.54 Å are diffracted by the atoms of a crystal, given that the interplanar distance is 4.04 Å.

SOLUTION :

Formula used

$$n\lambda = 2d \text{ Sin } \theta$$

Quantities given

$n = 1$ $\lambda = 1.54$ Å $d = 4.04$ Å

Substitution of values

$$1 \times 1.54\ \text{Å} = 2 \times 4.04\ \text{Å} \times \text{Sin}\ \theta$$

or $$\text{Sin}\ \theta = \frac{1.54\ \text{Å}}{2 \times 4.04\ \text{Å}} = 0.19059$$

or $$\theta = \sin^{-1} 0.19059 = \mathbf{10.987^o}$$

SOLVED PROBLEM 5. The ionic radii of Cs is 169 pm and Br is 195 pm. What kind of unit cell would be expected for CsBr crystal ? Calculate the unit cell dimensions and density of CsBr crystal (atomic mass of Cs = 133 ; Br = 80)

SOLUTION :

(i) To find out the type of unit cell for CsBr

$$\text{Radius ratio of CsBr Crystal, } \frac{r_+}{r_-} = \frac{169\ \text{pm}}{195\ \text{pm}} = 0.866$$

Since the ratio lies in the range 0.732 – 1 the co-ordination number will be 8 and the crystal would exit in **simple cubic unit cell.**

(ii) To calculate the unit cell dimensions and density of CsBr

$$\text{Length of the edge of simple cube} = 2 \times \text{radius of Br}^- \text{ ion} = 2 \times 195\ \text{pm} = 390\ \text{pm} = 390 \times 10^{-10}\ \text{cm}$$

$$\text{Volume of cubic unit cell, } a^3 = (390 \times 10^{-10}\ \text{cm})^3$$

$$\text{Molecular mass of CsBr} = 133 + 80 = 213\ \text{g mol}^{-1}$$

$$\text{Mass of the unit cell} = \frac{213\ \text{g mol}^{-1}}{\text{Avogadro's Number}} = \frac{213\ \text{g mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}} = 35.3644 \times 10^{-23}\ \text{g}$$

$$\text{Density of CsBr unit cell} = \frac{\text{Mass of CsBr unit cell}}{\text{Volume of CsBr unit cell}} = \frac{35.3644 \times 10^{-23}\ \text{g}}{(390 \times 10^{-10}\ \text{cm})^3} = \frac{35.3644 \times 10^7}{(390)^3}\ \text{g cm}^{-3} = \mathbf{5.96\ g\ cm^{-3}}$$

SOLVED PROBLEM 6. Platinum crystallises in a face-centred cubic lattice with all atoms at the lattice points. It has a density of 21.45 g cm^{-3} and an atomic mass of 195.08 amu. From these data, Calculate the length of a unit-cell edge.

SOLUTION :

Molecular mass of Pt = 195.08 amu (Given)

$\therefore$ Mass of one atom of Pt $= \dfrac{\text{Molecular mass}}{\text{Avogadro number}}$

$= \dfrac{195.08}{6.02 \times 10^{23}}$ g

$= 3.240 \times 10^{-22}$ g

Number of Pt atom in unit cell = 4 [$\because$ f c c structure]

$\therefore$ Mass of unit cell of Pt $= 4 \times 3.240 \times 10^{-22}$ g

$= 1.296 \times 10^{-21}$ g

and volume of the unit cell, $V = \dfrac{M}{D} = \dfrac{1.296 \times 10^{-21}\text{ g}}{21.45\text{ g cm}^{-3}}$

$= 6.042 \times 10^{-23}\text{ cm}^3$

Edge of the unit cell, $a = \sqrt[3]{6.042 \times 10^{-23}\text{ cm}^{-3}}$

$= \mathbf{3.924 \times 10^{-8}\ cm}$

SOLVED PROBLEM 7. A body centred cubic element of density 10.3 g cm^{-3} has a cell edge of 314 pm. Calculate the atomic mass of the element. (Avogadro's number = 6.023×10^{23})

SOLUTION :

Number of atoms in bcc structure $= 8 \times \dfrac{1}{8} + 1$ atoms

$=$ 2 atoms

Density of element $= 10.3\text{ g cm}^{-3}$

Edge of the unit cell, $l = 314\text{ pm} = 314 \times 10^{-10}\text{ cm}$

$\therefore$ Volume of the unit cell, $V = l^3 = (314 \times 10^{-10})^3\text{ cm}^3$

Mass of the unit cell = Density × Volume

$= 10.3\text{ g cm}^{-3} \times (314 \times 10^{-10})^3\text{ cm}^3$

$= 3.1188 \times 10^{-22}$ g

Mass of one atom $= \dfrac{3.1188 \times 10^{-22}}{2}$ g [$\because$ unit cell = 2 atoms]

$= 1.5594 \times 10^{-22}$ g

Atomic mass = Avogadro's number × mass of 1 atom

$= 6.023 \times 10^{23} \times 1.5594 \times 10^{-22}$ g

$= \mathbf{94\ g\ mol^{-1}}$

SOLVED PROBLEM 8. A crystal of lead (II) sulphide has an NaCl structure. In this crystal the shortest distance between a Pb^{2+} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide ? Also calculate the unit cell volume ($N = 6.023 \times 10^{23}\text{ mol}^{-1}$; At. masses Pb = 207.2; S = 32)

SOLUTION :

Length of the cell edge, $a = 2(r_+ + r_-)$

$= 2 \times 297$ pm

$= 594$ pm

$= \mathbf{594 \times 10^{-10}\ cm}$

and volume of the unit cell, $a^3 = (594 \times 10^{-10}\ \text{cm})^3$

$= \mathbf{2.0958 \times 10^{-22}\ cm^3}$

SOLVED PROBLEM 9. Sodium metal crystallises in bcc lattice with cell edge a = 4.29 Å. What is the radius of sodium atom ?

SOLUTION :

We know

For a body centred cube

$$4r = \sqrt{3}\,a$$

or

$$r = \frac{\sqrt{3}}{4} \times a$$

$$= \frac{1.73}{4} \times 4.29\ \text{Å}$$

$$= \mathbf{1.855\ Å}$$

ADDITIONAL PRACTICE PROBLEMS

1. The cell edge of a face-centred cubic element of atomic mass 108 is 409 pm. Calculate its denstiy. (Avogadro's constant = 6.023×10^{23})
   Answer. 10.48 g cm^{-3}
2. A body centred cubic element of density 10.3 g cm^{-3} has a cell edge of 314 pm. Calculate the atomic mass of element. (Avogadro's constant = 6.023×10^{23})
   Answer. 94 amu
3. An element (atomic mass = 60) having face centred cubic structure has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell. (Avogadro's constant = 6.023×10^{23} mol^{-1})
   Answer. 4×10^{-8} cm
4. Sodium chloride crystallises in face-centred cubic (fcc) structure. Its density is 2.165 g cm^{-3}. If the distance between Na^+ and its nearest Cl^- is 281 pm, find out the Avogadro's number (Na = 23 g mol^{-1} ; Cl = 35.44 g mol^{-1})
   Answer. 6.08×10^{-23} mol^{-1}
5. Crystalline CsBr has a bcc Structure. Calculate the unit cell length if the density of CsBr crystal is 4.29 g cm^{-3} ($N_o = 6.023 \times 10^{23}$ mol^{-1} ; Atomic masses, Cs = 133 ; Br = 80)
   Answer. 4.369×10^{-8} cm
6. Lead (II) Sulphide crystal has a NaCl structure. What is its density ? The edge length of the unit cell of PbS crystal is 500 pm. ($N_o = 6.023 \times 10^{23}$ mol^{-1} ; Atomic masses, Pb = 207.2 ; S = 32)
   Answer. 12.7 g cm^{-3}

7. KF has NaCl structure. What is the distance between K^+ and F^- in KF if its density is 2.48 g cm^{-3} ? (Atomic mass of K = 39.1, F = 19)

Answer. 2.689×10^{-8} cm

8. Sodium chloride crystal has fcc structure. Its density is 2.163×10^2 kgm^{-2}. Calculate the edge of the unit cell cube. ($M_{NaCl} = 58.45 \times 10^{-3}$ kg mol^{-1} ; $N_o = 6.023 \times 10^{23}$ mol^{-1})

Answer. 5.640×10^{-8} cm

9. Given for Fe a/pm = 286 ; ρ g cm^{-3} = 7.86. Find the type of cubic lattice to which the crystal belongs. Also calculate the radius of Fe. (At. mass of Fe = 55.85 amu)

Answer. bcc ; 123.84 pm

10. Copper crystal has fcc cubic lattice structure. Its density is 8.93 g cm^{-3}. What is the length of the unit cell? ($N_o = 6.023 \times 10^{23}$; Atomic mass of Cu = 63.5)

Answer. 3.614×10^{-8} cm^{-3}

11. A face centred cubic element (at. mass = 60) has a unit cell egde of 400 pm. What is its density ? ($N_o = 6.023 \times 10^{23}$ atoms mol^{-1})

Answer. 6.226 g cm^{-3}

12. Calculate the value of Avogadro's number from the data : Density of NaCl = 2.165 g cm^{-3} ; Distance between Na^+ and Cl^- in NaCl structure = 281 pm.

Answer. 6.089×10^{23}

13. The nearest neighbour distance in silver atoms in the silver crystal is 2.87×10^{-10} m apart. What is the density of silver ? Silver crystallizes in fcc form (Atomic mass of Ag = 108)

Answer. 10.73 g cm^{-3}

14. KF has NaCl type structure. What is the distance between K^+ and F^- in KF, if the density of KF is 2.48 g cm^{-3} ? (Atomic mass of K = 39.1 ; F = 19 ; Avogadro's Number = 6.023×10^{23} mol^{-1})

Answer. 268.9 pm

15. A unit cell of sodium chloride has four formula unit. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride ?

Answer. 2.1656 g cm^{-3}

13

Physical Properties and Chemical Constitution

CHAPTER

KEY CONCEPTS AND EQUATIONS

SURFACE TENSION AND CHEMICAL CONSTITUTION

The surface tension of a liquid is related to its density and density of vapour pressure at the same temperature by the relation.

$$\frac{\gamma^{1/4}}{D - d} = C$$

where γ is the surface tension, *D* its density and *d* the density of vapours at the same temperature and *C* is a constant. Multiplying both sides by *M*, the molecular mass of the liquid, we get

$$\frac{M\gamma^{1/4}}{D - d} = MC = [P]$$

The quantity [*P*] is called parachor. As *d* is negligible as compared to *D*, the equation reduces to

$$\frac{M}{D}\gamma^{1/4} = [P]$$

or $$V_m\gamma^{1/4} = [P]$$

or $\gamma = 1$ then $$V_m = [P]$$

Thus **Parachor [P]** may be defined as the molar volume of a liquid at a temperature that its surface tension is unity. The Parachor is very helpful in elucidating structure of molecules as it is both an additive and constitutive property.

VISCOCITY AND CHEMICAL CONSTITUTION

Viscosity is due to intermolecular attractions which resist the flow of a liquid.

If molecular volume [*M*/*d*] be multiplied by the eighth root of the coefficient of viscosity, it gives a constant value [*R*] termed as Rheochor.

$$\frac{M}{d} \times \eta^{1/8} = [R]$$

DIPOLE MOMENT

The dipole moment of a polar molecule is given by the product of the charge at one end and the distance between the opposite charges. Thus

$$\mu = q \times r$$

where q is charge in esu and r the distance is Å units (10^{-8} cm) The CGS unit for dipole moment is debye

$$\begin{aligned} 1 \text{ Debye} &= 10^{-10} \text{ esu} \times 10^{-8} \text{ cm} \\ &= 1 \times 10^{-18} \text{ esu cm} \end{aligned}$$

The dipole moment is a vector quantity. The net dipole moment of the molecule is the vector resultant of all the individual bonds.

DIPOLE MOMENT AND IONIC CHARACTER

The magnitude of the dipole moment of a diatomic molecule determines its ionic character. The % ionic character of a bond is calculated by using the formula

$$\% \text{ Ionic character} = \frac{\mu_{experimental}}{\mu_{ionic}} \times 100$$

MOLAR REFRACTION AND CONSTITUTION

The molar refraction of a molecule is a sum of contributions of the atomic refractions and bond refractions. It is helpful in elucidating the structure of molecules.

OPTICAL ACTIVITY AND CONSTITUTION

The optical activity is due to the pressure dissymmetry in the molecule. An optically active molecule exists in two or more forms which are non-superimposable mirror images of each other. These are called enantiomers. One of these enantiomers rotates the plane of polarised light towards right and is called dextro-rotatory and the other which rotates the plane of polarised light towards left is called leavorotatory.

MAGNETIC PROPERTIES

Substances can be classified as Diamagnetic or Paramagnetic depending upon their behaviour in a magnetic field.

Diamagnetic substances are slightly repelled or pushed out of magnetic field, and

Paramagnetic substances are slightly attracted or pulled into the magnetic field.

Paramagnetism is due to the presence of unpaired electrons in the ion or molecule whereas all electrons are paired in Diamagnetic substances.

The magnetic moment of a molecule is given by the formula

$$\mu = \sqrt{n(n+2)}$$

where μ is magnetic moment in magnetons and n is the number of unpaired electrons.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Parachor of decane is found to be 424.2. Each $-CH_2-$ group has a parachor value of 39. Find out the parachor of hydrogen and carbon.

SOLUTION :

Formula used

$$\text{Parachor of decane} = 2 \times \text{Parachor of } CH_3- \; + \; 8 \times \text{Parachor of } CH_2-$$

Quantities given

Parachor of decane = 424.2 *Parachor of* $-CH_2- = 39$

Substitution of values

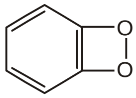
$$424.2 = 2 \times \text{Parachor of } CH_3- \; + \; 8 \times 39$$

or $$2 \times \text{Parachor of } CH_3- = 424.2 - 8 \times 39$$

or

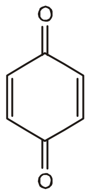
$$\begin{aligned}
\text{Parachor of } CH_3- &= \frac{112.2}{2} = 56.1 \\
\text{Parachor of } H &= \text{Parachor of } CH_3- \;-\; \text{Parachor of } -CH_2- \\
&= 56.1 - 39 = \mathbf{17.1} \\
\text{Parachor of } C &= \text{Parachor of } CH_3- \;-\; 3\times \text{Parachor of } C \\
&= 56.1 - 3 \times 17.1 \\
&= \mathbf{4.8}
\end{aligned}$$

SOLVED PROBLEM 2. For quinone, the following two structures are proposed :



(i)

and



(ii)

The experimental value of parachor of quinone is 237.0. Parachor values for $H = 17.1$, $C = 4.8$, $O = 20.0$, double bond $= 23.2$, 6-carbon ring $= 6.1$. Which constitution will you accept ?

SOLUTION :

$$\begin{aligned}
\text{Parachor of Structure (i)} &= 6\times P_C + 4\times P_H + 2\times P_O + P_{\textit{carbon ring}} + 3\times P_{\textit{double bond}} \\
&= 6\times 4.8 + 4\times 17.1 + 2\times 20.0 + 6.1 + 3\times 23.2 \\
&= 212.9 \\
\text{Parachor of structure (ii)} &= 6\times P_c + 4\times P_H + 2\times P_O + P_{\textit{carbon ring}} + 4\times P_{\text{double bond}} \\
&= 6\times 4.8 + 4\times 17.1 + 2\times 20 + 6.1 + 4\times 23.2 \\
&= 28.8 + 68.4 + 40 + 6.1 + 92.8 \\
&= 236.1
\end{aligned}$$

The value of Parachor structure (ii) is close to the experimental value. Thus the structure (ii) is accepted.

SOLVED PROBLEM 3. Predict the parachor for $CH_3–C_6H_4–CN$ if the parachor equivalent for C is 4.8 ; H, 17.1 ; N, 12.5 ; double bond, 23.2 ; triple Bond, 46.6 ; and six-membered ring, 6.1.

SOLUTION :

The predicted parachor is the sum of the equivalents *i.e.*

$$\begin{aligned}
8\,C &= 8\times 4.8 &&= 38.4 \\
7\,H &= 7\times 17.1 &&= 119.7 \\
1\,N &= 1\times 12.5 &&= 12.5 \\
\text{One six membered ring} &= 1\times 6.1 &&= 6.1 \\
\text{Triple bond (one)} &= 1\times 46.6 &&= 46.6 \\
\text{Three double bonds} &= 3\times 23.2 &&= 69.6 \\
&\text{Total} &&= \underline{\mathbf{292.9}}
\end{aligned}$$

SOLVED PROBLEM 4. The density of hexane at 25 ºC is 0.6874 g cm^{-3}. Calculate the surface tension of hexane if the parachors of ethane and propane are 110.5 and 150.8 respectively.

SOLUTION :

(i) To calculate the parachor of C_6H_{14}

$$[P]_{C_2H_6} = 2 \times [P]_{CH_3} = 110.5$$

$$[P]_{C_3H_8} = 2 \times [P]_{CH_3} + [P]_{CH_2} = 150.8$$

$$\therefore \quad [P]_{CH_2} = [P]_{C_3H_8} - [P]_{C_2H_6}$$

$$= 150.8 - 110.5 = 40.3$$

$$[P]_{C_6H_{14}} = [P]_{C_3H_8} + 3 \times [P]_{CH_2}$$

$$= 150.8 + 3 \times 40.3$$

$$= 271.7$$

Molar mass of Hexane = 86

(ii) To calculate the surface tension of C_6H_{14}

Formula used

$$\frac{M}{D}\gamma^{1/4} = [P]$$

Quantities given

$[P] = 271.7$ $\quad M = 86$ $\quad D = 0.6874 \text{ g cm}^{-3}$

Substitution of values

$$\frac{86}{0.6874} \times \gamma^{1/4} = 271.7$$

or $$\gamma^{1/4} = \frac{271.7 \times 0.6874}{86} \text{ dyne cm}^{-1}$$

$$\gamma^{1/4} = 2.172 \text{ dynes cm}^{-1}$$

and $$\gamma = (2.172)^4 \text{ dynes cm}^{-1}$$

$$= \mathbf{22.25 \text{ dyne cm}^{-1}}$$

SOLVED PROBLEM 4. The density of paraldehyde is 0.9943 g cm^{-3}. Calculate the parachor if the surface tension is 25.9 dyne cm^{-1}. The molar mass of paraldehyde is 132.16 g mol^{-1}.

SOLUTION :

Formula used

$$\frac{M}{D}\gamma^{1/4} = [P]$$

Quantities given

$M = 132.16 \text{ g mol}^{-1}$ $\quad D = 0.9943 \text{ g cm}^{-3}$ $\quad \gamma = 25.9 \text{ dyne cm}^{-1}$

Substitution of values

$$[P] = \frac{132.16}{0.9943} \times (25.9)^{1/4}$$

$$= 132.91 \times 2.256$$

$$= \mathbf{299.84}$$

ADDITIONAL PRACTICE PROBLEMS

1. The parachor equivalent for C is 4.8; for H, 17.1 ; and for O, 20.0 Calculate the parachor for methanol.

Answer. 93.2

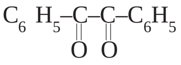
2. The parachor equivalents for C is 4.8 ; for H, 17.1 ; and for O, 20.0. Calculate the parachor for ethyl alcohol.

Answer. 132.2

3. Calculate the parachors of methanol and ethanol if $\gamma = 22 \times 10^{-3}\ \text{Nm}^{-1}$ for each alcohol and if $d = 0.7914 \times 10^3\ \text{kg m}^{-3}$ for methanol and $0.7893 \times 10^3\ \text{kg m}^{-3}$ for ethanol.

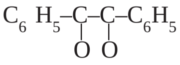
Answer. 87.6 and 126.2

4. For benzil, the following two structures have been proposed



$$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5$$

I



$$C_6H_5-\underset{\underset{O}{|}}{C}-\underset{\underset{O}{|}}{C}-C_6H_5$$

II

The experimental value of parachor of quinone is 479. Parachor values for H = 17.1, C = 4.8, O = 20., double bond = 23.2, 6-carbon ring = 6.1. Which constitution will you accept ?

Answer. I

5. A substance having the molecular formula C_3H_6O may be allyl alcohol ($CH_2 = CH - CH_2 - OH$) or acetone (CH_3–CO–CH_3). Determine the correct formula if the observed molar refractivity of the compound is 15.998 $\text{cm}^3\ \text{mol}^{-1}$. Given that refractivities of C = 2.418, H = 1.100, O (Carbonyl) = 2.211, O (hydroxyl) = 1.525 and C = C double bond = 1.733.

Answer. 16.06 acetone

6. For isocyanide, the following two structures have been suggested

$$-N\overset{\rightarrow}{\equiv}C \qquad\qquad - \overset{+}{N}=\overset{-}{C}$$

I II

The experimental value of parachor of quinone is 65. Parachor values for N = 12.5, C = 4.8, double bond 23.2. Which constitution will you accept ?

Answer. II

7. The molecule AsF_3 has a dipole moment of 2.59 D. Which of following geometries are possible? Trigonal planar, Trigonal pyramidal, T-shaped

Answer. Trigonal pyramidal

8. Which of the following molecules would be expected to have zero dipole moments on the basis of their geometry ? (a) H_2S (b) PF_3 (c) TeF_6 (d) BeF_2

Answer. (c) and (d)

9. Calculate the %age ionic character of H – Cl bond if the distance between the two atoms is 1.275 Å and its dipole moment is 1.03 D.

Answer. 16.885%

10. Each of the following molecules has a non zero dipole moment. Select the geometry that is consistent with this information.

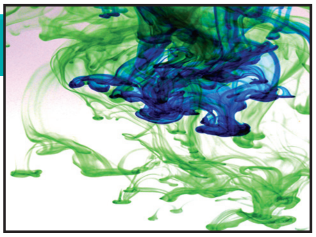
(a) SO_2 ; Linear, Bent

(b) PH_3 ; Trigonal planar, Trigonal pyramidal

Answer. (a) Bent (b) Trigonal pyramidal

14 Solutions

CHAPTER



KEY CONCEPTS AND EQUATIONS

SOLUTION AND ITS CONCENTRATION

A solution is a homogeneous mixture of two or more substances. The substance which is present in smaller amount is called a **solute** and the one which is present in a large amount is called **solvent.** The concentration of a solution is the amount of solute present in a given amount of solution *i.e.*

$$\text{Concentration} = \frac{\text{Amount of solute}}{\text{Volume of solution}}$$

WAYS OF EXPRESSING CONCENTRATION

(i) Percent by weight

It is the weight of solute as a per cent of the total weight of the solution *i.e.*

$$\text{\% by weight of solute} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

(ii) Mole Fraction

It is the ratio of number of moles of solute and the total number of moles of solute and solvent. Thus

$$X_{\text{solute}} = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}}$$

$$X_{\text{solute}} = \frac{n}{n+N} \quad \text{and} \quad X_{\text{solute}} = \frac{N}{n+N}$$

Where n is the number of moles of solute and N the number of moles of solvent.

(iii) Molarity

It is the number of moles of solute per litre of solution.

i.e. $$\text{Molarity, } M = \frac{\text{moles of solute}}{\text{volume of solution in litres}}$$

(iv) Molality

It is the number of solute per kilogram of solvent *i.e.*

$$\text{Molality, } m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

(v) Normality

It is defined as the number of gram equivalents of solute per litre of solution. Thus

$$\text{Normality, } N = \frac{\text{no. of gram equivalents of solute}}{\text{volume of solution in litres}}$$

(vi) Formality

It is the number of formula weight in grams dissolved per litre of solution. When formula weight is equal to the molecular weight, the formality and molarity are the same.

SOLUTION OF GASES IN GASES

When two gases which do not react chemically are mixed, a homogeneous solution is obtained. Such a mixture follows Dalton's law of partial pressure.

HENRY'S LAW

The solubility of a gas in a solvent depends upon the pressure and temperature. The effect of pressure on solubility of a gas can be predicted quantitatively by Henry's law which states that the solubility of a gas is directly proportional to the partial pressure of the gas above the solution. Mathematically,

$$C \propto P \qquad \text{or} \qquad C = k\,P$$

where C is the concentration of the gas in solution, k, the proportionality constant and P, the pressure of the gas.

VAPOUR PRESSURE OF MIXTURE OF NON-MISCIBLE LIQUIDS

In a mixture of non-miscible liquids, each component exerts its own vapour pressure independent of others and the total vapour pressure is equal to the sum of individual vapour pressures of all the liquids. This generalisation is the basic principle of steam distillation. The number of molecules of each component in the vapour will be proportional to its vapour pressure i.e. to the vapour pressure of the pure liquid at that temperature. Hence

$$\frac{n_1}{n_2} = \frac{p_1}{p_2}$$

where n_1 and n_2 are the number of moles of the two components, p_1 and p_2 are their vapour pressures.

We can also write

$$\frac{w_1 / M_1}{w_2 / M_2} = \frac{p_1}{p_2}$$

where w_1 and w_2 are the masses of two liquids with their molecular masses M_1 and M_2 respectively From this we can calculate the molecular mass of one component if that of other is given.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the molality of a solution of sodium hydroxide which contains 0.2 g of sodium hydroxide in 50 g of the solvent.

SOLUTION :

Formula used

$$\textit{Molality, } m = \frac{\textit{No. of moles of solute}}{\textit{mass of solvent in kg}}$$

Quantities given

$$\textit{amount of NaOH} = 0.2 \text{ g and } \textit{no. of moles of NaOH} = \frac{0.2 \text{ g}}{40 \text{ g mol}^{-1}}$$

$$\textit{mass of solvent} = 50 \text{ g} = 50 \times 10^{-3} \text{ kg} = 0.005 \text{ kg}$$

Substitution of values

$$\text{Molality, } m = \frac{0.005}{50 \times 10^{-3}} = \mathbf{0.1\ m}$$

SOLVED PROBLEM 2. Calculate the normality of a solution containing 6.3 g of oxalic acid crystals (molecular mass = 126) dissolved in 500 ml of the solution.

Formula used

$$\textit{Normality, } N = \frac{\textit{No. of gram equivalents}}{\textit{volume of solution in litres}}$$

Quantities given

$$\textit{Amount of oxalic acid in 500 ml solution} = 6.3\text{ g}$$

$$\textit{No. of gram equivalents of oxalic acid} = \frac{\textit{Amt. of solute}}{\textit{gram equivalent weight}} = \frac{6.3\text{ g}}{63\text{ g equiv}^{-1}} = 0.1\text{ equiv}$$

$$\text{volume of solution} = 500\text{ ml} = 0.5\text{ lit.}$$

Substitution of values

$$\text{Normality, } N = \frac{0.1}{0.5} = \mathbf{0.2\ N}$$

SOLVED PROBLEM 3. A sample of spirit contains 92% ethanol by weight, the rest being water. What is the mole fraction of its constituents ?

SOLUTION :

Let the weight of a sample of ethanol be = 100 g

Amount of ethanol in the sample = 92 % = 92 g

and Amount of water in the sample = 8% = 8 g

Formula used

$$X_A = \frac{\textit{No. of moles of A}}{\textit{Total no. of moles}}$$

Quantities given

$$\textit{No. of moles of ethanol} = \frac{\textit{Amount}}{\textit{Molar mass}} = \frac{92\text{ g}}{46\text{ g mol}^{-1}} = 2\text{ moles}$$

$$\textit{No. of moles of water} = \frac{\textit{Amount}}{\textit{Molar mass}} = \frac{8\text{ g}}{18\text{ g mol}^{-1}} = 0.444\text{ mole}$$

Substitution of values

$$X_{ethanol} = \frac{2\text{ moles}}{2\text{ moles} + 0.444\text{ mole}} = \frac{2\text{ mole}}{2.444\text{ mole}} = \mathbf{0.818}$$

and

$$X_{H_2O} = \frac{0.444\text{ mole}}{2\text{ moles} + 0.444\text{ mole}} = \frac{0.444\text{ mole}}{2.444\text{ mole}} = \mathbf{0.182}$$

SOLVED PROBLEM 4. Calculate the ionic strength of a solution containing 0.2 M NaCl and 0.1 M Na_2SO_4.

SOLUTION :

Since $NaCl \equiv Na^+$

Amount of Na^+ from 0.2 M NaCl = 0.2 × Atomic mass of Na^+

$= 0.2 \times 23$

$= 4.6 \text{ g lit}^{-1}$

and $Na_2SO_4 \equiv 2\,Na^+$

Amount of Na^+ from 0.1 *M* Na_2SO_4 $= 2 \times 0.1 \times$ Atomic mass of Na^+

$= 2 \times 0.1 \times 23$

$= 4.6 \text{ g lit}^{-1}$

Thus total strength of Na^+ ions $= 4.6 \text{ g lit}^{-1} + 4.6 \text{ g lit}^{-1}$

$= \mathbf{9.2 \text{ g lit}^{-1}}$

Now $NaCl \equiv Cl^-$

Amount of Cl^- from 0.2 *M* NaCl $= 0.2 \times$ Formula mass of Cl^-

$= 0.2 \times 35.5$

$= \mathbf{7.1 \text{ g lit}^{-1}}$

and Amount of SO_4^{2-} from 0.1 *M* Na_2SO_4 $= 0.1 \times$ Formula mass of SO_4^{2-}

$= 0.1 \times 96$

$= \mathbf{9.6 \text{ g lit}^{-1}}$

SOLVED PROBLEM 5. Determine the molality of a solution containing 86.53 g of sodium carbonate (molar mass = 105.99) per litre in water at 20°C. The density of the solution at this temperature is 1.0816 g ml^{-1}.

SOLUTION :

(i) To calculate the amount of Na_2CO_3 in 1000 g of water

Density of solution $= 1.0816 \text{ g ml}^{-1}$

$\therefore$ Mass of 1 litre solution $= 1.0816 \text{ g ml}^{-1} \times 1000 \text{ ml}$ [$\because$ M = density × vol.]

$= 1081.6 \text{ g}$

Amt. of sodium carbonate in 1081.6 g of $= 86.53$ g (given)

$\therefore$ Amt. of Na_2CO_3 in 1000 g of water $= \dfrac{86.53 \times 1000}{1081.6}$ g

$= 80.0 \text{ g}$

(ii) To calculate the molality

Formula used

$$\textit{Molality, } m = \frac{\textit{Amount of } Na_2CO_3 \textit{ in 1000 g of water}}{\textit{molar mass}}$$

Quantities given

Amount of Na_2CO_3 in 1000 g of water $= 80.0 \text{ g}$

Molar mass of Na_2CO_3 $= 105.99 \text{ g mol}^{-1}$

Substitution of values

$$\textit{Molality, m} = \frac{80 \text{ g}}{105.99 \text{ g mol}^{-1}}$$

$= \mathbf{0.7548 \text{ m}}$

SOLVED PROBLEM 6. A solution contains 25% water, 25% ethanol and 50% ethanoic acid. Calculate the mole fraction of each component.

SOLUTION :

(i) To calculate the total number of moles

Let the mass of solution be $= 100 \text{ g}$

$$\text{Amount of } H_2O = 25\,\% = 25\text{ g}$$
$$\text{Amount of } C_2H_5OH = 25\,\% = 25\text{ g}$$
$$\text{Amount of } CH_3COOH = 50\,\% = 50\text{ g}$$
$$\text{Number of moles of water} = \frac{25\text{ g}}{18\text{ g mol}^{-1}} = 1.3888\text{ moles}$$
$$\text{Number of moles of } C_2H_5OH = \frac{25\text{ g}}{46\text{ g mol}^{-1}} = 0.5435\text{ mole}$$
$$\text{Number of moles of } CH_3COOH = \frac{50\text{ g}}{60\text{ g mol}^{-1}} = 0.8333\text{ moles}$$
$$\text{Total number of moles} = 1.3888 + 0.5434 + 0.8333\text{ moles}$$
$$= 2.7655\text{ moles}$$

(ii) To calculate the mole fraction of each component

Formula used

$$X_{Component} = \frac{\text{No. of moles of component}}{\text{Total no. of moles}}$$

Substitution of values

$$\text{Mole fraction of } H_2O,\ X_{H_2O} = \frac{1.3888\text{ moles}}{2.7655\text{ moles}} = \mathbf{0.502}$$
$$\text{Mole Fraction of } C_2H_5OH,\ X_{C_2H_5OH} = \frac{0.5435\text{ mole}}{2.7655\text{ moles}} = \mathbf{0.1965}$$
$$\text{Mole Fraction of } CH_3COOH,\ X_{CH_3COOH} = \frac{0.8333\text{ mole}}{2.7655\text{ mole}} = \mathbf{0.3013}$$

SOLVED PROBLEM 7. What is molarity and molality of a 13% solution (by weight) of sulphuric acid ? Its density is 1.09 g ml^{-1}.

SOLUTION :

$$\text{Let the mass of solution be} = 100\text{ g}$$
$$\text{Amount of } H_2SO_4 \text{ in solution} = 13\text{ g}$$
$$\text{Amount of } H_2O \text{ in solution} = 87\text{ g}$$
$$\text{Number of moles of } H_2SO_4 = \frac{13\text{ g}}{98\text{ g mol}^{-1}} = 0.1326\text{ mol}$$

(i) To calculate the molality

Formula used

$$\textit{Molality, m} = \frac{\textit{No. of moles of } H_2SO_4}{\textit{Mass of solvent in kg}}$$

Quantities given

$$\text{No. of moles } H_2\,SO_4 = 0.1326$$
$$\text{Mass of solvent} = 87\text{ g} = 87 \times 10^{-3}\text{ kg}$$

Substitution of value

$$\text{Molality, } m = \frac{0.1326}{87 \times 10^{-3}\text{ kg}}$$
$$= \mathbf{1.524\ m}$$

(ii) To calculate the molarity

$$\text{Volume of 100 g of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100\text{ g}}{1.09\text{ g ml}^{-1}}$$

$$= 91.74 \text{ ml}$$

$$= 0.09174 \text{ lit}$$

$$\text{Molarity, } M = \frac{\text{No. of moles of } H_2\,SO_4}{\text{Volume of solution in litre}}$$

$$= \frac{0.1326}{0.09174}$$

$$= \mathbf{1.4459\ M}$$

SOLVED PROBLEM 8. 49 g of H_2SO_4 are dissolved in 250 ml of solution. Calculate the molarity of the solution.

Solution :

$$\text{Amount of } H_2SO_4 \text{ in 250 ml solution} = 49 \text{ g}$$

$$\text{Amount of } H_2SO_4 \text{ in 1 lit solution} = \frac{49 \times 1000}{250} \text{ g}$$

$$= 196 \text{ g}$$

$$\text{No. of moles of } H_2SO_4 \text{ in 1 lit solution} = \frac{196 \text{ g}}{98 \text{ g mol}^{-1}}$$

$$= 2 \text{ moles}$$

$$\text{Molarity, } M = \frac{\text{No. of moles of } H_2SO_4}{\text{Volume of solution in litre}}$$

$$= \frac{2 \text{ moles}}{1 \text{ lit}}$$

$$= \mathbf{2\ M}$$

SOLVED PROBLEM 9. 45 g of glucose, $C_6H_{12}O_6$, are dissolved in 500 g of water. Calculate the molality of the solution.

SOLUTION :

$$\text{Amount of glucose in 500 g water} = 45 \text{ g}$$

$$\text{No. of moles of glucose in 500 g water} = \frac{45\text{g}}{180 \text{ g mol}^{-1}}$$

$$= 0.25 \text{ mol}$$

$$\text{Mass of water} = 500 \text{ g}$$

$$= 500 \times 10^{-3} \text{ kg}$$

$$\textit{Molality, m} = \frac{\text{No. of moles of glucose}}{\text{Mass of water in kg}}$$

$$= \frac{0.25}{500 \times 10^{-3}}$$

$$= \mathbf{0.5\ m}$$

SOLVED PROBLEM 10. Nitrobenzene is completely miscible with water. A mixture of two liquids boils at 99°C and 753 torr pressure. The vapour pressure of water is 733 torr at this temperature. Find out the weight composition of liquid mixture.

SOLUTION :

Formula used

$$\frac{w_1}{w_2} = \frac{p_1}{p_2} \times \frac{M_1}{M_2}$$

Quantities given

$$p_1 = \text{Vap. pressure of mixture} - \text{vap. pressure of water} = 753 \text{ torr} - 733 \text{ torr} = 20 \text{ torr}$$

P_2 = 733 torr $\qquad$ M_1 of Nitrobenzene ($C_6H_5NO_2$) = 123 $\qquad$ M_2 of water = 18

Substitution of values

$$\frac{w_1}{w_2} = \frac{20 \text{ torr}}{733 \text{ torr}} \times \frac{123}{18} = 5.36$$

$$\frac{w_1}{w_2} = \frac{5.36}{1}$$

or $\qquad \mathbf{w_1 : w_2 = 5.36 : 1}$

SOLVED PROBLEM 11. Calculate the mole fraction of water in a mixture of 12 g of water, 108 g of acetic acid and 92 g of ethyl alcohol.

SOLUTION :

(i) To calculate the total number of moles

$$\text{No. of moles of } H_2O = \frac{12 \text{ g}}{18 \text{ g mol}^{-1}} = 0.667 \text{ mole}$$

$$\text{No. of moles of } CH_3COOH = \frac{108 \text{ g}}{60 \text{ g mol}^{-1}} = 1.80 \text{ mole}$$

$$\text{No. of moles of } C_2H_5OH = \frac{92 \text{ g}}{46 \text{ g mol}^{-1}} = 2.0 \text{ mole}$$

$$\text{Total number of moles} = 0.667 \text{ moles} + 1.80 \text{ moles} + 2.0 \text{ moles} = 4.467 \text{ moles}$$

(ii) To calculate the mole fraction of H_2O

Formula used

$$X_{H_2O} = \frac{\text{Number of moles of } H_2O}{\text{Total number of moles}} = \frac{0.667 \text{ mole}}{4.467 \text{ mole}} = \mathbf{0.1493}$$

SOLVED PROBLEM 12. Calculate the molality of 1M solution of sodium nitrate, the density of solution is 1.25 g cm^{-3}.

SOLUTION :

$$\text{Mass of 1 litre solution of } NaNO_3 = \text{Density} \times \text{volume} = 1.25 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 = 1250 \text{ g}$$

$$\text{Molar mass of } NaNO_3 = 23 + 14 + 48 = 85 \text{ g mol}^{-1}$$

$$\text{Mass of water in one litre solution} = 1250 \text{ g} - 85 \text{ g} = 1165 \text{ g} = 1.165 \text{ kg}$$

$$\text{Molality of } NaNO_3 = \frac{\text{Number of moles of } NaNO_3}{\text{Mass of water in kg}}$$

$$= \frac{1\,\text{mole}}{1.165\,\text{kg}}$$

$$= \mathbf{0.8583\ m}$$

SOLVED PROBLEM 13. 2.82 g of glucose (mol mass = 180) are dissolved in 30 g of water. Calculate the (i) molality of the solution (ii) mole fraction of glucose and water.

SOLUTION :

(i) To calculate the molality of the solution

$$\text{Number of moles of glucose} = \frac{\text{mass of glucose}}{\text{molar mass}}$$

$$= \frac{2.82\,\text{g}}{180\,\text{g mol}^{-1}} = 0.01567$$

$$\text{Amount of solvent} = 30\,\text{g} = 30 \times 10^{-3}\,\text{kg}$$

$$\text{Molality of glucose, } m = \frac{\text{No. of moles of glucose}}{\text{amt. of water in kg}}$$

$$= \frac{0.01567}{30 \times 10^{-3}}$$

$$= \mathbf{0.5223\ m}$$

(ii) To calculate the mole fraction of glucose and water

$$\text{No. of moles of } H_2O = \frac{30\,\text{g}}{18\,\text{g mol}^{-1}} = 1.6667\,\text{mole}$$

$$\text{Number of moles of glucose} = 0.01567\,\text{mole}$$

$$\text{Total number of glucose} = 0.01567 + 1.6667\,\text{mole}$$

$$= 1.68237$$

Formula used

$$X_{component} = \frac{\text{No. of moles of component}}{\text{Total number of moles}}$$

$$X_{glucose} = \frac{0.01567\,\text{mole}}{1.68237\,\text{mole}} = \mathbf{0.0093}$$

$$X_{H_2O} = \frac{1.6667\,\text{mole}}{1.68237\,\text{mole}} = \mathbf{0.9907}$$

SOLVED PROBLEM 14. Calculate the mole fraction of ethyl alcohol in a solution of total volume 86 ml prepared by adding 50 ml of ethyl alcohol ($d = 0.789\ \text{g ml}^{-1}$) to 50 ml of water (density = $1.0\ \text{g ml}^{-1}$)

SOLUTION :

$$\text{Mass of 50 ml ethyl alcohol} = \text{Density} \times \text{volume} = 0.789\,\text{g ml}^{-1} \times 50\,\text{ml}$$

$$= 39.45\,\text{g}$$

$$\text{Number of moles of } C_2H_5OH = \frac{\text{Amt of } C_2H_5OH}{\text{molar mass of } C_2H_5OH} = \frac{39.45\,\text{g}}{46\,\text{g mol}^{-1}}$$

$$= 0.8576\,\text{mole}$$

$$\text{Mass of 50 ml of water} = \text{Density} \times \text{volume}$$

$$= 1.0\,\text{g ml}^{-1} \times 50\,\text{ml}$$

$$= 50\,\text{g}$$

$$\text{Number of moles of } H_2O = \frac{50\,\text{g}}{18\,\text{g mol}^{-1}} = 2.777\,\text{moles}$$

Mole fraction of ethyl alcohol, $X_{C_2H_5OH} = \dfrac{\text{No. of moles } C_2H_5OH}{\text{Total no. of moles}}$

$= \dfrac{0.8576 \text{ mole}}{0.8576 \text{ mole} + 2.777 \text{ moles}}$

$= \mathbf{0.2359}$

SOLVED PROBLEM 15. The density of a 3 M sodium thiosulphate solution is 1.25 g ml^{-1}. Calculate (i) the % by weight of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate, and (iii) the molality of Na^+ and $S_2O_3^{2-}$ ions.

SOLUTION :

(i) To calculate the % by weight of sodium thiosulphate

Density of the solution $= 1.25 \text{ g ml}^{-1}$

Mass of 1000 ml of solution $=$ Density × volume

$= 1.25 \text{ g ml}^{-1} \times 1000 \text{ ml} = 1250 \text{ g}$

Amt of $Na_2S_2O_3$ in 3 M solution $= 3 \times$ molar mass of $Na_2S_2O_3$

$= 3 \times 158 \text{ g}$

$= 474 \text{ g}$

1250 g of solution contains $Na_2S_2O_3$ $= 474 \text{ g}$

% by weight of $Na_2S_2O_3$ $= \dfrac{474 \text{ g}}{1250 \text{ g}} \times 100$

$= \mathbf{37.92\ \%}$

(ii) To calculate the mole fraction of $Na_2S_2O_3$

Amount of $Na_2S_2O_3$ in 100g solution $= 37.92$

Amount of H_2O in 100 g solution $= 100 - 37.92 = 62.08 \text{ g}$

Number of moles of $Na_2S_2O_3$ $= \dfrac{37.92 \text{ g}}{158 \text{ g mole}} = 0.24 \text{ mole}$

Number of moles of water $= \dfrac{62.08 \text{ g}}{18 \text{ g mol}^{-1}} = 3.449 \text{ mol}$

Total no. of moles $= 0.24 \text{ mole} + 3.449 \text{ mole} = 3.689 \text{ moles}$

Mole fraction of $Na_2S_2O_3$, $X_{Na_2S_2O_3} = \dfrac{0.24 \text{ mole}}{3.689 \text{ mole}} = \mathbf{0.065}$

(iii) To calculate molality of Na^+ and $S_2O_3^{2-}$ ions

No. of moles of Na_2 in 68.02 g water $= 0.24 \text{ mole}$

No. of moles of $Na_2S_2O_3$ in 1000g water $= 3.528 \text{ mole}$

Molality of Na^+ ions $= 2 \times 3.528 \text{ moles}$ $[\because Na_2S_2O_3 \equiv 2\,Na^+]$

$= \mathbf{7.056\ m}$

and Molality of $S_2O_3^{2-}$ ions $= 1 \times 3.528 \text{ moles}$ $[\because Na_2S_2O_3 \equiv S_2O_3^{2-}]$

$= \mathbf{3.528\ m}$

SOLVED PROBLEM 16. Calculate the molality of water in pure water.

SOLUTION :

Mass of 1 litre of pure water $=$ Density × volume

$= 1.0 \text{ g ml}^{-1} \times 1000 \text{ ml}$

$= 1000 \text{ g}$

Molar mass of H_2O $= 18 \text{ g mol}^{-1}$

$\therefore$ No. of moles of H_2O in 1000 g of pure water $= \dfrac{1000\text{ g}}{18\text{ g mol}^{-1}}$

Molality, $m = \mathbf{55.55\ m}$

SOLVED PROBLEM 17. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution.

SOLUTION :

Mass of Glauber's salt, $Na_2SO_4.10H_2O$ dissoloved $= 8.0575 \times 10^{-2}$ kg

Molar mass of $Na_2SO_4.10H_2O = 46 + 32 + 64 + 180 = 322\text{ g mol}^{-1}$

$$\text{Number of moles of } Na_2SO_4.10H_2O = \frac{8.0575 \times 10^{-2}}{322 \times 10^{-3}\text{ kg mol}^{-1}}$$
$$= 0.25\text{ mole}$$

Mass of 1 dm^3 (1 lit.) solution of $Na_2SO_4.10H_2O$ = Density × volume

$$= 1077.2\text{ kg m}^{-3} \times 10^{-3}\text{ m}^3$$
$$= 1.0772\text{ kg}$$

322 g of $Na_2SO_4.10H_2O$ contains Na_2SO_4 = 142 g

$$8.0575{\times}10^{-2}\text{ kg of } Na_2SO_4.10H_2O \text{ contains } Na_2SO_4 = \frac{142 \times 8.0575 \times 10^{-2}\text{ kg}}{322}$$
$$= 3.553 \times 10^{-2}\text{ kg}$$

Mass of water in 1 dm^3 solution (1litre) $= 1.0772\text{ kg} - 3.553 \times 10^{-2}$ kg $= 1.04167$ kg

(i) To calculate molarity of Na_2SO_4

Formula used

$$\textit{Molarity, } M = \frac{\textit{No of moles of } Na_2SO_4}{\textit{Vol. of solution in } dm^3 \textit{ (litre)}}$$
$$= \frac{0.25\text{ mole}}{1\text{ dm}^3} = \mathbf{0.25\ M}$$

(ii) To calculate molality of Na_2SO_4

Formula used

$$\textit{Molality, } m = \frac{\text{No of moles of } Na_2SO_4}{\text{Mass of water in kg}}$$
$$= \frac{0.25\text{ mole}}{1.04167\text{ kg}} = \mathbf{0.2400\ m}$$

(iii) To calculate mole fraction of Na_2SO_4

Formula used

$$\textit{Mole fraction of } Na_2SO_4,\ X_{Na_2SO_4} = \frac{\textit{No of moles of } Na_2SO_4}{\textit{Total no. of moles}}$$
$$= \frac{0.25\text{ mole}}{\dfrac{1.04167 \times 10^3}{18} + 0.25\text{ mole}}$$
$$= \frac{0.25\text{ mole}}{57.87 + 0.25\text{ mole}}$$
$$= \frac{0.25\text{ mole}}{58.12\text{ mole}} = \mathbf{0.0043}$$

ADDITIONAL PRACTICE PROBLEMS

1. A solution contains 100 g of NaCl and 900 g of water. Calculate the mole fraction of the components of the solution.

   Answer. 0.0331 and 0.9669

2. Calculate the molarity of a solution containing 331g of HCl dissolved in sufficient water to make 2 dm^3 of solution.

   Answer. 4.534 *M*

3. Calculate the molality of a solution containing 100 g of H_2SO_4 dissolved in 2 kg of water.

   Answer. 0.51 *m*

4. How many grams of Na_2CO_3 should be added to 2000 g of water in order to prepare 0.100 *m* solution of Na_2CO_3 ?

   Answer. 21.2 g

5. What is the normality of a solution containing 28.0 g of KOH dissolved in sufficient water to make 400 ml of solution ?

   Answer. 1.25 *N*

6. Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 172 ml obtained by adding 100 ml ethyl alcohol (d = 0.789 g ml^{-1}) to 100 ml of water (d = 1.0 g ml^{-1})

   Answer. 9.953 *M* ; 17.12 *m* ; 0.0299

7. Calculate the molality and mole fraction of the solute in a aqueous solution containing 5.0 g of urea in 250 g of water. (molecular mass of urea = 60)

   Answer. 0.0833 *m* ; 0.00596

8. A solution has 20% water, 20% ethyl alcohol and 60% acetic acid by mass. Calculate the mole fraction of each component.

   Answer. 0.437 ; 0.170 ; 0.393

9. Calculate the molarity and normality of a solution containing 5.3 g of Na_2CO_3 dissolved in 1000 ml solution.

   Answer. 0.05 *M* ; 0.10 *N*

10. Calculate the molarity of the diluted solution obtained by diluting 1 litre of 12 M HCl to 20 litre.

    Answer. 0.6 *m*

11. Water was added to 25.0 ml of 98 percent H_2SO_4, density 1.84 g ml^{-1} to make 100 ml solution. Calculate the normality and molarity of the solution.

    Answer. 9.2 *N* ; 4.6 *M*

12. A 6.90 M solution of KOH in water contains 30% by weight of KOH. Calculate the density of the solution.

    Answer. 1.288 g ml^{-1}

13. Concentrated NH_4OH has a density of 0.90 g ml^{-1} and is 28 percent by weight. What is its normality ?

    Answer. 15 N

14. Calculate the molarity and molality of a solution of K_2CO_3 containing 22% of the salt by weight and has a density of 1.21 g ml^{-1}.

    Answer. 1.93 *M* ; 2.04 *m*

15. What is molarity of Fe^{2+} ions in a solution containing 200 g of $FeCl_3$ per litre of solution ?

Answer. 1.574 *M*

16. 5 g of NaCl is dissolved in 1 kg of water. If the density of the solution is 0.997 g ml^{-1}, calculate the molarity, molality and mole fraction of the solute.

Answer. 0.085 *M*, 0.0847 *m*, 0.00153

17. How many kilograms of wet $AlCl_3$ containing 24% water are required to prepare 100 litres of 0.5 M solution.

Answer. 8.782 kg

18. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate (i) molal concentration and (ii) mole fraction of sugar in syrup.

Answer. (i) 0.556 m ; (ii) 0.0099

19. A water solution contains 8.0% sugar by weight and has a density of 1.03 g ml^{-1}. How many grams of sugar are there in 400 ml of the solution ?

Answer. 33.0 g

20. Calculate the amount of Na^+ and Cl^- ions in grams present in 500 ml of 1.5 *M* NaCl solution.

Answer. 17.3 g Na^+ and 26.6 g Cl^-

21. Calculate the number of molecules of sugar present in 1 ml of 10% sugar solution having density = 1.20 g ml^{-1}.

Answer. 2.1×10^{20}

22. The acid solution in a fully charged lead storage battery contains one-third of sulphuric acid by weight and has a density of 1.25 g ml^{-1}. Calculate the molarity and molality and mole fraction of the acid solution.

Answer. 4.21 M ; 5.02 *m*

15

Theory of Dilute Solutions

CHAPTER

KEY CONCEPTS AND EQUATIONS

COLLIGATIVE PROPERTIES

Certain properties of solutions which depend only on the concentration (number of particles) of solute particles are called colligative properties. These are independent of the size or nature of the particles. Colligative properties may be used to measure the concentration of solute. In this way, we can determine the molecular weight of the solute.

LOWERING OF VAPOUR PRESSURE - RAOULT'S LAW

When a non-volatile solute is dissolved in a solvent, the vapour pressure of the pure solution is lowered than that of pure solvent. This lowering of vapour pressure relative to the vapour pressure of the pure solvent is equal to the mole fraction of the solute in dilute solution. (Raoult's law) *i.e.*

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

where p is the vapour pressure of the pure solvent, p_s the vapour pressure of solution, n the number of moles of solute and N the number of moles of solvent.

DETERMINATION OF MOLECULAR MASS

If w is the mass of the solute of molecular mass m dissolved in W grams of solvent of molecular mass M, we can write :

$$\frac{p - p_s}{p} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

For a very dilute solution w/m is very small and is negligible in the denominator, then we have

$$\frac{p - p_s}{p} = \frac{w/m}{W/M} = \frac{wM}{Wm}$$

From this we can calculate the molecular mass of the solute if other parameters are given.

BOILING POINT ELEVATION

The addition of non-volatile solute lowers the vapour pressure and the solution has to be heated to a higher temperature in order to make its vapour pressure equal to the atmospheric pressure. *i.e.*

Elevation in boiling point occurs. The elevation in boiling point, ΔT is given by

$$\Delta T_b = T - T_b$$

where T is the boiling point of the solution and T_b, the boiling point of pure solvent. The elevation in boiling point, ΔT is directly proportional to the relative lowering of vapour pressure, *i.e.*

$$\Delta T_b \propto \frac{p - p_s}{p}$$

From Raoult's law we can write

$$\Delta T_b \propto \frac{w\,M}{W\,m} \qquad \left[\because \frac{p - p_s}{p} = \frac{w\,M}{W\,m}\right]$$

or $$\Delta T_b = K_b \times \frac{w}{m} \times \frac{1}{W} \qquad \text{[since } M \text{ is constant]}$$

where K_b is a constant called **Boiling point constant** or **Molal Elevation constant. It is defined as the boiling point elevation produced when 1 mole of the solute is dissolved in 1 kg (1000g) of the solvent.** If the mass of the solvent (W) is given in grams, it has to be converted into kilograms. Then we have

$$\Delta T_b = K_b \times \frac{w}{m} \times \frac{1}{W/1000}$$

or the molecular mass, $$m = \frac{K_b \times 1000 \times w}{\Delta T_b \times W}$$

The molal elevation constant is characterstic of a particular solvent used. It can also be calculated by using the relation.

$$K_b = \frac{R\,T_b^2}{1000 \times L_v}$$

where R is gas constant, T_b, the boiling point of the solvent used and L_v the molar latent heat of vaporisation.

FREEZING POINT DEPRESSION

The addition of a non-volatile solute lowers the vapour pressure and the freezing point decreases. This difference of the freezing point of pure solvent and the solution is called depression in freezing point, denoted by ΔT_f. It is given by

$$\Delta T_f = T_f - T$$

where T_f is the freezing point of pure solvent and T, the freezing point of the solution. It is directly proportional to the relative lowering of vapour pressure *i.e.*

$$\Delta T_f \propto \frac{p - p_s}{p}$$

From Raoult's law we can write

$$\Delta T_f \propto \frac{w\,M}{W\,m} \qquad \left[\because \frac{p - p_s}{p} = \frac{w\,M}{W\,m}\right]$$

or $$\Delta T_f \propto \frac{w}{W\,m} \qquad \text{[since } M \text{ is constant]}$$

or $$\Delta T_f \propto \frac{w}{m} \times \frac{1}{W}$$

$$= K_f \times \frac{w}{m} \times \frac{1}{W}$$

where K_f is called the **Freezing point constant or Molal depression constant. It is defined as the freezing point depression produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent.** If the mass of solvent (W) is in grams, it has to be converted into kilograms, then we can write

$$\Delta T_f = K_f \times \frac{w}{m} \times \frac{1}{W/1000}$$

or molecular mass of solute, $m = \dfrac{K_f \times 1000 \times w}{\Delta T_f \times W}$

The molal depression constant is characteristic of a particular solvent used. It can also be calculated by using the relation.

$$K_f = \frac{R\,T_f^2}{1000 \times L_f}$$

COLLIGATIVE PROPERTIES OF ELECTROLYTES

The electrolytes ionise in solution and yield more than one particle per formula unit in the solution. Therefore, the colligative effect of an electrolyte is always greater than that of a non-electrolyte of the same molal concentration. To account for the effect of electrolytes, a factor known as van't Hoff factor, *i*, was introduced. **It is defined as ratio of the colligative effect produced by an electrolyte solution to corresponding effect for the same concentration of a non-electrolyte solution,** *i.e.*

$$i = \frac{\Delta T_f}{[\Delta T_f]_0} = \frac{\Delta T_b}{[\Delta T_b]_0} = \frac{\Delta p}{[\Delta p]_0}$$

where ΔT_f, ΔT_b and Δp are elevation in boiling point, depression in freezing point and lowering of vapour pressure for the electrolyte solution and $[\Delta T_f]_0$, $[\Delta T_b]_0$ and $[\Delta p]_0$ are corresponding colligative properties for non-electrolyte solution of the same molal concentrations.

The vant Hoff factor, *i*, can be calculated by using any colligative property *eg.*

$$\Delta T_b = \frac{i \times 1000 \times K_b \times w}{m \times W}$$

ABNORMAL MOLECULAR MASSES OF ELECTROLYTES

In case of electrolytes, which dissociate into ions, the experimental molecular mass will always be less than the theoretical value calculated from the formula. The van't Hoff factor, *i*, is also equal to the ratio of number of particles in solution to the number obtained assuming no ionisation, *i.e.*

$$i = \frac{\text{Actual number of particles}}{\text{Number of particles for no ionisation}}$$

The degree of dissociation is the fraction of a electrolyte which is dissociated into ions in aqueous solution. It is denoted by λ and is related to the van't Hoff factor by the relation

$$\lambda = \frac{i - 1}{v - 1}$$

where *v* is the no. of ions formed on complete dissociation of 1 mole of an electrolyte.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A Solution containing 10.0 g of a compound in 100 g of water lowers the vapour pressure from 17.5 mm of Hg to 17.41 mm of Hg at 20ºC. Calculate the molecular mass of the compound.

SOLUTION :

Formula used $\dfrac{p - p_s}{p} = \dfrac{w \times M}{m \times W}$

Quantities given

p = 17.5 mm of Hg $\quad$ p_s = 17.41 mm of Hg $\quad$ w = 18 g

w = 10 g $\quad$ W = 100 g

Substitution of values

$$\frac{17.5\,\text{mm} - 17.41\,\text{mm}}{17.5\,\text{mm}} = \frac{10\text{g} \times 18}{m \times 100\text{g}}$$

or
$$\frac{0.09}{17.5} = \frac{10 \times 18}{m \times 100}$$

or
$$m = \frac{10 \times 18 \times 17.5}{0.09 \times 100}$$
$$= \mathbf{350}$$

SOLVED PROBLEM 2. 10 g of a non-volatile solute was dissolved in 100 g of acetone (molecular mass = 58) at 25 ºC. The vapour pressure of the solution was found to be 192.5 mm Hg. Calculate the molecular mass of the solute. The vapour pressure of pure acetone at 25 ºC is 195 mm Hg.

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

p = 195 mm Hg $\quad$ p_s = 192.5 mm Hg $\quad$ w = 10 g

W = 100 g $\quad$ M = 58

Substitution of values

$$\frac{195\,\text{mm} - 192.5\,\text{mm}}{195\,\text{mm}} = \frac{10\text{ g} \times 58}{100\text{ g} \times m}$$

or
$$\frac{2.5}{195} = \frac{10 \times 58}{100 \times m}$$

or
$$m = \frac{10 \times 58 \times 195}{100 \times 2.5}$$
$$= \mathbf{452.4}$$

SOLVED PROBLEM 3. Napthalene freezes at 80.1 ºC. It has a molal depression constant 6.89 ºC kg mol^{-1}. A solution of 3.2 g of sulphur in 100 g of napthalene freezes at a temperature 0.86 ºC lower than pure napthalene. What is the molecular formula of sulphur in napthalene ?

SOLUTION :

Formula used

$$\text{Molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

K_f = 6.89 ºC kg mol^{-1} $\quad$ w = 3.2 g $\quad$ ΔT_f = 0.86 ºC

W = 100 g

Substitution of values

$$m = \frac{1000 \times 6.89\text{ ºC kg mol}^{-1} \times 3.2\text{ g}}{0.86\text{ ºC} \times 100\text{g}}$$
$$= 256$$

$$\text{Number of sulphur atoms in napthalene} = \frac{\text{Calculated mol. mass}}{\text{Atomic mass of S}}$$

$$= \frac{256}{32} = \mathbf{8}$$

Thus, the molecular formula of sulphur in napthalene is S_8.

SOLVED PROBLEM 4. A Solution of urea in water has a freezing point of – 0.400 ºC. Calculate the boiling point of the solution. ($K_f = 1.86$; $K_b = 0.51$)

SOLUTION :

Formula used

$$\text{molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W} \quad \text{... (i)}$$

and $$\text{molecular mass, } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W} \quad \text{... (ii)}$$

Quantities given

$\Delta T_f = 0.4\,^\circ\text{C}$ $K_f = 1.86\,^\circ\text{C}$ $K_b = 0.51^\circ\text{C}$

Substitution in (i) and (ii) we have

$$m = \frac{1000 \times 1.86\,^\circ\text{C} \times w}{0.4\,^\circ\text{C} \times W} \quad \text{and} \quad m = \frac{1000 \times 0.51\,^\circ\text{C} \times w}{\Delta T_b \times W}$$

On equating we get

$$\frac{1000 \times 1.86\,^\circ\text{C} \times w}{0.4\,^\circ\text{C} \times W} = \frac{1000 \times 0.51 \times w}{\Delta T_b \times W}$$

or $$4650 = \frac{510}{\Delta T_b}$$

or $$\Delta T_b = \frac{510}{4650} = 0.10968\,^\circ\text{C}$$

$\therefore$ Boiling point of the solution = Boiling point of water + Elevation in boiling point

$$= 100\,^\circ\text{C} + 0.10968\,^\circ\text{C}$$

$$= \mathbf{100.10968\,^\circ C}$$

SOLVED PROBLEM 5. Boiling point of 2.5 m solution of glucose (mol mass = 180) in water was 101.3 ºC. Calculate the molal elevation constant of water.

SOLUTION :

Formula used

$$\Delta T_b = m \times K_b \quad \text{or} \quad K_b = \frac{\Delta T_b}{m}$$

Quantities given

$\Delta T_b = 101.3\,^\circ\text{C} - 100\,^\circ\text{C} = 1.3\,^\circ\text{C}$ $m = 2.5$

Substitution of values

$$K_b = \frac{1.3\,^\circ\text{C}}{2.5} = \mathbf{0.52\,^\circ C}$$

SOLVED PROBLEM 6. A solution of 8.585 g of sodium nitrate in 100 g of water freezes at – 3.04 ºC. Calculate the molecular mass of sodium nitrate. (K_f for water = 1.86 K mol^{-1})

SOLUTION :

Formula used

$$\text{molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$K_f = 1.86 \text{ K mol}^{-1}$ $\quad \Delta T_f = 3.04\ ^\circ\text{C} = 3.04 \text{ K}$ $\quad w = 8.585 \text{ g}$ $\quad W = 100 \text{ g}$

Substitution of values

$$m = \frac{1000 \times 1.86 \text{ K mol}^{-1} \times 8.585 \text{ g}}{3.04 \text{ K} \times 100 \text{ g}}$$

$$= \mathbf{52.52}$$

SOLVED PROBLEM 7. A 0.1 molar solution of urea at the room temperature freezes at – 0.25 ºC at normal pressure. What would be the approximate freezing point of 0.1 molal aqueous solution of aluminium chloride at room temperature assuming complete ionisation ?

SOLUTION :

Formula used

$$\Delta T_f = K_f \times m \qquad \text{or} \qquad K_f = \frac{\Delta T_f}{m}$$

Quantities given

$\Delta T_f = 0.25\ ^\circ\text{C}$ $\quad m = 0.1$

Substitution of values

$$K_f = \frac{0.25\ ^\circ\text{C}}{0.1} = 2.5\ ^\circ\text{C}$$

Now, for $AlCl_3$

$$\Delta T_f = K_f \times m$$

$$= 2.5\ ^\circ\text{C} \times 0.1$$

$$= \mathbf{0.25\ ^\circ C}$$

SOLVED PROBLEM 8. The values of molal elevation constant and molal depression constant for water are 0.52 and 1.86 ºC kg mol^{-1} respectively. If the elevation in boiling point by dissolving a solute in water is + 0.2 ºC, what will be the depression in freezing point of this solution ?

SOLUTION :

Formula used

$$\Delta T_b = K_b \times m \qquad \text{and} \qquad \Delta T_f = K_f \times m$$

or

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}$$

Quantities given

$\Delta T_b = 0.2\ ^\circ\text{C}$ $\quad K_b = 0.52\ ^\circ\text{C kg mol}^{-1}$ $\quad K_f = 1.86\ ^\circ\text{C kg mol}^{-1}$

Substitution of values

$$\frac{0.2\ ^\circ\text{C}}{\Delta T_f} = \frac{0.52\ ^\circ\text{C kg mol}^{-1}}{1.86\ ^\circ\text{C kg mol}^{-1}}$$

or

$$\Delta T_f = \frac{1.86 \times 0.2\ ^\circ\text{C}}{0.52}$$

$$= \mathbf{0.715\ ^\circ C}$$

SOLVED PROBLEM 9. 1.065 g of an organic solute dissolved in 30.14 g of diethyl ether raises the boiling point by 0.296 ºC. The molal elevation constant of ether is 2.11. Calculate the molecular mass of the solute.

SOLUTION :

Formula used

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$K_b = 2.11$°C $\quad w = 1.065$ g $\quad \Delta T_b = 0.296$ °C $\quad W = 30.14$ g

Substitution of values

$$m = \frac{1000 \times 2.11\,°\text{C} \times 1.065\text{ g}}{0.296\,°\text{C} \times 30.14\text{ g}}$$

$$= \mathbf{251.88}$$

SOLVED PROBLEM 10. A 0.5 percent solution of potassium chloride was found to freeze at – 0.24 °C. Calculate the degree of dissociation of potassium chloride. (Molal depression constant for water = 1.80 °C)

SOLUTION :

(i) To calculate the molecular mass of KCl

Formula used

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

Quantities given

$K_b = 1.80$ °C $\quad \Delta T_f = 0.24$ °C $\quad w = 5$ g $\quad W = 99.5\,g$

Substitution of values

$$m = \frac{1000 \times 1.80\,°\text{C} \times 0.5\text{ g}}{0.24\,°\text{C} \times 99.5\text{ g}}$$

$$= \mathbf{37.69}$$

(ii) To calculate the degree of dissociation of KCl

The observed molecular mass = 37.69

and the normal molecular mass = 38 + 35.5 = 73.5

$$\text{van't Hoff factor, } i = \frac{\text{Normal molecular mass}}{\text{observed molecular mass}}$$

$$= \frac{73.5}{37.69} = 1.950$$

The degree of dissociation is related to van't Hoff factor by the relation

$$i = 1 + \alpha$$

or $$1.950 = 1 + \alpha$$

or $$\alpha = \mathbf{0.95} \text{ or } \mathbf{95\%}$$

SOLVED PROBLEM 11. 10 g of a substance is dissolved in 100 g of water at 25 °C. The vapour pressure of water is lowered from 17.5 mm to 17.2 mm. Calculate the molecular mass of the solute.

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$p = 17.5$ mm $\quad p_s = 17.2$ mm $\quad w = 10$ g

$W = 100$ g $\quad M = 18$

Substitution of values

$$\frac{17.5\,\text{mm} - 17.2\,\text{mm}}{17.5\,\text{mm}} = \frac{10\,\text{g} \times 18}{m \times 100\,\text{g}}$$

or
$$\frac{0.3\,\text{mm}}{17.5\,\text{mm}} = \frac{10 \times 18}{m \times 100\,\text{g}}$$

or
$$m = \frac{10 \times 18 \times 17.5}{100 \times 0.3}$$
$$= \mathbf{105}$$

SOLVED PROBLEM 12. 20 g of a non-volatile substance (mol mass = 60) was dissolved in 100 g of water. Calculate the vapour pressure of the solution at 100 ºC.

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$p = 760\,\text{mm}$ $\quad w = 20\,\text{g}$ $\quad W = 100\,\text{g}$

$m = 60$ $\quad M = 18$

Substitution of values

$$\frac{760\,\text{mm} - p_s}{760\,\text{mm}} = \frac{20\,\text{g} \times 18}{60 \times 100\,\text{g}}$$

or
$$760\,\text{mm} - p = \frac{760\,\text{mm} \times 20 \times 18}{60 \times 100}$$

or
$$760\,\text{mm} - p = 45.6\,\text{mm}$$
$$p_s = 760\,\text{mm} - 45.6\,\text{mm}$$
$$= \mathbf{714.4\,mm}$$

SOLVED PROBLEM 13. The molecular mass of a water soluble non-electrolyte is 58. Compute the boiling point of a solution containing 24 g of the solute and 600 g of water at atmospheric pressure. (K_{1000} of water = 0.573)

SOLUTION :

Formula used

$$\Delta T_b = \frac{1000 \times K_b \times w}{m \times W}$$

Quantities given

$K_b = 0.573\,ºC$ $\quad w = 24\,\text{g}$ $\quad W = 600\,\text{g}$ $\quad m = 58$

Substitution of values

$$\Delta T_b = \frac{1000 \times 0.573ºC \times 24\,\text{g}}{58 \times 600\,\text{g}}$$
$$= 0.395\,ºC$$

Thus the boiling point of solution = Boiling point of water + ΔT_b

$$= 100\,ºC + 0.395\,ºC$$
$$= \mathbf{100.395\,ºC}$$

SOLVED PROBLEM 14. When a certain amount of solute is added to 100 g of water at 25 ºC, the vapour pressure reduces to one half of that for pure water. The vapour pressure of water is 23.76 mm Hg. Find out the amount of salt added.

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

p = 23.76 mm $\qquad P_s$ = ½ p = ½ × 23.76 mm = 11.88 mm

W = 100 g $\qquad M$ = 18

Substitution of values

$$\frac{23.76\,\text{mm} - 11.88\,\text{mm}}{23.76\,\text{mm}} = \frac{w}{m} \times \frac{18}{100}$$

or
$$\frac{11.88\,\text{mm}}{23.76\,\text{mm}} = \frac{w}{m} \times \frac{18}{100}$$

or
$$\frac{w}{m} = \frac{1}{2} \times \frac{100}{18}$$

$$= \mathbf{2.78\ mole}$$

SOLVED PROBLEM 15. 0.3×10^{-3} kg of camphor (molar mass 154.5×10^{-3} kg mol^{-1}) when added to 25.2×10^{-3} kg of chloroform raised the boiling point of the solvent by 0.299 K. Calculate the molecular elevation constant of chloroform.

SOLUTION :

Formula used

$$m = \frac{K_b \times 1000 \times w}{\Delta T_b \times W} \quad \text{or} \quad K_b = \frac{m \times \Delta T_b \times W}{1000 \times w}$$

Quantities given

m = 154.5 g mol^{-1} = 154.5×10^{-3} kg mol^{-1} $\qquad W$ = 25.2×10^{-3} kg

w = 0.3×10^{-3} kg $\qquad \Delta T_b$ = 0.299 K

Substitution of values

$$K_b = \frac{154.5 \times 10^{-3}\,\text{kg mol}^{-1} \times 0.299\,\text{K} \times 25.2 \times 10^{-3}\,\text{kg}}{1000 \times 0.3 \times 10^{-3}\,\text{kg}}$$

$$= \mathbf{3.88} \times 10^{-3}\ \text{K kg mol}^{-1}$$

SOLVED PROBLEM 16. When 0.946 g of sugar is dissolved in 150 g of water, the resulting solution is observed to have a freezing point of 0.0651 °C. What is the molecular mass of sugar ? (K_f for water is 1.86 °C).

SOLUTION :

Formula used

$$\text{molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

K_f = 1.86 °C $\qquad w$ = 0.946 g $\qquad \Delta T_f$ = 0.0651 °C $\qquad W$ = 150 g

Substitution of values

$$m = \frac{1000 \times 1.86\,°\text{C} \times 0.946\,\text{g}}{0.0651\,°\text{C} \times 150\,\text{g}}$$

$$= \mathbf{180}$$

SOLVED PROBLEM 16. An immiscible liquid system composed of water and an organic liquid boils at 95ºC when the barometer reads 740 mm. The vapour pressure of pure liquid at this temperature is 63 mm. The distillate contains 55% of the weight of the organic compound. Calculate the molecular mass of the organic compound.

SOLUTION :

Formula used

$$\frac{w_1}{w_2} = \frac{p_1}{p_2} \times \frac{M_1}{M_2}$$

Quantities given

$w_1 = 45$ $\quad$ $w_2 = 55$ $\quad$ $M_1 = 18$

p_1 (water) = Vap. pressure of mixture – Vap. pressure of liquid = 740 mm – 63 mm = 677 mm

Substitution of values

$$\frac{45}{55} = \frac{677\,\text{mm}}{63\,\text{mm}} \times \frac{18}{M_2}$$

or

$$M_2 = \frac{677 \times 18 \times 55}{63 \times 45}$$

$$= \mathbf{236}$$

SOLVED PROBLEM 17. A solution containing 7.5 g of urea (mol mass 60) in one kg of water freezes at the same temperature as another solution containing 15 g of solute *S* in the same amount of water. Calculate the molecular mass of *S*.

SOLUTION :

Formula used

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

(i) For urea

Quantities given

$w = 7.5$ g $\quad$ $m = 60$ $\quad$ $W = 1$ kg $= 1000$ g

Substitution of values

$$\Delta T_f = \frac{1000 \times K_f \times 7.5\text{ g}}{60 \times 1000\text{g}} = 0.125\, K_f$$

(ii) For solute S

Quantities given

$w = 15$ g $\quad$ $W = 1000$ g

Substitution of values

$$\Delta T_f = \frac{1000 \times K_f \times 15\text{ g}}{m \times 1000\text{g}} = 15\,\frac{K_f}{m}$$

Since ΔT_f, is the same in both cases, we have

$$0.125\, K_f = 15\,\frac{K_f}{m}$$

or

$$m = \frac{15}{0.125}$$

$$= \mathbf{120}$$

SOLVED PROBLEM 18. A solution containing 12.5 g of unknown solute in 170 g water gave a boiling point elevation of 0.63 K. Calculate the molar mass of the solute ($K_b = 0.52$ K).

SOLUTION :

Formula used

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

K_b = 0.52 K $\quad w$ = 12.5 g $\quad W$ = 170 g $\quad \Delta T_b$ = 0.63 K

Substitution of values

$$m = \frac{1000 \times 0.52\,\text{K} \times 12.5\,\text{g}}{0.63\,\text{K} \times 170\,\text{g}}$$

$$= \mathbf{60.69}$$

SOLVED PROBLEM 19. The relative molar mass of an ionic compound is 58.5. If the experimentally observed molar mass is 30, calculate van't Hoff factor.

SOLUTION :

Formula used

$$\text{van't Hoff factor, } i = \frac{\textit{Normal molecular mass}}{\textit{Observed molecular mass}}$$

Quantities given

Normal molecular mass = 58.5 $\quad$ Observed molecular mass = 30

Substitution of values

$$\text{van't Hoff factor, } i = \frac{58.5}{30}$$

$$= \mathbf{1.95}$$

SOLVED PROBLEM 20. 1.8 of glucose (mol mass 180) is dissolved in 100 grams of water. Calculate the freezing and boiling point of the solution. Molal freezing point constant of water = 1.86. Molal boiling point constant of water = 0.513

SOLUTION :

(i) To calculate the freezing point of the solution

Formula used

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

Quantities given

K_f = 1.86 °C $\quad w$ = 1.8 g $\quad m$ = 180 $\quad W$ = 100 g

Substitution of values

$$\Delta T_f = \frac{1000 \times 1.86\,°\text{C} \times 1.8\,\text{g}}{180 \times 100\,\text{g}}$$

$$= 0.186\,°\text{C}$$

$$\therefore \quad \text{The freezing point of solution} = 0\,°\text{C} - \Delta T_f$$

$$= 0\,°\text{C} - 0.186\,°\text{C}$$

$$= -0.186\,°\text{C}$$

(ii) To calculate the boiling point of the solution

Formula used

$$\Delta T_b = \frac{1000 \times K_b \times w}{m \times W}$$

Quantities given

K_b = 0.513 ºC w = 1.8 g m = 180 W = 100 g

Substitution of values

$$\Delta T_b = \frac{1000 \times 0.513\,ºC \times 1.8\,g}{180 \times 100\,g}$$

$$= 0.0513\,ºC$$

∴ The boiling point of solution $= 100\,ºC + \Delta T_b$

$$= 100 + 0.0513\,ºC$$

$$= \mathbf{100.0513\,ºC}$$

SOLVED PROBLEM 21. Calculate the value of K_b for water, given that pure water boils at 100 ºC and latent heat of its vaporisation is 540 cal g^{-1}.

SOLUTION :

Formula used

$$K_b = \frac{R \times T_b^{\,2}}{1000 \times L_v}$$

Quantities given

R = 1.99 cal T_b = 100 + 273 = 373 K L_v = 540 cal g^{-1}

Substitution of values

$$K_b = \frac{1.99\,cal \times (373\,K)^2}{1000 \times 540\,cal}$$

$$= \mathbf{0.512\,K}$$

SOLVED PROBLEM 22. The molal elevation constant K_b and the boiling point for carbon tetrachloride are 5.02 deg/molal and 76.80 ºC respectively. Calculate boiling point of 1.0 molal solution of naphthalene in carbon tetrachloride.

SOLUTION :

Formula used

$$\Delta T_b = K_b \times m$$

Quantities given

K_b = 5.02 ºC/molal m = 1.0 (for naphthalene)

Substitution of values

$$\Delta T_b = 5.02\,ºC/molal \times 1.0\,molal$$

$$= 5.02\,ºC$$

∴ The boiling point of 1 molal solution of naphthalene in chloroform

$$= \text{boiling point of chloroform} + \Delta T_b$$

$$= 76.8\,ºC + 5.02\,ºC$$

$$= \mathbf{81.82\,ºC}$$

SOLVED PROBLEM 23. 8.0 g of solute dissolved in 100 g of water boils at 100.255 ºC. Determine the molecular mass of the solute. (K_b for water 0.51)

SOLUTION :

Formula used

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$K_b = 0.51\,^{\circ}\text{C}$ $w = 8.0\text{ g}$ $\Delta T_b = 0.255\,^{\circ}\text{C}$

Substitution of values

$$m = \frac{1000 \times 0.51^{\circ}\text{C} \times 8.0\text{ g}}{0.255\,^{\circ}\text{C} \times 100\text{ g}}$$

$$= \mathbf{160}$$

SOLVED PROBLEM 24. A solution containing 5.0 g of KCl per litre of water boils at 100.065 ºC at 760 mm pressure. Determine the degree of dissociation of KCl. (K_b for water = 0.54 ºC)

SOLUTION :

(i) To calculate the molecular mass of KCl.

Formula used

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$m = 5.0\text{ g}$ $K_b = 0.54\,^{\circ}\text{C}$ $\Delta T_b = 0.065\,^{\circ}\text{C}$ $W = 1000\text{ g}$

Substitution of values

$$m = \frac{1000 \times 0.54\,^{\circ}\text{C} \times 5.0\text{ g}}{0.065\,^{\circ}\text{C} \times 1000\text{ g}}$$

$$= 41.53$$

(ii) To calculate the degree of dissociation

Formula used

$$i = \frac{\textit{Normal molecular mass}}{\textit{Observed molecular mass}}$$

$$= \frac{74.5}{41.53} = 1.7939$$

and $i = 1 + \alpha$

or $1.7939 = 1 + \alpha$

or $\alpha = \mathbf{0.7959 \text{ or } 79.59\%}$

SOLVED PROBLEM 25. The boiling point of a solution containing 0.20 g of non-volatile substance *X* in 20 g of solvent is 0.17 higher than that of pure solvent. Calculate the molecular mass of *X*. Boiling point elevation constant of solvent per kg is 2.16 K.

SOLUTION :

Formula used

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times \text{W}}$$

Quantities given

$K_b = 2.16\text{ K}$ $w = 0.20\text{ g}$ $\Delta T_b = 0.17\text{ K}$ $W = 20\text{ g}$

Substitution of values

$$m = \frac{1000 \times 2.16\text{ K} \times 0.2\text{ g}}{0.17\text{ K} \times 20\text{ g}}$$

$$= \mathbf{127}$$

SOLVED PROBLEM 26. Molal elevation constant of Chloroform is 3.63 kg mol^{-1}. A solution of same organic solute boils at 0.15 K higher than Chloroform. What is the molality of the solution ?

SOLUTION :

Formula used

$$\Delta T_b = K_b \times m \qquad \text{or} \qquad m = \frac{\Delta T_b}{K_b}$$

Quantities given

$\Delta T_b = 0.15\ \text{K}$ $\qquad$ $K_b = 3.63\ \text{K kg mol}^{-1}$

Substitution of values

$$m = \frac{0.15\ \text{K}}{3.63\ \text{K kg mol}^{-1}}$$

$$= \mathbf{0.0413\ m\ kg^{-1}}$$

SOLVED PROBLEM 27. The molal depression constant for benzene is 5.12 K mol^{-1}. A solution containing 1g solute per 100 g benzene freezes at 5.1 ºC. What is the molar mass of the solute? (Freezing point of pure benzene is 5.5 ºC)

SOLUTION :

Formula used

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

Quantities given

$K_f = 5.12\ \text{K}$ $\qquad$ $w = 1\ \text{g}$

$W = 100\ \text{g}$ $\qquad$ $\Delta T_f = 5.5\ º\text{C} - 5.1\ º\text{C} = 0.4\ º\text{C} = 0.4\ \text{K}$

Substitution of values

$$m = \frac{1000 \times 5.12\ \text{K} \times 1\text{g}}{0.4\ \text{K} \times 100\ \text{g}}$$

$$= \mathbf{128}$$

SOLVED PROBLEM 28. The vapour of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance ?

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{\dfrac{w}{m}}{\dfrac{w}{m} + \dfrac{W}{M}}$$

Quantities given

$p = 640\ \text{mm}$ $\qquad$ $p_s = 600\ \text{mm}$ $\qquad$ $w = 2.175\ \text{g}$

$W = 39.0\ \text{g}$ $\qquad$ $M = 78$

Substitution of values

$$\frac{640 - 600\ \text{mm}}{640\ \text{mm}} = \frac{\dfrac{2.175\ \text{g}}{m}}{\dfrac{2.175\ \text{g}}{m} + \dfrac{39\ \text{g}}{78}}$$

$$\frac{40\ \text{mm}}{640\ \text{mm}} = \frac{2.175}{2.175 + 0.5\,m}$$

or $$2.175 + 0.5\,m = \frac{2.175 \times 640}{40}$$

or $$0.5\,m = 34.8 - 2.175$$

or $$m = \mathbf{65.25}$$

SOLVED PROBLEM 29. 2.0 g of benzoic acid dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant K_f of benzene is 4.9 K kg mol^{-1}. What is the percentage association of the acid ?

SOLUTION :

(i) To calculate the molecular mass of benzoic acid

Formula used

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

Quantities given

K_f = 4.9 K kg mol^{-1} w = 2 g ΔT_f = 1.62 K W = 25 g

Substitution of values

$$m = \frac{1000 \times 4.9\ \text{K kg mol}^{-1} \times 2\ \text{g}}{1.62\ \text{K} \times 25\ \text{g}}$$

$$= \mathbf{241.975}$$

(ii) To calculate the degree of association of benzoic acid

observed mol. mass of benzoic acid = 241.975

normal mol. mass of benzoic acid = 122

$$\text{van't Hoff factor, } i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$= \frac{122}{241.975} = 0.504$$

$$2\,CH_3COOH \longrightarrow (C_6H_5COOH)_2$$

Degree of association x is related to van't Hoff factor by the relation

$$i = 1 - \frac{x}{2}$$

or $$0.504 = 1 - \frac{x}{2}$$

or $$1.008 = 2 - x$$

or $$x = 2 - 1.008$$

$$= \mathbf{0.992 \text{ or } 99.2\%}$$

SOLVED PROBLEM 30. The degree of dissociation of Calcium nitrate in dilute aqueous solution containing 7.0 g of the salt per 100 g of water at 100 ºC is 70%. If the vapour pressure of water at 100ºC is 760 mm. Calculate the vapour pressure of the solution.

SOLUTION :

(i) To calculate the number of moles of $Ca\,(NO_3)_2$ and H_2O

The dissociation of Calcium nitrate is represented by

$$Ca\,(NO_3)_2 \longrightarrow Ca^{2+} + 2\,NO_3^-$$

	$Ca\,(NO_3)_2$	Ca^{2+}	$2\,NO_3^-$
Initial Conc.	1	0	0
Equilibrium Conc.	1 – 0.7	0.7	2 × 0.7

Total number of moles of equilibrium $= (1 - 0.7) + 0.7 + 2 \times 0.7$

$= 2.4$

Number of moles at equilibrium when the conc. of $Ca(NO_3)_2$ is 7.0 g

$$= \frac{2.4 \times 7\ \text{g}}{164\ \text{g mol}^{-1}} = 0.1024\ \text{mole}$$

Number of moles of water in 100 g $= \dfrac{100\ \text{g}}{18\ \text{g mol}^{-1}} = 5.55$ moles

(ii) To calculate the vapour pressure of the solution

Formula used

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

Quantities given

$p = 760$ mm $\quad n = 0.1024$ mole $\quad N = 5.55$ moles

Substitution of values

$$\frac{760\ \text{mm} - p_s}{760\ \text{mm}} = \frac{0.1024\ \text{mole}}{0.1024\ \text{mole} + 5.55\ \text{mole}}$$

or $\quad 760\ \text{mm} - p_s = \dfrac{0.1024 \times 760\ \text{mm}}{5.6524}$

or $\quad 760\ \text{mm} - p_s = 13.76$ mm

or $\quad p_s = 760\ \text{mm} - 13.76\ \text{mm}$

$= \mathbf{746.24\ mm}$

SOLVED PROBLEM 31. Addition of 0.643 g of a compound to 50 ml of benzene (density 0.879 g ml^{-1}) lowers the freezing point from 5.51 ºC to 5.03 ºC. If K_f for benzene is 5.12 K kg mol^{-1}, calculate the molar mass of the compound.

SOLUTION :

Formula used

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

Quantities given

$K_f = 5.12\ \text{K kg mol}^{-1}$ $\quad \Delta T_f = 5.51\ ºC - 5.03\ ºC = 0.48\ ºC = 0.48\ \text{K}$

$w = 0.643\ \text{g}$ $\quad W = 50\ \text{ml} \times 0.879\ \text{g ml}^{-1} = 43.95\ \text{g}$

Substitution of values

$$m = \frac{1000 \times 5.12\ \text{K kg mol}^{-1} \times 0.643\ \text{g}}{0.48\ \text{K} \times 43.95\ \text{g}}$$

$= \mathbf{156.056}$

SOLVED PROBLEM 32. In a cold climate water gets frozen causing damage to the radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at – 6 ºC. (K_f for water = 1.85 K kg mol^{-1})

SOLUTION :

Formula used

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

Quantities given

$K_f = 1.85\ \text{K kg mol}^{-1}$ $\quad \Delta T_f = 6\ ºC = 6\ \text{K}$

m of ethylene glycol [$OHCH_2-CH_2OH$] = 62 $\quad W = 4\ \text{kg} = 4 \times 10^3\ \text{g}$

Substitution of values

$$62 = \frac{1000 \times 1.85 \text{ K kg mol}^{-1} \times w}{6 \text{ K} \times 4 \times 10^3 \text{ g}}$$

or $$w = \frac{62 \times 6 \times 4 \times 10^3 \text{ g}}{1000 \times 1.85} = \mathbf{804.324 \text{ g}}$$

SOLVED PROBLEM 33. What mass of the non-volatile solute, urea, (NH_2 CO NH_2) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution ?

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Quantities given

$p = p$ mm (say) $\qquad p_s = 75\%$ of p mm $= \frac{3p}{4}$ mm

$m = 60 \qquad W = 100$ g $\qquad M = 18$

Substitution of values

$$\frac{p - \frac{3}{4}p}{p} = \frac{\frac{w}{60}}{\frac{w}{60} + \frac{100}{18}}$$

$$4 \times \frac{w}{60} = \frac{w}{60} + 5.55$$

or $$\frac{4w}{60} - \frac{w}{60} = 5.55$$

or $$\frac{3w}{60} = 5.55$$

or $$w = \frac{60 \times 5.55}{3} = \mathbf{111 \text{ g}}$$

or $$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

$$= \frac{111 \text{ g}}{60 \text{g mol}^{-1} \times 100 \times 10^{-3} \text{ kg}}$$

$$= \mathbf{18.50 \text{ m}}$$

SOLVED PROBLEM 34. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45 °C. Calculate the degree of association of acetic acid in benzene. (K_f for benzene is 5.12 K mol^{-1} kg)

SOLUTION :

(i) To calculate the molecular mass of acetic acid

Formula used

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

Quantities given

K_f = 5.12 K kg mol^{-1} $\quad$ w = 0.2 g

ΔT = 0.45 K $\quad$ W = 20.0 g

Substitution of values

$$m = \frac{1000 \times 5.12 \text{ K kg mol}^{-1} \times 0.2 \text{ g}}{0.45 \text{ K} \times 20.0 \text{ g}}$$

$$= 113.778$$

(ii) To calculate the degree of association of acetic acid

$$2\,CH_3COOH \longrightarrow (CH_3COOH)_2$$

$$\text{The van't Hoff factor, } i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$= \frac{60}{113.378} = 0.527$$

Let the degree of association of acetic acid be $= x$

and $\quad$ van't Hoff factor, $i = 1 - \frac{x}{2}$

or $\quad$ $0.527 = 1 - \frac{x}{2}$

or $\quad$ $x = 2 - 2 \times 0.527$

$= \mathbf{0.946 \text{ or } 94.6\ \%}$

SOLVED PROBLEM 35. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g of water to 9.3. (K_f for water = 1.86 K mol^{-1} kg)

SOLUTION :

Formula used

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

or

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

Quantities given

K_f = 1.86 K kg mol^{-1} $\quad$ w = 50 g

molecular mass, m, of glycol (HO $CH_2 - CH_2$ OH) = 62 $\quad$ ΔT_f = 9.3 K

Substitution of values

$$W = \frac{1000 \times 1.86 \text{ K kg mol}^{-1} \times 50 \text{ g}}{9.3 \text{ K} \times 62}$$

$$= 161.29 \text{ g}$$

Amt. of ice separated from 200 g water = 200 g – 161.29 g

= **38.71 g**

ADDITIONAL PRACTICE PROBLEMS

1. Calculate the freezing point of a one molar aqueous solution (density = 1.04 g ml^{-1}) of KCl. K_f for water is 1.86 K kg mol^{-1} (Atomic mass K = 39, Cl = 35.5)

Answer. 269.15 K

2. Calculate the boiling point of one molar aqueous solution (density = 1.04 g ml^{-1}) of potassium Chloride, K_b for water is 0.52 K kg mol^{-1}. (Atomic mass of K = 39, Cl = 35.5)

Answer. 374.077 K

3. 12.5 g of the solute when dissolved in 170 g of water results in elevation of boiling point by 0.63 K. Calculate molecular mass of the solute. K_b for water = 0.52 K kg mol^{-1}.

Answer. 60.69

4. The normal freezing point of nitrobenzene is 278.82 K. A 0.25 molal solution of a certain solute in nitrobenzene causes a freezing point depression of 2 degrees. Calculate the value of K_f for nitrobenzene.

Answer. 8 K kg mol^{-1}

5. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2K.

Answer. 80.1 g

6. The boiling point of water is 100 °C and it becomes 100.52 °C if 3 g of a non-volatile solute is dissolved in 200 g of it. Calculate the molecular mass of the solute. (K_b for water = 0.52 K kg mol^{-1}).

Answer. 15

7. The vapour pressure of methyl alcohol at 298 K is 96 torr. Its mole fraction in a solution with ethyl alcohol is 0.305, what is its vapour pressure if it obeys Raoult's law.

Answer. 29.28 torr

8. Benzene and toluene form ideal solutions. At 323 K, the vapour pressure of pure benzene is 269 torr and that of pure toluene is 926 torr. What is the total vapour pressure at 323 K if a solution is prepared from 39.0 g benzene and 23 g toluene ?

Answer. 299.9 torr

9. The capacity of the radiator of a car is 5 dm^3. If the car is to be used in Srinagar when the temperature is 263.15 K, calculate the mass of ethylene glycol ($C_2H_6O_2$) which must be added so that it does not freeze. K_f for water = 1.86 kg dm^3).

Answer. 1.426 kg

10. The vapour pressure of a dilute solution of glucose ($C_6H_{12}O_6$) is 750 mm of Hg at 373 K. Calculate the molality and mole fraction of the solute ?

Answer. 0.7404 m ; 0.132

11. An aqueous solution contain 5 % and 10 % of urea and glucose respectively (by weight). Calculate the depression in freezing point of solution (K_f for water = 1.86°)

Answer. 3.03 °C

12. Benzene, C_6H_6 (boiling point 353.1 K) and toluene, C_7H_8 (boiling point 383.6) are two hydrocarbons that form a very nearly ideal solution. At 313 K, the vapour pressure of pure liquids are benzene = 160 mm Hg and toluene = 60 mm Hg. Assuming an ideal behaviour, calculate the partial pressures of benzene and toluene and the total pressure over the solution obtained by mixing equal number of moles of benzene and toluene.

Answer. 80 mm, 30 mm and 110 mm

13. Ethyl alcohol and methyl alcohol form a solution which is almost ideal. The vapour pressure of ethyl alcohol is 44.5 mm and that of methyl alcohol is 88.7 mm at 293 K. Calculate the partial pressures and total pressure of the solution obtained by mixing 100 g of ethyl alcohol with 50 g of methyl alcohol.

Answer. 96.73 mm ; 138.59 mm ; 235.32 mm

14. An aqueous solution contains 30 % by weight of a liquid A (molecular mass 120) has a vapour pressure of 160 mm at 310 K. Find the vapour pressure of pure liquid A (the vapour pressure of water at 310 K is 150 mm)

Answer. 1715 mm

15. Calculate the Molal elevation constant for benzene if its boiling point is 353 K and ΔH_{vap} is 30.8 kJ mol^{-1}

Answer. 2.62 K kg m^{-1}

16. The boiling point of a solution containing 2.56 g of substance A per 100 g of water is higher by 0.052 ºC than the boiling point of pure water. Calculate the molar mass of the substance if molar elevation constant of water is 0.512 K kg m^{-1}.

Answer. 252 g mol^{-1}

17. Calculate the molal depression constant of benzene if its enthalpy of fusion at 30.05 cal g^{-1} and it freezes at 5.48 ºC.

Answer. 5.11 K kg m^{-1}

18. 50 g of sucrose is dissolved in 300 g of water. Calculate the boiling point and freezing point of the solution. (R = 8.314 J K^{-1} mol^{-1} and ΔH_{vap} = 40.67 kJ mol^{-1})

Answer. 100.26 ºC ; – 0.95 ºC

19. Calculate the amount of CS_2 present as an impurity in 50 g of Chloroform which raises the boiling point of Chloroform by 0.3 ºC.

Answer. 3.14 g

20. Calculate the molar mass of a solute, 1 g of which in solution depresses the freezing point of benzene by 0.516 ºC. (K_f = 5.12 ºC kg mol^{-1})

Answer. 198.4

21. Phenol (C_6H_5OH) associates in water to form associated molecules. 0.6677g of phenol dissolved in 35.5 g of water decreases the freezing point of water by 0.215 ºC. Calculate the degree of association of phenol. (K_f for water = 1.85ºC kg mol^{-1})

Answer. 83.8 %

22. The depression in freezing point of a solution containing 1.5 g of Barium nitrate [$Ba(NO_3)_2$] in 100 g of water is 0.72 ºC. Calculate the degree of dissociation of the salt. K_f for water is 1.86 ºC (At mass of Ba = 137, N = 14 and O = 16)

Answer. 0.81 or 81 %

23. A very small amount of non-volatile solute (that does not dissociate) is dissolved in 5.68 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.85 mm Hg while that of benzene is 100 m m Hg. Find the molality of this solution. If the freezing point of this solution is 0.073º lower than that of benzene, what is the value of molal freezing point depression constant of benzene.

Answer. 0.144 m ; 5.7 K

24. Calculate the boiling point of a solution containing 0.61 g of benzene acid in 50 g of CS_2 assuming 84% dimerisation of the acid. The boiling point and K_b of CS_2 are 46.2 ºC and 2.3 K kg mol^{-1} respectively.

Answer. 46.333 ºC

25. How much ethyl alcohol must be added to 1.00 litre of water so that the solution will breeze at 14º F ? (K_f for water = 1.86 ºC /mole)

Answer. 247.3 g

16

Osmosis and Osmotic Pressure

CHAPTER

KEY CONCEPTS AND EQUATIONS

OSMOSIS

The flow of the solvent through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentrated solution is termed Osmosis.

OSMOTIC PRESSURE

The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semipermeable membrane is called Osmotic Pressure.

It may also be defined as the external pressure applied to the solution in order to stop the Osmosis of solvent into solution separted by a semipermeable membrane.

VAN'T HOFF EQUATION FOR SOLUTION

It has been shown by experiments that for *n* moles of the solute dissolved in *V* litres of the solution, the Osmotic pressure π at temperature *T* is given by

$$\pi V = n R T$$

where *R* is gas constant

or

$$\pi = \frac{nRT}{V}$$

$$= C R T$$

where *C* is the molar concentration of the solution. At a given temperature, both *R* and *T* are constants. Therefore $\pi \propto C$

Thus osmotic pressure depends upon the molar concentration of solution and is, therefore , colligative property.

DETERMINATION OF MOLECULAR MASS FROM OSMOTIC PRESSURE MEASUREMENTS

According to van't Hoff equation.

$$\pi = \frac{n}{V} R T \qquad \text{........ (i)}$$

where *n* is the number of moles of solute. It may be written as

$$n = \frac{w}{M}$$

where *w* is the mass of the solute and *M* its molecular mass. Substituting this in equation (i) we have

$$\pi = \frac{w}{M} \times \frac{RT}{V}$$

or molecular mass of the solute, $M = \dfrac{w\,R\,T}{V \times \pi}$

ABNORMAL MOLECULAR MASSES

The molecular masses of some substances as determined experimentally by osmotic pressure measurements are different from those calculated theoretically from their chemical formula. In such cases either association or dissociation of molecules takes place. The number of particles decrease or increase as compared to the number of particles if no ionisation or association takes place. Since the osmotic pressure is a colligative property (dependent on the number of particles) it shows deviations. In such cases van't Hoff equation may be written as

$$\pi V = i\,n\,R\,T$$

where i is called van't Hoff factor and is given by

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association $i < 1$ and

in case of dissociation $i > 1$

The van't Hoff factor, i is related to the degree of dissociation, α, by the relation.

$$i = 1 + \alpha$$

The value of i will lie between 1 and 2.

RELATION BETWEEN OSMOTIC PRESSURE AND VAPOUR PRESSURE

It has been found experimentally that the osmotic pressure is directly proportional to the relative lowering of vapour pressure, *i.e.*

$$\pi \propto \frac{p - p_s}{p}$$

where p is the vapour pressure of the solvent and p_s, the vapour pressure of the solution at a given temperature.

RAOULT'S LAW AND THE OSMOTIC VAPOUR PRESSURE

We know $\pi V = n\,R\,T$

or $\pi = \dfrac{n}{V} R\,T$

and the relative lowering of vapour pressure is proportional to the osmotic pressure *i.e.*

$$\frac{p - p_s}{p} \propto \pi \qquad \text{..... (ii)}$$

or

$$\frac{p - p_s}{p} = \frac{n}{N} \qquad \text{..... (iii)}$$

where n is the number of moles of the solute and N the number of moles of solvent.

From equation (ii) and (iii) we have

$$\pi \propto \frac{n}{N}$$

This is Raoult's law equation.

ISOTONIC SOLUTIONS

Isotonic solutions are those solutions which have the same osmotic pressure. For two isotonic solution at the same temperature we have

$$C_1 = C_2$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the osmotic pressure of a 5% solution of glucose at 27 °C.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R\ T$$

Quantities given

$$n = \frac{5\text{g}}{180\text{g mol}^{-1}} = 0.02778 \text{ mol} \qquad V = \frac{1}{10} \text{ lit} = 0.1 \text{ lit}$$

$$R = 0.0821 \text{ atm lit K}^{-1}\text{mol}^{-1} \qquad T = 27 + 273 = 300\text{K}$$

Subsitition of values

$$\pi = \frac{0.02778 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1}\text{ mol}^{-1} \times 300 \text{ K}}{0.1 \text{ lit}}$$

$$= \mathbf{6.8422\ atm}$$

SOLVED PROBLEM 2. A 0.100 molal aqueous solution of NH_4Cl freezes at 0.344 °C. Calculate *i*. (K_f = 1.86 °C)

SOLUTION : (i) To calculate the molecular mass of the solute

Formula Used

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

Quantities given

K_f = 1.86 °C $\qquad w = 0.1\text{m} = 0.1\text{m} \times 53.5 \text{ g mol}^{-1} = 5.35 \text{ g}$

ΔT_f = 0.344 °C $\qquad W = 1000 \text{ g}$

Substitution of values

$$m = \frac{1000 \times 1.86\,°\text{C} \times 5.35\text{g}}{1000\text{g} \times 0.344\,°\text{C}}$$

$$= \mathbf{28.9}$$

ii) To calculate the van't Hoff factor *i*

Formula used

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$= \frac{53.5}{28.9}$$

$$= \mathbf{1.849}$$

SOLVED PROBLEM 3. Calculate the osmotic pressure of a 5% solution of glucose ($C_6H_{12}O_6$) at 18 °C. $R = 0.0820$ atm lit K^{-1} $mol^{-1.}$

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R\,T$$

Quantities given

$$n = \frac{5g}{180\text{ g mol}^{-1}} = 0.02778 \text{ mol} \qquad V = \frac{1}{10}\text{ lit} = 0.10 \text{ lit}$$

$$T = 18 + 273 = 291\text{ K} \qquad R = 0.0820 \text{ atm lit K}^{-1}\text{ mol}^{-1}$$

Substitution of values

$$\pi = \frac{0.02778\text{ mol} \times 0.0820\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 291\text{K}}{0.10\text{ lit}}$$

$$= \mathbf{6.628\ atm}$$

SOLVED PROBLEM 4. An aqueous solution contains 20 g of glucose per litre. Calculate the pressure of the solution at 25 °C (molecular mass of glucose = 180).

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R\,T$$

Quantities given

$$n = \frac{20g}{180g\text{ mol}^{-1}} = 0.111\text{ mol} \qquad V = 1\text{ lit.}$$

$$T = 25 + 273 = 298K \qquad R = 0.0821\text{ atm lit K}^{-1}\text{mol}^{-1}$$

Substitution of values

$$\pi = \frac{0.111\text{ mol} \times 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 298K}{1\text{ lit.}}$$

$$= \mathbf{2.71\ atm}$$

SOLVED PROBLEM 5. A 1% solution of potassium chloride is 80% dissociated. What is its osmotic pressure at 300 K ? ($R = 0.082$ atm lit K^{-1} mol^{-1} ; $K = 39$; $Cl = 35.5$)

SOLUTION : (i) To calculate the van't Hoff factor, *i*

$$\text{No. of moles of KCl in 1\% solution} = \frac{1\text{ g}}{74.5\text{ g mo1}^{-1}} = 0.01342\text{ mo1}^{-1}$$

	KCl $\longrightarrow$	K	+ Cl^{-1}
Initial Concentration	0.01342	0	0
Final Concentration	(0.01342 – α)	0.01342α	0.01342α

$$\text{Total number of particles} = 0.01342\,(1-\alpha) + 0.01342\alpha + 0.01342\alpha$$

$$= 0.01342\,(1+\alpha)$$

Since α = 80% or 0.8, we have

$$\text{Total number of particles} = 0.01342\,(1+0.8)$$

$$= 0.024126$$

$$\text{van't Hoff factor, } i = \frac{0.02416}{0.01342}$$

$$= 1.80$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = \frac{i\ \mathrm{n R T}}{\mathrm{V}}$$

Quantities given

i = 1.8 $\quad$ n = 0.01342 mol $\quad$ $V = \frac{1}{10}$ lit = 0.1lit

R = 0.082 atm lit K^{-1} mol^{-1} $\quad$ T = 300 K

Substitution of values

$$\pi = \frac{1.8 \times 0.01342\ \text{mol} \times 0.082\ \text{atm lit K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{0.1\ \text{lit}}$$

$$= \mathbf{5.94\ atm}$$

SOLVED PROBLEM 6. Calculate the molality and osmotic pressure of 0.5% solution of urea (molecular mass = 60) in water at 0 °C. (R = 0.082 atm lit K^{-1} mol^{-1}).

SOLUTION : **(i) To calculate the molality**

Formula used

$$\text{molality, } m = \frac{\text{mass of urea} \times 1000}{\text{mol mass of urea} \times \text{mass of solvent}}$$

Quantities given

mass of urea = 0.5 g $\quad$ mass of solvent = 99.5 g

mol mass of urea = 60 g mol^{-1}

Substitution of values

$$\text{molality, } m = \frac{0.5\ \text{g} \times 1000}{60\ \text{g mol}^{-1} \times 99.5\ \text{g}}$$

$$= 0.0838\ \text{m}$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = \frac{n}{V}\ \mathrm{R T}$$

Quanities given

$n = \dfrac{0.5\text{ g}}{60\text{ g mol}^{-1}} = 0.00833\text{ mol}$ $\qquad R = 0.082\text{ atm lit K}^{-1}\text{mol}^{-1}$

$V = \dfrac{1}{10}\text{ lit} = 0.1\text{ lit}$ $\qquad T = 273\text{ K}$

Substitution of values

$$\pi = \frac{0.00833\text{ mol} \times 0.082\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 273\text{ K}}{0.1\text{ lit}}$$
$$= 1.86 \text{ atm}$$

SOLVED PROBLEM 7. Calculate the osmotic pressure of 0.01 M solution of cane sugar at 30 °C.

SOLUTION :

Formula used

$$\pi = C\,R\,T$$

Quantities given

$C = 0.01\text{ M}$ $\qquad R = 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1}$ $\qquad T = 30 + 273 = 303\text{ K}$

Substitution of values

$$\pi = 0.01\text{ mol} \times 0.0821\text{atm lit K}^{-1}\text{mol}^{-1} \times 303\text{ K}$$
$$= \mathbf{0.249\text{ atm}}$$

SOLVED PROBLEM 8. What is the concentration of cane sugar which is isotonic with solution containing 6 g of urea per litre? (mol mass of urea and cane sugar are 60 and 340 respectively).

SOLUTION : (i) To calculate the osmotic pressure of urea solution

Formula used

$$\pi = \frac{n}{V}\,R\,T$$

Quantities given

$n = \dfrac{6\text{ g}}{60\text{ g mol}^{-1}} = 0.1\text{ mol}$ $\qquad V = 1\text{ lit}$

Substitution of values

$$\pi = \frac{0.1\text{ mol} \times R \times T}{1\text{ lit}}$$
$$= 0.1\,R\,T$$

(ii) To calculate the concentration of cane sugar

Formula used

$$\pi = C\,R\,T$$

Quantities given

$$\pi = 0.1\text{ R T}$$

Subsitution of values

$$0.1\,R\,T = C\,R\,T$$

or

$$\text{C} = 0.1\text{ mol}$$
$$= \frac{342}{10}\text{ g lit}^{-1}$$
$$= \mathbf{34.2\text{ g lit}^{-1}}$$

SOLVED PROBLEM 9. Calculate the osmotic pressure of 0.745% solution of KCl at 27 °C assuming to be 86% dissociated.

SOLUTION : (i) To calculate the van't Hoff factor *i*

$$\text{Number of moles of KCl in 0.745\% solution} = \frac{0.745\text{ g}}{74.5\text{ g mol}^{-1}} = 0.01\text{ mol}$$

	KCl	$\longrightarrow$	K^+	$+$	Cl^{-1}
Initial Concentration	0.01		0		0
Final Concentration	$0.01(1-\alpha)$		0.01α		0.01α

$$\text{Total number of particles} = 0.01(1-\alpha) + 0.01\alpha + 0.01\alpha$$
$$= 0.01\,(1+\alpha)$$

Since $\alpha = 86\%$ or 0.86, we have

$$\text{Total number of particles} = 0.01(1 + 0.86)$$
$$= 0.0186$$
$$\text{van't Hoff factor, } i = \frac{0.0186}{0.01} = 1.86$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = i\,\frac{n}{V}\,RT$$

Quantities given

$i = 1.86$ $\quad n = 0.01$ m $\quad T = 300$ K

$R = 0.0820$ atm lit K^{-1} mol^{-1} $\quad V = \frac{1}{10}$ lit $= 0.01$ lit

Substitution of values

$$\pi = \frac{1.86 \times 0.01\text{ m} \times 0.0820\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 300\text{ K}}{0.10\text{ lit}}$$
$$= \mathbf{4.576\ atm}$$

SOLVED PROBLEM 10. Is 5% solution of cane sugar (mol mass = 342) isotonic with 0.877% solution of urea?

Formula used

$$\pi = \frac{n}{V}\,RT$$

Quantities given

$n = \dfrac{5\text{g}}{342\text{ g mol}^{-1}} = 0.01462$ mol $\quad V = \frac{1}{10}$ lit $= 0.1$ lit

Substitution of values

$$\pi = \frac{0.01462\text{ mol}^{-1}}{0.1\text{ lit}}\,RT$$
$$= \mathbf{0.1462\,RT}$$

(ii) To calculate the osmotic pressure of 8.77% urea solution

Quantities given

$n = \dfrac{0.877\text{ g}}{60\text{ g mol}^{-1}} = 0.1462$ mol $\quad V = \frac{1}{10}$ lit $= 0.1$ lit

Substitution of values

$$\pi = \frac{0.1462 \text{ mol} \times RT}{0.1 \text{ lit}}$$

$$= \mathbf{1.462\ R\ T}$$

Since both solutions have the same osmotic pressure, they are isotonic.

SOLVED PROBLEM 11. Calculate the concentration (g/litre) of aqueous glucose (mol mass = 180) which is isotonic with blood (Osmotic pressure for blood is 7.65 atm at 37 °C and $R = 0.0821$ atm lit K^{-1} mol^{-1})

SOLUTION :

Formula used

$$\pi = C\,R\,T \qquad \text{or} \qquad C = \frac{\pi}{R\,T}$$

Quantities given

π = 7.65 atm $\qquad R$ = 0.0821 atm lit K^{-1} mol^{-1} $\qquad T$ = 310 K

Substitution of values

$$C = \frac{7.65 \text{ atm}}{0.0821 \text{ atm lit K}^{-1} \text{mol}^{-1} \times 310 \text{ K}}$$

$$= 0.3005 \text{ mol lit}^{-1}$$

$$= 0.03005 \times 180\text{g lit}^{-1} \quad [\because 1 \text{ mol of glucose} = 180\text{g}]$$

$$= \mathbf{54.1\ g\ lit^{-1}}$$

SOLVED PROBLEM 12. Calculate osmotic pressure of solution at 25 °C containing (i) 5.85g of NaCl and (ii) 5.0 g of urea per litre of solution.

SOLUTION : (i) To calculate the osmotic pressure of NaCl solution

Formula used

$$\pi = \frac{n}{V}\,R\,T$$

Quantities given

$n = \dfrac{5.85 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.1$ m $\qquad R$ = 0.0821 atm lit K^{-1} mol^{-1}

T = 25 + 273 = 298 K $\qquad V$ = 1 lit

Substitution of values

$$\pi = \frac{0.1 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{mol}^{-1} \times 298 \text{ K}}{1 \text{ lit}}$$

$$= \mathbf{2.45\ atm}$$

(ii) To calculate the osmotic pressure of urea solution

Quantities given

$n = \dfrac{5\text{g}}{60\text{g mol}^{-1}} = 0.0833$ mol $\qquad R$ = 0.0821 atm lit k^{-1} mol^{-1}

T = 25 + 273 = 298 K $\qquad V$ = 1 litre

Substitution of values

$$\pi = \frac{0.0833 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{mol}^{-1} \times 298 \text{ K}}{1 \text{ lit}}$$

$$= \mathbf{2.038\ atm}$$

SOLVED PROBLEM 13. 10 g of urea of molecular mass 60 is dissolved in one litre of water. Calculate the osmotic pressure of the solution at 20 °C.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R\,T$$

Quantities given

$$n = \frac{10\text{ g}}{60\text{g mol}^{-1}} = 0.1667\text{ mol} \qquad R = 0.0821\text{ atm lit k}^{-1}\text{ mol}^{-1}$$

$$T = 20 + 273 = 293\text{ K} \qquad V = 1\text{ lit}$$

Substitution of values

$$\pi = \frac{0.1667\text{ mol} \times 0.0821\text{ atm lit K}^{-1}\text{mol}^{-1} \times 293\text{ K}}{1\text{ lit}}$$

$$= \mathbf{4.01\ atm}$$

SOLVED PROBLEM 14. A solution containing 8.6 g per dm^3 of urea (mol mass 60) was found to be isotonic with a 5% solution of an organic non-volatile solution. Calculate the molecular mass of the latter.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R\,T$$

(i) For urea

Quantities given

$$n = \frac{8.6\text{ g}}{60\text{ g mol}^{-1}} = 0.1433\text{ mol} \qquad V = 1\text{ lit}$$

Substitution of values

$$\pi = \frac{0.1433\text{ mol } R\,T}{1\text{ lit}} = 0.1433\,R\,T$$

(ii) For organic non-volatile solute

Quantities given

$$n = \frac{5\text{g}}{M\text{ g mol}^{-1}} = \frac{5}{M}\text{ mol} \qquad V = 0.1\text{ lit}$$

Substitution of values

$$\pi = \frac{5/M\text{ mol}^{-1} \times R\,T}{0.1\text{ lit}} = \frac{50}{M} R\,T$$

Since both solutions are isotonic we have

$$0.1433\,R\,T = \frac{50}{M} R\,T$$

or

$$M = \frac{50}{0.1433}$$

$$= \mathbf{348.9}$$

SOLVED PROBLEM 15. A solution contains 5g of urea (mol mass 60) per 100g of water. If the density of water at 25 °C is 0.998 g cm^{-3}, calculate the osmotic pressure of the solution at the same temperature ($R = 0.082$ atm lit K^{-1} mol^{-1}).

SOLUTION : **(i) To calculate the volume of 100g of water**

$$\text{Density of water} = 0.998 \text{ g cm}^{-3}$$

$$\text{Volume of 100g of water} = 100 \text{ g} \div 0.998 \text{ g cm}^{-3} \qquad [\because V = \frac{M}{D}]$$

$$= 100.2 \text{ cm}^3$$

$$= 0.1002 \text{ lit} \qquad [\because 1 \text{ lit} = 1000 \text{ cm}^3]$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = \frac{n}{V} R T$$

Quantiities given

$$n = \frac{5\text{g}}{60\text{g mol}^{-1}} = 0.0833 \text{ mol} \qquad R = 0.0821 \text{ atm lit K}^{-1}\text{mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K} \qquad V = 0.1002 \text{ lit}$$

Subsitution of values

$$\pi = \frac{0.0833 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{0.1002 \text{ lit}}$$

$$= \mathbf{20.34 \text{ atm}}$$

SOLVED PROBLEM 16. 3.58 g of NaCl was dissolved in 120 g of water at 77 °C. If the osmotic pressure of solution is 26.31 atm, then calculate the degree of dissociation of NaCl.

SOLUTION : **(i) To calculate van't Hoff Factor, *i***

Formula used

$$\pi = i \frac{n}{V} R T$$

Quantities given

$$\pi = 26.31 \text{ atm} \qquad R = 0.821 \text{ atm lit K}^{-1}\text{mol}^{-1} \qquad T = 77 + 273 = 350 \text{ K}$$

$$n = \frac{3.58 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.0612 \text{ mol} \qquad V = \frac{120}{1000} = 0.12 \text{ lit}$$

Substitution of values

$$26.31 \text{ atm} = i \times \frac{0.0612 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1}\text{mol}^{-1} \times 350 \text{ K}}{0.12 \text{ lit}}$$

or $$i = 1.7954$$

(ii) To calculate the degree of dissociation

Formula used

$$i = 1 + \alpha$$

or $$\alpha = i - 1$$

$$= 1.7954 - 1$$

$$= \mathbf{0.7954} \text{ or } \mathbf{79.54\ \%}$$

SOLVED PROBLEM 17. A 5% solution of cane sugar (mol mass 342) is isotonic with 0.877% solution of substance X. Find out the molecular mass of X.

SOLUTION :

$$\text{Concentration of cane sugar} = \frac{50\ \text{g lit}^{-1}}{342\ \text{g mol}^{-1}}$$

$$= \frac{50}{342}\ \text{mol lit}^{-1}$$

$$\text{Concentration of unknown substance} = 0.877\ \text{g}/100\ \text{ml}$$

$$= 8.77\ \text{g lit}^{-1}$$

$$= \frac{8.77\text{g lit}^{-1}}{M\ \text{g mol}^{-1}}$$

$$= \frac{8.77}{M}\ \text{mol lit}^{-1}$$

Since both solutions are isotonic, their concentration must be equal *i.e.*

$$\frac{50}{342}\ \text{mol lit}^{-1} = \frac{8.77}{M}\ \text{mol lit}^{-1}$$

or

$$M = \frac{342 \times 8.77}{50}$$

$$= \mathbf{60}$$

SOLVED PROBLEM 18. Calculate the osmotic pressure of glucose containing 1.75 in 150 ml of solution at 17 ºC.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R\,T$$

Quantities given

$$n = \frac{1.75\ \text{g}}{180\ \text{g mol}^{-1}} = 0.009722\ \text{mol} \qquad V = 150\ \text{ml} = 0.15\ \text{lit}$$

$$R = 0.0821\ \text{atm lit K}^{-1}\text{mol}^{-1} \qquad T = 17 + 273 = 290\ \text{K}$$

Substitution of values

$$\pi = \frac{0.009722\ \text{mol} \times 0.0821\ \text{atm lit K}^{-1}\text{mol}^{-1} \times 290\ \text{K}}{0.15\ \text{lit}}$$

$$= \mathbf{1.543\ atm}$$

SOLVED PROBLEM 19. Calculate the freezing point of an aqueous solution of a non-elctrolyte having an osmotic pressure of 2.0 atm at 300 K. ($K_f = 1.86$ K kg mol^{-1} ; $R = 0.821$ atm lit K^{-1} mol^{-1}).

SOLUTION : (i) To calculate the concentration of the solution

Formula used

$$\pi = C\,R\,T \qquad \text{or} \qquad C = \frac{\pi}{R\,T}$$

Quantities given

$$\pi = 2.0\ \text{atm} \qquad R = 0.0821\ \text{atm lit K}^{-1}\ \text{mol}^{-1} \qquad T = 300\ \text{K}$$

Substitution of values

$$C = \frac{2.0\ \text{atm}}{0.0821\ \text{atm lit K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$

$$= 0.0812 \text{ mol lit}^{-1}$$

$$\text{molality, } m = 0.0812 \text{ mol kg}^{-1} \qquad [\because 1 \text{ lit } H_2O = 1 \text{ kg } H_2O]$$

(ii) To calculate the depression in freezing point

Formula used

$$\Delta T_f = K_f \times m$$

Quantities given

$m = 0.0812 \text{ mol kg}^{-1}$ $\qquad K_f = 1.86 \text{ K kg mol}^{-1}$

Substitution of values

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0812 \text{ mol kg}^{-1}$$

$$= 0.151 \text{ K}$$

$$\therefore \quad \text{Freezing Point of solution} = 273 \text{ K} - 0.151 \text{ K}$$

$$= \mathbf{272.849 \text{ K}}$$

ADDITIONAL PRACTICE PROBLEMS

1. Calculate the osmotic pressure of 2% solution of glucose in water at 25 ºC. Molecular mass of glucose = 180; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Answer. $2.75 \times 10^5 \text{ Nm}^{-2}$

2. A solution of sucrose (mol mass 342 g mol^{-1}) is prepared by dissolving 30 g of it per litre of solution. Calculate the osmotic pressure at 300 K ($R = 0.082$ atm lit $\text{K}^{-1} \text{ mol}^{-1}$).

Answer. 2.15 atm

3. A solution containing 3.0 g of a solute in 100 cm^3 of the solution exhibits an osmotic pressure of 2.05 atm at 27 ºC. Calculate the molecular mass of the solute.

Answer. 360

4. The osmotic pressure of a solution containing 2.0 g of protein in 200 ml of aqueous solution is 0.2 atm at 300K. Calculate the molar mass of the protein. ($R = 0.082$ atm lit $\text{K}^{-1} \text{ mol}^{-1}$)

Answer. 1230 g mol^{-1}

5. Calculate the molecular mass of a solute when 10 g of it is present in 100 ml of the solution at 27 ºC which has an osmotic pressure of 2.85 atm. $R = 0.0821$ atm lit $\text{K}^{-1} \text{ mol}^{-1.}$

Answer. 864

6. Osmotic pressure of a solution containing 2.0 g of dissolved protein in 250 ml of solution is 20 mm of Hg at 300 K. Calculate the molecular mass of the protein. ($R = 0.0821$ atm lit $\text{K}^{-1} \text{ mol}^{-1}$)

Answer. 7487

7. Calculate the osmotic pressure of a mixture solution obtained by mixing 1 litre of 7.5% solution of substance *A* with mol mass = 75 and two litres of a 5% solution of substance B (with molecular mass 60 at 453 K.)

Answer. 7.95 atm

8. Calculate the osmotic pressure of a glucose solution containing 15 g in 100 ml solution at 27 °C.

Answer. 20.5 atm

9. An aqueous solution contains 20 g of glucose in one litre of the solution. Assuming the solution to be ideal, calculate its osmotic pressure at 25 °C.

Answer. 2.718 atm

10. Calculate the osmotic pressure of a sugar solution in which 3.42 g of sugar has been dissolved in 100 cm^3 of solution at 300 K.

Answer. 2.477 atm

11. The osmotic pressure of solution containing 5×10^{-3} kg sugar in 250 cm^{-3} is 1.45×10^5 Nm^{-2} at 298 K. What is the molar mass of sugar cane ?

Answer. 341.7 g mol^{-1}

12. A 1.8% solution of an unknown solute is isotonic with 10.26% solution of sugar cane (molecular mass = 342). Calculate the molar mass of the solute.

Answer. 60 g mol^{-1}

13. The average osmotic pressure of human blood at body temperature 37 °C is 7.6 atm. Calculate the total concentration of various solutes in blood.

Answer. 0.298 mol^{-1}

14. Calculate the osmotic pressure of a 10% solution of urea (molecular mass = 60; R = 0.0821 atm lit $K^{-1}mol^{-1}$) at 300 K.

Answer. 40.05 atm

15. Calculate the osmotic pressure of a solution obtained by mixing 100 ml of 5% solution of urea (molecular mass = 60) and 100 ml of 4% solution of sucrose at 300 K. (molecular mass = 342) R = 0.0821 atm lit K^{-1} mol^{-1})

Answer. 11.70 atm

16. Calculate the osmotic pressure of a solution at 25 °C obtained by mixing 100 cm^3 of 4.6 % of glucose and 200 cm^3 of 4.5% solution of glucose.

Answer. 8.332 atm

17. The formula for starch is $(C_6H_{10}H_5)_n$ where n = 200. When 1.0 g of starch is dissolved in 100 ml of water solution, what is the osmotic pressure of 27 °C ?

Answer. 7.60×10^{-3} atm

18. The osmotic pressure of blood at 37 °C is 7.6 atm. A solution that is given intravenously must have the same osmotic pressure as blood. What should be the molarity of a glucose solution to give an osmotic pressure of 7.6 atm at 37 °C ?

Answer. 0.298 mol^{-1}

19. A solution containing 4 g of a non-volatile organic solute per litre was found to have an osmotic pressure 360mm of Hg at 27 ^{o}C. Calculate the molecular mass of the solute.

Answer. 197

20. A 5% solution of glucose (molecular mass 60) is isotonic with 3% solution of an unknown compound. Calculate the molecular mass of the unknown substance.

Answer. 36

21. A solution of sucrose (molar mass 342 g mol^{-1}) is prepared by dissolving 68.4 of it per litre of the solution. What is its osmotic pressure at 300 K ? (R = 0.082 lit atm deg^{-1} mol^{-1})

Answer. 4.92 atm

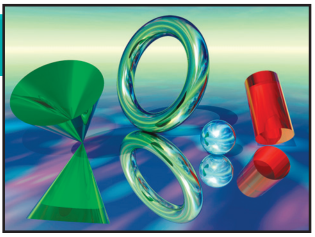
22. A 1.2% solution of NaCl is isotonic with 7.2% solution of glucose. Calculate van't Hoff factor of NaCl solution .

Answer. 1.95

17

Chemical Equilibrium

CHAPTER



KEY CONCEPTS AND EQUATIONS

CHEMICAL EQUILIBRIUM

The state of a reversible reaction when the two opposing reactions occur at the same rate is called Chemical equilibrium. At equilibrium the concentrations of reactants and products do not change with time. Thus at equilibrium

$$\textit{Rate of forward reaction} = \textit{Rate of backward reaction}$$

LAW OF MASS ACTION

The rate of a chemical reaction is proportional to the active masses of the reactants. For the reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{Products}$$

we can write

$$\text{Rate of reaction} \propto [\mathrm{A}]\,[\mathrm{B}] = k\,[\mathrm{A}]\,[\mathrm{B}]$$

and for the reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow \text{Products}$$

we have

$$\text{Rate of reaction} \propto [\mathrm{A}]^a\,[\mathrm{B}]^b = \mathrm{K}\,[\mathrm{A}]^a\,[\mathrm{B}]^b$$

EQUILIBRIUM CONSTANT

The product of the equilibrium concentration of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balance equation is called the Equilibrium constant.

For the reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

the equilibrium constant is given by

$$K_c = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

EQUILIBRIUM CONSTANT IN TERMS OF PARTIAL PRESSURE

The partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. For the reaction

$$l\,\mathrm{L}_{(g)} + m\,\mathrm{M}_{(g)} \rightleftharpoons y\,\mathrm{Y}_{(g)} + z\,\mathrm{Z}_{(g)}$$

the equilibrium constant K_p is given by

$$K_p = \frac{(p_Y)^y\,(P_Z)^z}{(p_L)^l\,(p_M)^m}$$

RELATION BETWEEN K_P AND K_C

For the reaction

$$jA + kB \rightleftharpoons lC + mD$$

$$K_p = K_c \times (RT)^{\Delta n}$$

where $\Delta n = (l + m) - (j + k)$

when $\Delta n = 0$ $K_p = K_c$

RELATION BETWEEN ΔG AND THE EQUILIBRIUM CONSTANT

The change in free energy of a reaction and the equilibrium constant K are related to each other by the relation

$$\Delta G = -RT \ln K$$

Case I when ΔG is –ve the forward reaction is spontaneous.

Case II when ΔG *is* 0 the reaction is at equilibrium.

Case III when ΔG *is* +ve the reverse reaction is spontaneous.

TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT (VAN'T HOFF EQUATION)

The value of equilibrium constant changes with temperature. The reaction between equlibrium constants at two different temperatures and the enthalpy change is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303\, R}\left[\frac{T_2 - T_1}{T_1\, T_2}\right]$$

where K_{p_2} is the equilibrium constant at temperature T_2 and K_{p_1} is the equilibrium constant at temperature T_1

In terms of ΔE the equation becomes

$$\log \frac{K_{c_2}}{K_{c_1}} = \frac{\Delta E}{2.303\, R}\left[\frac{T_2 - T_1}{T_1\, T_2}\right]$$

LIQUID SYSTEMS

The reaction between acetic acid and ethyl alcohol to form ethyl acetate and water is represented by

	$CH_3COOH_{(l)}$	+ $C_2H_5OH_{(l)}$	$\rightleftharpoons$ $CH_3COOC_2H_{5\,(l)}$	+ $H_2O_{(l)}$
Initial conc.	a	b	0	0
Eq. conc.	$a - x$	$b - x$	x	x

The equilibrium constant may be written as

$$K = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{a-x}{V}\right) \times \left(\frac{b-x}{V}\right)} \quad \text{or} \quad \frac{x^2}{(a-x)\ (b-x)}$$

where V is the volume

HETEROGENEOUS EQUILIBRIA

The equilibria in which the reactants and products are not all in the same phase are called heterogeneous equilibria. The examples with their equilibrium constants are

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)} \qquad K_p = p_{CO_2}$$

$$2H_2O_{(l)} \rightleftharpoons 2\,H_{2\,(g)} + O_{2\,(g)} \qquad K_p = p^2_{H_2} \times p_{O_2}$$

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)} \qquad K_p = p_{NH_3} \times p_{HCl}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. The equilibrium constant at 444 °C for the reaction

$$2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$$

is 1.39×10^{-2}. Calculate the equilibrium constant at the same temperature for the reaction

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{\,(g)}$$

SOLUTION :

Formula used

$$K' = \frac{1}{K}$$

Quantity given

$$K = 1.39 \times 10^{-2}$$

Substitution of value

$$K' = \frac{1}{1.39 \times 10^{-2}}$$

$$= \frac{100}{1.39}$$

$$= \mathbf{71.94}$$

SOLVED PROBLEM 2. One mole of PCl_5 is heated in closed two-litre vessel. At equilibrium 40% of PCl_5 is dissociated. Calculate the equilibrium constant of the reaction

SOLUTION :

The dissociation of PCl_5 is represented by

	$PCl_5 \rightleftharpoons$	PCl_3	+ Cl_2
Initial concentration	1.0 mole	0	0
Equilibrium concentration	0.6 mole	0.4 mole	0.4 mole

Formula used

$$K = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

Quantities given

$$[PCl_5] = \frac{0.6 \text{ mole}}{2 \text{ lit}} = 0.3 \text{ mol lit}^{-1} \qquad [PCl_3] = \frac{0.4 \text{ mole}}{2 \text{ lit}} = 0.2 \text{ mol lit}^{-1}$$

$$[Cl_2] = \frac{0.4 \text{ mole}}{2 \text{ lit}} = 0.2 \text{ mol lit}^{-1}$$

Substitution of value

$$K = \frac{0.2 \text{ mol lit}^{-1} \times 0.2 \text{ mol lit}^{-1}}{0.3 \text{ mol lit}^{-1}}$$

$$= \mathbf{0.133 \text{ mol lit}^{-1}}$$

SOLVED PROBLEM 3. The concentration equilibrium constant K_C for the reaction

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

at 400 ^{0}C is 0.5. Find the value of K_p ($R = 0.0821$ atm lit K^{-1} mol^{-1})

SOLUTION :

Formula used

$$K_p = K_c \times (R\,T)^{\Delta n}$$

Quantities given

$$\Delta n = n_P - n_R = 2 - 4 = -2 \qquad K_c = 0.5$$

$$T = 400 + 273 = 673\text{ K} \qquad R = 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} K_p &= 0.5 \times (0.0821 \times 673)^{-2} \\ &= 0.5 \times (55.2533)^{-2} \\ &= \mathbf{0.000164} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the equilibrium constant of the reaction from the data given below:

$$\text{A} + \text{B} \rightleftharpoons 2\,\text{C}$$

The reaction was started with 2.0 moles litre^{-1} of A and 2.0 moles litre^{-1} of B and the equilibrium constant of C was found to be 0.32 mol litre^{-1}.

SOLUTION : The equilibrium reaction is

	A	+	B	$\rightleftharpoons$	2 C
Initial conc.	2.0 mole		2.0 mole		0
Eq. conc.	1.84 mole		1.84 mole		0.32 mole

Formula used

$$K = \frac{[C]^2}{[A]\ [B]}$$

Quantities given

$[C] = 0.32\text{ mol lit}^{-1}$ $\qquad [A] = 1.84\text{ mol lit}$ $\qquad [B] = 1.84\text{ mol lit}^{-1}$

Substitution of values

$$\begin{aligned} K &= \frac{(0.32\text{ mol lit}^{-1})^2}{(1.84\text{ mol lit}^{-1}) \times (1.84\text{ mol lit}^{-1})} \\ &= \mathbf{0.0302\ mol\ lit^{-1}} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the ratio of K_p to K_c at 27 ^{o}C for the equilibrium reaction :

$$\text{COCl}_{2\,(g)} \rightleftharpoons \text{CO}_{(g)} + \text{Cl}_{2\,(g)}$$

SOLUTION :

The equilibrium reaction is

$$\text{COCl}_{2\,(g)} \rightleftharpoons \text{CO}_{(g)} + \text{Cl}_{2\,(g)}$$

Formula used

$$K_p = K_c(RT)^{\Delta n} \quad \text{or} \quad \frac{K_p}{K_c} = (RT)^{\Delta n}$$

Quantities given

$\Delta n = n_P - n_R = 2 - 1 = 1$ mole $\qquad R = 0.082\text{ atm lit K}^{-1}\text{ mol}^{-1}$

$T = 27 + 273 = 300\text{ K}$

Substitution of values

$$\begin{aligned} \frac{K_p}{K_c} &= (0.082 \times 300)^{-1} \\ &= (24.63)^{-1} = \mathbf{0.406} \end{aligned}$$

SOLVED PROBLEM 6. On heating in a closed vessel PCl_5 dissociates into PCl_3 & Cl_2. At 200 ^{o}C the vapour density of the gaseous mixture is 75.5 Calculate the degree of dissociation of PCl_5 (P = 31; Cl = 35.5).

SOLUTION :

Formula used

$$\frac{\rho_1}{\rho_2} = \frac{1+x}{1}$$

Quantities given

ρ_1, the density of undissociated gas $= \dfrac{\text{mol. mass of } PCl_5}{2} = \dfrac{31+5\times35.5}{2} = 104.25$

ρ_2, the density of dissociated gas $= 75.5$

Substitution of values

$$\frac{104.25}{74.5} = \frac{1+x}{1}$$

or $\quad 1.399 = 1 + x$

or $\quad x = 1.399 - 1$

$\quad = \mathbf{0.399}$

SOLVED PROBLEM 7. Calculate the free energy change (ΔG^o) associated with chemical reaction for which the equilibrium constant at 298 K is 0.01 ($R = 8.314\ J\ K^{-1} mol^{-1}$)

SOLUTION :

Formula used

$$\Delta G^o = -2.303\, R\, T \log K$$

Quantities given

$R = 8.314\ J\ K^{-1} mol^{-1}$ $\quad T = 298\ K$ $\quad K = 0.01$

Substitution of values

$$\begin{aligned}\Delta G^o &= -2.303 \times 8.314\ J\ K^{-1} mol^{-1} \times 298\ K^{-1} \times \log 0.01\\ &= -5705.84\ J \times \log 0.01\\ &= -5705.84\ J \times -2\\ &= \mathbf{11411.68\ J}\end{aligned}$$

SOLVED PROBLEM 8. For the reaction

$$CO_{2\,(g)} + H_{2\,(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

The equilibrium constant at 1000 K is 0.53.

(a) If a mixture at equilibrium in a 1 dm^3 vessel contains 0.25 mole of CO, 0.5 mole of CO_2 and 0.6 mole of H_2, how many moles of H_2O are there in the vessel ?

(b) 5 moles of inert gas are added to the equilibrium mixture containing 1 mole of H_2 and 1 mole of CO_2 Predict the equilibrium concentration of CO_2 and H_2O.

SOLUTION : (a)

Formula used

$$K = \frac{[CO]\ [H_2O]}{[CO_2]\ [H_2]}$$

Quantities given

$K = 0.53$ $\quad [CO] = 0.25$ $\quad [CO_2] = 0.5$ $\quad [H_2] = 0.6$

Substitution of values

$$0.53 = \frac{0.25 \times [H_2O]}{0.5 \times 0.6}$$

$$[H_2O] = \frac{0.53 \times 0.5 \times 0.6}{0.25}$$

$$= \mathbf{0.636}$$

SOLVED PROBLEM 9. The equilibrium constant K_p for the reaction

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

is 1.64 × 10^{-4} at 673 K and 0.144 × 10^{-4} at 773 K. Calculate the mean heat of formation of ammonia from its elements in this temperature range.

SOLUTION :

Formula used

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

Quantities given

$K_{P_2} = 0.144 \times 10^{-4}$ $T_2 = 773\text{ K}$ $R = 8.314\text{ J K}^{-1}\text{mol}^{-1}$

$K_{P_1} = 1.64 \times 10^{-4}$ $T_1 = 673\text{ K}$

Substitution of values

$$\log \frac{0.144 \times 10^{-4}}{1.64 \times 10^{-4}} = \frac{\Delta H}{2.303 \times 8.314}\left[\frac{773 - 673}{773 \times 673}\right]$$

$$1.05648 = \frac{\Delta H}{19.14714}\left[\frac{100}{673 \times 773}\right]$$

or

$$\Delta H = -\frac{1.05648 \times 19.14714 \times 673 \times 773}{100}$$

$$= \mathbf{-105.235\ kJ}$$

This is the heat of reaction in which two moles of NH_3 are formed.

$$\text{The mean heat of formation of } NH_3 = -\frac{105.235\text{ kJ}}{2}$$

$$= \mathbf{-52.6174\ kJ}$$

SOLVED PROBLEM 10. For the reaction

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

K_p is 1.64 × 10^{-4} at 673 K. Calculate (i) ΔG ; (ii) ΔG when the partial pressure of N_2, H_2 and NH_3 are 10 atm, 30 atm and 3 atm respecitvely ; (iii) Is the reaction spontaneous ?

SOLUTION :

(i) To calculate ΔG

Formula used

$$\Delta G = -2.303\,R\,T\,\log K_p$$

Quantities given

$R = 8.314\text{ J K}^{-1}\text{mol}^{-1}$ T = 673K $K_p = 1.64 \times 10^{-4}$

Substitution of values

$$\Delta G = -2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 673\ \text{K} \times \log(1.64 \times 10^{-4})$$
$$= -12886.027\ \text{J} \times (-3.78515)$$
$$= 48775.5\ \text{J}$$
$$= \mathbf{48.7755\ J}$$

(ii) To calculate ΔG when partial pressures are given

Formula used

$$\Delta G = -2.303\, RT \log K_p$$

Quantities given

$$K_p = \frac{P^2\, NH_3}{PN_2 \times P^3 H_2} = \frac{3^2}{10 \times 30^3} = 0.0000333 = 3.33 \times 10^{-5}$$

$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ $\qquad T = 673\ \text{K}$

Soubstitution of values

$$\Delta G = -2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 673\ \text{K} \times \log(3.33 \times 10^{-5})$$
$$= -12886.027\ \text{J} \times (-4.47755)$$
$$= 57697.8\ \text{J}$$
$$= \mathbf{57.6978\ kJ}$$

(iii) No - the reaction is not spontaneous since ΔG is positive.

SOLVED PROBLEM 11. The equilibrium constant K_p for a reaction

$$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$$

is 10^{-12} at 327 ^{0}C and 10^{-7} at 427 ^{0}C, Calculate the enthalpy of the reaction ($R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$)

SOLUTION :

Formula used

$$\log \frac{Kp_2}{Kp_1} = \frac{\Delta H}{2.303\, R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

Quantities given

$Kp_2 = 10^{-7}$ $\qquad R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ $\qquad T_2 = 427 + 273 = 700\text{K}$

$Kp_1 = 10^{-12}$ $\qquad T_1 = 327 + 273 = 600\text{K}$

Substitution of values

$$\log \frac{10^{-7}}{10^{-12}} = \frac{\Delta H}{2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}} \times \left[\frac{700\ \text{K} - 600\ \text{K}}{700\ \text{K} \times 600\ \text{K}}\right]$$

or
$$\Delta H = \frac{\log 10^5 \times 2.303 \times 8.314\ \text{J} \times 600 \times 700}{100}$$
$$= 402089.98\ \text{J}$$
$$= \mathbf{402.08998\ kJ}$$

SOLVED PROBLEM 12. For the dissociation of water

$$H_2O_{(g)} \rightleftharpoons H_{2\,(g)} + {}^1/_2\, O_{2\,(g)}$$

at 1773 K the value of K_p is 1.87×10^{-6} atm. Assuming ideal behaviour of gases, Calculate the value of K_c

SOLUTION :

Formula used

$$K_p = K_c\,(RT)^{\Delta n}$$

or $$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

Quantities given

$K_p = 1.87 \times 10^{-6}$ atm $R = 0.082$ atm lit K^{-1} mol $^{-1}$ T = 1773 K

$\Delta n = n_p - n_R = 1^1/_2 - 1 = {}^1/_2$

Substitution of values

$$K_c = \frac{1.87 \times 10^{-6}}{(0.082 \times 1773)^{1/2}}$$

$$= \frac{1.87 \times 10^{-6}}{12.0576}$$

$$= \mathbf{1.55 \times 10^{-7}}$$

SOLVED PROBLEM 13. For the reaction

$$CO_{(g)} + 2H_{2\,(g)} \rightleftharpoons CH_3OH_{(g)}$$

hydrogen gas introduced into a five litre flask at 327 °C containing 0.2 mole of $CO_{(g)}$ and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $CH_3OH_{(g)}$ is formed. Calculate the equilibrium constant K_p and K_c.

SOLUTION :

(i) To calculate the total number of moles of all gas at equilibrium

Formula used

$$PV = nRT \quad \text{or} \quad n = \frac{PV}{RT}$$

Quantities given

$P = 4.92$ atm $V = 5$ litres $R = 0.082$ atm lit K^{-1} mol^{-1}

$T = 327 + 273 = 600$K.

Substitution of values

$$n = \frac{4.92 \text{ atm} \times 5 \text{ lit}}{0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 600 \text{ K}}$$

$$= \mathbf{0.5 \text{ mole}}$$

(ii) To calculate the value of K_c

Formula used

$$K_c = \frac{[CH_3OH]}{[CO]\,[H_2]^2}$$

Quantites given

No. of moles of CH_3OH = 0.1 $\therefore [CH_3OH] = \frac{0.1}{5} = 0.02$ mol lit^{-1}

No. of moles of CO = 0.1 $\therefore [CO] = \frac{0.1}{5} = 0.02$ mol lit^{-1}

No. of moles of H_2 = 0.5 – (0.1 + 0.1)

= 0.3 $\therefore [H_2] = \frac{0.3}{5} = 0.06$ mol lit^{-1}

Substitution of values

$$K_c = \frac{0.02 \text{ mol lit}^{-1}}{0.02 \text{ mol lit}^{-1} \times (0.06 \text{ mol lit}^{-1})^2}$$

$$= \mathbf{277.78 \text{ mol}^{-2} \text{ lit}^2}$$

(iii) To calculate the value of K_p

Formula used

$$K_p = K_c \times (RT)^{\Delta n}$$

Quantities given

$K_c = 277.78$

$T = 600\text{K}$

$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$

$\Delta n = n_P - n_R = 1 - 3 = -2$

Substitution of values

$$\begin{aligned} K_p &= 277.78 \text{ mol}^{-2} \text{ lit}^{-1} \times (0.082 \text{ atm litK}^{-1} \text{ mol}^{-1} \times 600 \text{ K})^{-2} \\ &= 277.78 \times (49.2 \text{ atm})^{-2} \\ &= \mathbf{0.11475 \text{ atm}^{-2}} \end{aligned}$$

SOLVED PROBLEM 14. When sulphur in the form of S_8 is heated at 900 K the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of equilibrium constant for the reaction.

SOLUTION :

The equilibrium reaction is

	S_8	$\rightleftharpoons$	$4\,S_{2\,(g)}$
Initial pressure	1 atm		0
Equilibrium pressure	$(1-\alpha)$ atm		$4\,\alpha$ atm

At Equilibrium $\quad \alpha = 29\%$ or 0.29

$\therefore \quad 1-\alpha = 1 - 0.29 = 0.71$

and $\quad 4\,\alpha = 4 \times 0.29 = 1.16$

Formula used

$$K_p = \frac{p^4_{S_2}}{p_{S_8}} = \frac{(4\,\alpha)^4}{1-\alpha}$$

Quantities given

$4\,\alpha = 1.16 \text{ atm}$

$1-\alpha = 0.71 \text{ atm}$

Substitution of values

$$\begin{aligned} K_p &= \frac{(1.16 \text{ atm})^2}{0.71 \text{ atm}} = \frac{1.3456}{0.71} \\ &= \mathbf{1.8952 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 15. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 at 1.1 atm pressure respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.

SOLUTION :

(i) To calculate the value K_p

$$\underset{0.28 \text{ atm}}{N_2O_{4\,(g)}} \rightleftharpoons \underset{1.1 \text{ atm}}{2\,NO_{2\,(g)}}$$

Formula used

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$

Quantities given

$p_{NO_2} = 1.1 \text{ atm}$

$p_{N_2O_4} = 0.28 \text{ atm}$

Substitution of values

$$K_p = \frac{(1.\ 1 \text{ atm})^2}{0.28 \text{ atm}} = 4.32 \text{ atm}$$

(ii) To calculate the new equilibrium pressures when volume is doubled

When volume is doubled the pressure reduces to one half we have

	$N_2O_{4\,(g)}$ $\rightleftharpoons$	$2NO_{2\,(g)}$
Initial pressure	0.28/2 atm	1.1/2 atm
Equilibrium pressure	(0.14 – x) atm	(0.55 + 2x) atm

Formula used

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$

Quantities given

p_{NO_2} = (0.55 + 2x) atm $\qquad$ $p_{N_2O_4}$ = (0.14 – x) atm

K_p = 4.32 atm

Substitution of values

$$4.32 \text{ atm} = \frac{(0.55 + 2x)^2 \text{ atm}^2}{(0.14 - x) \text{ atm}}$$

or $$4x^2 + 2.2x + 0.3025 = 0.6048 - 4.32x$$

or $$4x^2 + 6.52x - 0.3023 = 0$$

or $$x = \frac{-6.52 \pm \sqrt{42.510 + 4.837}}{8} \qquad \left[x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$= \frac{-6.52 \pm 6.88}{8}$$

$$= 0.045 \text{ or } -1.675$$

∴ $$p_{NO_2} = 0.55 + 2 \times 0.045 = \mathbf{0.64\ atm} \qquad \text{(Rejecting} -1.675)$$

and $$p_{N_2O_4} = 0.14x = \mathbf{0.095\ atm}$$

SOLVED PROBLEM 16. The equilibrium constant for the reaction

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$$

is 0.63. A mixture of 1 mole of water vapour and 3 moles of CO is allowed to come to equilibrium at a total pressure of 2 atmospheres. Calculate

(i) the no. of moles of hydrogen present at equilibrium

(ii) the partial pressure of each gas in the equilibrium mixture.

SOLUTION :

(i) To calculate the no. of moles of hydrogen at equilibrium

The reaction equilibrium is

	$CO_{(g)}$	+ $H_2O_{(g)}$ $\rightleftharpoons$	$CO_{2\,(g)}$	+ $H_{2\,(g)}$
Initial concentration	3	1	0	0
Equilibrium concentration	(3 – x)	(1– x)	x	x

Total number of moles at equilibrium $= (3 - x) + (1 - x) + x + x$

$= (3 + 1)$

Formula used

$$K_p = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

Quantities given

K_p = 0.63 $\qquad$ [CO] = 3 – x $\qquad$ [H_2O] = 1 – x

Substitution of values

$$0.63 = \frac{x \times x}{3 - x \times 1 - x}$$

or $$0.63 \times (x^2 - 4x + 3) = x^2$$

or $$0.373x^2 + 2.52x - 1.89 = 0$$

or $$x = 0.68$$

Thus the no. of moles of hydrogen at equilibrium = **0.68**

(ii) To calculate the partial pressure of each gas

Formula used

$$\textit{Partial pressure} = \frac{\textit{No. of moles of the gas}}{\textit{Total no. of moles}} \times \textit{Total pressure}$$

Quantities given

Total pressure = 2 atm

Total no. of moles = 4

Subtitution of values

$$p_{CO_2} = \frac{x \times 2\text{atm}}{4} = \frac{0.68 \times 2\text{atm}}{4} = \mathbf{0.34\ atm}$$

$$p_{H_2} = \frac{x \times 2\text{ atm}}{4} = \frac{0.68 \times 2\text{ atm}}{4} = \mathbf{0.34\ atm}$$

$$p_{CO} = \frac{(3 - x) \times 2\text{ atm}}{4} = \frac{2.32 \times 2\text{ atm}}{4} = \mathbf{1.16\ atm}$$

$$p_{H_2O} = \frac{(1 - x) \times 2\text{ atm}}{4} = \frac{0.32 \times 2\text{ atm}}{4} = \mathbf{0.16\ atm}$$

SOLVED PROBLEM 17. Calculate the percent dissociation of $H_2S_{(g)}$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K. For the reaction.

$$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$$

the value of K_c is 1.0×10^{-6}.

SOLUTION :

The chemical equation representing the equilibrium is

	$2H_2S_{(g)}$ $\rightleftharpoons$	$2H_{2(g)}$ +	$S_{2(g)}$
Initial concentration	0.1	0	0
Equilibrium concentration	$0.1 - x$	x	$x/2$
Molar Concentrations	$\frac{0.1 - x}{V}$	$\frac{x}{V}$	$\frac{x}{2V}$

Formula used

$$K_c = \frac{[H_2]^2\,[S_2]}{[H_2S]^2}$$

Quantities given

$K_c = 1.0 \times 10^{-6}$

$[H_2] = \frac{x}{V}$

$[S_2] = \frac{x}{2V}$

$[H_2S] = \frac{0.1 - x}{V}$ where $V = 0.4$ litre

Subsitution of values

$$1.0 \times 10^{-6} = \frac{\left(\frac{x}{V}\right)^2 \left(\frac{x}{2V}\right)}{\left(\frac{0.1 - x}{V}\right)^2}$$

$$\text{or} \quad 1.0 \times 10^{-6} = \frac{x^3}{2V\,(0.1)^2} \qquad [\because\ 0.1 - x \simeq 0.1]$$

$$\text{or} \quad x^3 = 2 \times 0.4 \times 0.01 \times 1.0 \times 10^{-6} \qquad [\because V = 0.4 \text{ litre}]$$

$$\text{or} \quad x^3 = 8 \times 10^{-9}$$

$$x = \sqrt{8 \times 10^{-9}}$$

$$= 2 \times 10^{-3}$$

$$= 0.002$$

$$\%\ \text{Dissociation} = \frac{\text{Amt. dissociated}}{\text{Initial concentration}} \times 100$$

$$= \frac{0.002}{0.1} \times 100$$

$$= \mathbf{2\%}$$

SOLVED PROBLEM 18. At temperature T, a compound AB_2 dissociates according to the reaction

$$2\,AB_{2\,(g)} \rightleftharpoons 2\,AB_{\,(g)} + B_{2\,(g)}$$

with a degree of dissociation, x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p, and the total pressure P.

SOLUTION :

The chemical equation representing the equilibrium is

	$2\,AB_{2\,(g)}$	$\rightleftharpoons$	$2\,AB_{\,(g)}$	+	$B_{2\,(g)}$
Initial concentration	1 mole		0 mole		0 mole
Initial concentration	$1 - x$ mole		x mole		$\frac{x}{2}$ mole

$$\text{Total number of moles at equilibrium} = (1 - x) + x + \frac{x}{2}$$

$$= 1 + \frac{x}{2} = \frac{2 + x}{2}$$

(i) To deduce the expression for the total Pressure

Formula used

$$\textit{Partial pressure} = \frac{\textit{No. of moles of the gas}}{\textit{Total no. of moles}} \times \textit{Total Pressure}$$

Substitution of values

$$p_{AB2} = \frac{1 - x}{\frac{2 + x}{2}} \times p = \frac{2\,(1 - x)}{2 + x}\,p$$

$$p_{AB} = \frac{x}{\frac{2 + x}{2}} \times p = \frac{2\,x}{2 + x}\,p$$

$$p_{B2} = \frac{x}{\frac{2 + x}{2}} \times p = \frac{2\,x}{2 + x}\,p$$

$$\textit{Total pressure} = p_{AB_2} + p_{AB} + p_{B_2}$$

$$= \frac{2\,(1 - x)}{2 + x}\,p + \frac{2\,x}{2 + x}\,p + \frac{x}{2 + x}\,p$$

$$= \frac{1}{2 + x}\,[\,1 - x + 2\,x + 2\,]\,p$$

$$= \frac{1-x}{2+x} + p$$

(ii) To deduce the expression for K_p

Formula used

$$K_p = \frac{p^2_{AB} \times p_{B_2}}{p^2_{AB_2}}$$

Substitution of values

$$K_p = \frac{\left(\frac{2\,x}{2+x}\,p\right)^2 \left(\frac{2}{2+x}\,p\right)^2}{\left[\frac{2\,(1-x)}{2+x}\right]^2}$$

$$= \frac{x^3\,p}{(2+x)\,(1-x)^2}$$

SOLVED PROBLEM 19. At 700 K, hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8. Calculate the amount of H_2 Br_2 and H Br at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of Br_2 is heated to 700 K.

SOLUTION :

The chemical equation representing the chemical equilibrium is

	H_2 +	$Br_{2(g)}$ $\rightleftharpoons$	$2\,HBr_{(g)}$
Initial concentration	0.6 mole	0.2 mole	0 mole
Equilibrium concentration	$(0.6 - x)$ mole	$(0.2 - x)$ mole	$2x$ mole

Formula used

$$K_c = \frac{[\,HBr\,]^2}{[H_2]\,[Br_2]}$$

Quantities given

$K_c = 5 \times 10^8$ $\quad$ $[HBr]^2 = 2\,x$ mole

$K_c = 5 \times 10^8$ $\quad$ $[Br_2] = (0.2 - x)$ mole

Substituting of values

$$5 \times 10^8 = \frac{(2x\text{ mole})^2}{(0.6 - x\text{ mole})\,(0.2 - x\text{ mole})}$$

$$x = 0.6\text{ mole or }0.2\text{ mole}$$

Rejecting the value 0.6 mole since it can not be greater than the initial concentration (= 0.2 mole)

Thus $[H_2] = 0.6\text{ mole} - 0.2\text{ mole} = 0.4\text{ mole}$

$[Br_2] = 0.2\text{ mole} - 0.2\text{ mole} = 0\text{ mole}$

$[HBr] = 2 \times 0.2\text{ mole} = 0.4\text{ mole}$

SOLVED PROBLEM 20. 20% of N_2O_4 molecules are dissociated in a sample of gas at 27 °C and 760 torr. Calculate the density of the equilibrium mixture.

SOLUTION :

The chemical equation representing the decomposition of N_2O_4 is

	N_2O_4 $\rightleftharpoons$	$2\,NO_2$
Initial concentration	1 mole	0 mole
Equilibrium concentration	(1 – 0.2) mole	2 × 0.2 mole

Total no. of moles at equilibrium $= (1 - 0.2)$ mole $+ 2 \times 0.2$ mole

$= 0.8$ mole $+ 0.4$ mole

$= 1.2$ mole

Formula used

$$P\,V = n\,R\,T \qquad \text{or} \qquad V = \frac{n\,R\,T}{P}$$

Quantities given

$n = 1.2$ mole

$R = 0.82$ atm lit K^{-1} mol^{-1}

T $= 27 + 273 = 300$ K

$P = 760$ torr $= 1$ atm

Substitution of values

$$V = \frac{1.2 \text{ mole} \times 0.082 \text{ atm lit } K^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{1 \text{ atm}}$$

$$= 29.52 \text{ lit}$$

To calculate the density

Formula used

$$Density = \frac{Molecular\ mass}{Volume}$$

Quantities given

Molar mass of $N_2O_4 = 92$ g

$V = 20.52$ lit

Substitution of values

$$Density = \frac{92 \text{ g}}{29.52 \text{ lit}}$$

$$= \mathbf{3.116\ g\ lit^{-1}}$$

SOLVED PROBLEM 21. At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which at which PCl_5 will be 20% dissociated, temperature remaining the same.

SOLUTION :

The chemical equation representing the dissociation of PCl_5

	$PCl_{5\,(g)}$	$\rightleftharpoons$ $PCl_{3\,(g)}$	$+$ $Cl_{2\,(g)}$
Initial concentration	1 mole	0 mole	0 mole
Equilibrium concentration	$(1 - \alpha)$	α mole	α mole

Total number of moles at equilibrium $= 1 - \alpha + \alpha + \alpha$ moles

$= 1 + \alpha$ moles

(i) To calculate the value of K_p

Formula used

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

Quantities given

$$P_{PCl_3} = \frac{\alpha}{1 + \alpha}\,P \qquad P_{Cl_2} = \frac{\alpha}{1 + \alpha}\,P$$

$$P_{PCl_5} = \frac{1 - \alpha}{1 + \alpha}\,P \qquad \text{where } P = 4 \text{ atm and } \alpha = 0.1$$

Substitution of values

$$K_p = \frac{\dfrac{\alpha}{1 + \alpha}\,P \times \dfrac{\alpha}{1 + \alpha}\,P}{\dfrac{1 - \alpha}{1 + \alpha}\,P}$$

$$K_p = \frac{\alpha^2\ P}{1-\alpha^2}$$

$$= \frac{(0.1)^2 \times 4 \text{ atm}}{1-0.1^2}$$

$$= \frac{0.01 \times 4 \text{ atm}}{1-0.01} = \frac{0.04}{0.99} \text{ atm} = 0.040 \text{ atm}$$

(ii) To calculate the pressure when α = 0.2

Formula used

$$K_p = \frac{\alpha^2\ p}{1-\alpha^2}$$

Qunatities given

K_p = 0.04 atm α = 0.2

Substitution of values

$$0.04 \text{ atm} = \frac{0.2^2 \times 0.2 \times P'}{1-(0.2)^2}$$

$$= \frac{0.04 \times P'}{1-0.04}$$

or $$P' = \frac{0.04 \times 0.096}{0.04} \text{ atm} = \mathbf{0.96\ atm}$$

ADDITIONAL PRACTICE PROBLEMS

1. The equilibrium constant K_p of the reaction

$$2\,SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,SO_{2\,(g)}$$

is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial partial pressures of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

Answer. 0.023 atm; 2.0115 atm; 0.977 atm

2. N_2O_4 is 25% dissociated at 37 ºC and 1 atm pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and 37 ºC.

Answer. 2.66×10^{-1} atm; 63.2%

3. For the reaction

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2\,CN^-$$

the equilibrium constant at 25 ºC is 4.0×10^{-19}. Calculate the equilibrium concentration in a solution which was originally 0.1 molar in KCN and 0.03 molar in $AgNO_3$

Answer. 7.5×10^{-18} M

4. One mole of H_2, two moles of I_2 and three moles of HI are injected in 1 litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 490 ºC? The equilibrium constant for the reaction at 490 ºC is 45.9.

Answer. 0.316 mol lit^{-1}; 1.316 mol lit^{-1}; 4.368 mol lit^{-1}

5. Find K_p for the following reaction

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

when the degree of dissociation is 63% at 78 ºC and total pressure is 1 atm.

Answer. 0.656 atm

6. Calculate the equilibrium constant K_p for the reaction

$$NH_4HS_{(s)} \rightleftharpoons NH_{3\,(g)} + H_2S_{(g)}$$

when the total pressure of the mixture is 10 atm.

Answer. 25 atm

7. A sample of $CaCO_{3(s)}$ is introduced into a sealed container of volume 0.500 litre and heated to 800 K until equilibrium is reached. The equilibrium constant for the reaction

$$CaCO_{3(g)} \rightleftharpoons CaO_{(g)} + CO_{2\,(g)}$$

is 3.9×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

Answer. 2.97×10^{-4} mol or 0.0166 g

8. Determine the value of K_p for the following reaction

$$CO_{(g)} + H_{2(g)} \rightleftharpoons CO_{2(g)} + H_{2\,(g)}$$

The value of K_c is 23.2 at 327 ºC.

Answer. 23.2

9. Determine the value of equilibrium constant for the reaction

$$P + 2\,Q \rightleftharpoons 2\,R$$

if 1.0 mol of P and 1.5 mol of Q are placed in 2.0 litre container and allowed to come to equilibrium. The equilibrium concentration of R is 0.35 mol lit^{-1}.

Answer. 2.36 mol lit^{-1}

10. At 25 ºC and 1 atm pressure the partial pressure in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25 ºC and a total pressure of 5 atm.

Answer. 4.47 atm and 0.53 atm

11. PCl_5 dissociates according to the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The density of the gas mixture at 473 K and 523 K is 70.2 and 57.9 respectively. Calculate the percentage dissociation of PCl_5 at these temperatures.

Answer. 48.5% and 80%

12. Calculate the value of K_c for the following reaction

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

when K_p is 0.113 atm at 25 ºC.

Answer. 4.624×10^{-3} mol lit^{-1}

13. Alcohol and acetic acid were mixed in equimolar proportions in aqueous medium at room temperature. At equilibrium 50% alcohol is converted into ester. Calculate how much ester will be formed if 2 moles of acetic acid and 1 mole of alcohol were mixed.

Answer. 0.67 mole]

14. Calculate the percentage dissociation of H_2S if 1.0 mole of H_2S is introduced into 1.1 litre vessel at 1000 ºC. The value of K_c for the reaction

$$2\,H_2S_{(g)} \rightleftharpoons 2\,H_{2\,(g)} + S_{2(g)}$$

is 1.0×10^{-6}.

Answer. 1.3

15. The equilibrium constant K_p for the equation

$$2\,HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$$

at 425 ºC is 1.84. What is the value of K_c for the following equation?

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

Answer. 0.543

16. The value of K_c for the following reaction at 1173K is 0.28.

$$CS_{2\,(g)} + 4\,H_{2\,(g)} \rightleftharpoons CH_{4\,(g)} + 2\,H_2S_{(g)}$$

Calculate the value of K_p at this temperature.

Answer. 3×10^{-5}

17. The reaction

$$SO_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightleftharpoons SO_{3\,(g)}$$

has K_c equal to 56.30 at 627 ºC. What is the value of K_p at this temperature?

Answer. 6.55

18. Phosgene, $COCl_2$, is prepared according to the equation

$$CO_{(g)} + Cl_{2\,(g)} \rightleftharpoons COCl_{2\,(g)}$$

An equilibrium mixture at 395 ºC contains 0.012 mole of CO and 0.025 mole of Cl_2 per litre as well as $COCl_2$. if the value of K_c at 395 ºC is 1.23×10^3.

Answer. 0.37 m

19. At 27 ºC and 1 atm pressure N_2O_4 is 20% dissociated in the NO_2. Calculate the value of K_p under these conditions.

Answer. 0.17 atm

20. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.0025 mole of nitrogen is converted to ammonia by the following reaction :

$$N_{2\,(g)} + 2\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$

Calculate the equilibrium constant K_c for the reaction :

$$\tfrac{1}{2}\,N_{2\,(g)} + H_{2\,(g)} \rightleftharpoons NH_{3\,(g)}$$

Answer. 3.82×10^{-3} lit mol^{-1}

18

Distribution Law

CHAPTER

KEY CONCEPTS AND EQUATIONS

NERNST'S DISTRIBUTION LAW

If a solute X distributes itself between two non-miscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents, then

$$\frac{\text{Concentration of } X \text{ in solvent } A}{\text{Concentration of } X \text{ in solvent } B} = K_D \text{ or } K$$

where K_D or K is the Distribution coefficient or Partition coefficient.

MODIFICATION OF NERNST DISTRIBUTION LAW

Case I. When solute undergoes Association

Let the solute X present in solvent A as simple molecules and in solvent B association of n molecules of X takes place to form X_n. Then, we have

$$\frac{C_1}{\sqrt[n]{C_2}} = K$$

when association occurs in solvent B.

Case II. When solute undergoes dissociation

Let the solute X be present in solvent A as simple molecules and in solute B it dissociates to Y and Z and the degree of dissociation is α. Then we have

$$\frac{C_1}{C_2(1-\alpha)} = K$$

when dissociation occurs in solvent B.

HENRY'S LAW

At a constant temperature the solubility of a gas in a liquid is proportional to the pressure of the gas above it. *i.e.*

$$C = k \times P$$

where C is solubility or concentration, k is a constant and P is the pressure of the gas, k is called Henry's constant.

EXTRACTION WITH A SOLVENT

The removal of an organic substance from an aqueous solution is done by shaking the aqueous solution with a non-miscible organic solvent. After some time the aqueous and organic solvent layers separate in the funnel when most of the organic substance passes into the organic layer. It has been found that multistep extraction is more efficient than single step extraction as the amount of solute recovered is 2/3 *A* in a single step extraction as compared to 3/4 *A* in multistep extraction.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Succinic acid was shaken with a mixture of water and ether. The concentration of acid in two layers are as follows per 100 of the solution :

Concentration in water layer (C_W)	25.4	33.2	42.6
Concentration in ether layer (C_E)	4.2	5.5	7.1

Find out the partition coefficient. If succinic acid has normal molecular mass 118 in water, find its molecular mass in ether.

SOLUTION :

Formula used

$$\text{Partition coefficient, } K = \frac{C_W}{C_E}$$

Quantities given

$$C_W = 25.4 \qquad 33.2 \qquad 42.6$$
$$C_E = 4.2 \qquad 5.5 \qquad 7.1$$

Substitution of values

$$K = \frac{25.4}{4.2} = 6.05 \qquad K = \frac{33.2}{5.5} = 6.05 \qquad K = \frac{42.6}{7.1} = 6.0$$

$$\text{Average value } = 6.02$$

Since the values of *K* are almost equal, molecular mass of succinic acid in ether will be the same as in water *i.e.* **118**.

SOLVED PROBLEM 2. 12 g of an organic substance A is present in 100 g of its aqueous solution. How much of it would be left behind after extracting the solution with two successive applications of 50 ml each of ether ? The distribution coefficient of A between water and ether is 2 in favour of ether.

SOLUTION :

Formula used

$$K = \frac{C_E}{C_W} = \frac{x_1/50}{(A-x_1)/100} \quad \text{for the first step}$$

Quantities given

$$K = 2 \qquad A = 12\text{ g}$$

Substitution of values

$$2 = \frac{x_1/50}{(12-x_1)/100}$$

$$2 = \frac{2\ x_1}{12-x_1}$$

or $$12 - x_1 = x_1$$

or $$x_1 = 6\text{ g}$$

Now Amount left, $A_1 = 12\text{ g} - 6\text{ g} = 6\text{ g}$

Again using the formula $K = \dfrac{x_2 / 50}{(A_1 - x_2)/100}$

Quantities given

$K = 2$ $A_1 = 6\text{ g}$

Substitution of values

$$2 = \frac{x_2/50}{(6 - x_2)/100} = \frac{2\,x_2}{6 - x_2}$$

or $6 - x_2 = x_2$

or $x_2 = 3\text{ g}$

The total amount of succinic acid extracted $= 6\text{ g} + 3\text{ g} = 9\text{ g}$

∴ the amount of succinic acid left $= 12\text{ g} - 9\text{ g} = \mathbf{3\ g}$

SOLVED PROBLEM 3. If the distribution coefficient of benzoic acid between water and benzene is 3.304 at 20°C, calculate the number of moles of benzoic acid which may be extracted from 100 ml of 0.2 molar aqueous solution by 10 ml of benzene.

SOLUTION :

Formula used

$$K = \frac{C_{benzene}}{C_{water}} = \frac{x/V}{(A - x)\ v}$$

Quantities given

$K = 3.304$ $V = 10\text{ ml}$ $v = 100\text{ ml}$

$A - x = 0.2\text{ mole}$

Substitution of values

$$3.304 = \frac{\dfrac{x}{10}}{\dfrac{0.2}{100}}$$

or $\dfrac{x}{10} \times \dfrac{100}{0.2} = 3.304$

or $\dfrac{10\,x}{0.2} = 3.304$

or $x = \dfrac{0.6608}{10} = \mathbf{0.0668\ mole}$

SOLVED PROBLEM 4. Benzoic acid was shaken between benzene and water. From the following concentrations of the acid in grams in 10 ml of the aqueous and benzene layers, show that acid exists in benzene as $(C_6H_5COOH)_2$

Acid in H_2O layer	0.150	0.195	0.289
Acid in Benzene layer	0.242	0.412	0.970

SOLUTION :

Formula used

$$K = \frac{C_1}{\sqrt[n]{C_2}}$$

Quantities given

$n = 2$ (dimerisation)

$C_1 = 0.150 \qquad 0.195 \qquad 0.289$

$C_2 = 0.242 \qquad 0.412 \qquad 0.970$

Substitution of values

$$K = \frac{0.150}{\sqrt[2]{0.242}} = 0.3061$$

$$K = \frac{0.195}{\sqrt[2]{0.412}} = 0.3047$$

$$K = \frac{0.289}{\sqrt[2]{0.970}} = 0.2934$$

Since the value of K is almost constant, benzoic acid exists as dimer in benzene.

SOLVED PROBLEM 5. The solubility of a substance is twice as great in ether as in water. Compare the quantities extracted from 100 cc of aqueous solution by

(i) 100 cc ether in single operation

(ii) 50 cc ether in two successive operations.

SOLUTION :

(i) Single step extraction

Formula used

$$K = \frac{x / V}{(A - x)\, v}$$

Quantities gives

$K = \frac{C_{ether}}{C_{water}} = 2 \qquad V = 100 \text{ ml} \qquad v = 100 \text{ ml}$

Substitution of values

$$2 = \frac{x / 100}{(A - x)/100}$$

or $$2\,(A - x) = x$$

or $$x = A\frac{2}{3}$$

(ii) Two step extraction

Formula used

$$K = \frac{x_1 / V}{(A - x_1)/v} \quad \text{for first operation}$$

Quantities given

$K = 2 \qquad V = 50 \text{ ml} \qquad v = 100 \text{ ml}$

Substitution of values

$$2 = \frac{x_1 / 50}{(A - x_1)/100}$$

or $$2\,(A - x_1) = 2x_1$$

or $$x_1 = A/2$$

Formula used

$$K = \frac{x_2 / V}{\left(\frac{A}{2} - x_2\right)/v} \quad \text{for the second operation}$$

Quantities given

$K = 2$ $V = 50$ ml $v = 100$ ml

Substitution of values

$$2 = \frac{x_2/50}{(A/2 - x_2)/100}$$

or $$2 = \frac{x_2}{50} \times \frac{100}{A/2 - x_2}$$

or $$A/2 - x_2 = x_2$$

or $$x_2 = A/4$$

Thus the total amount extracted $= A/2 + A/4 = \mathbf{\dfrac{3A}{4}}$

SOLVED PROBLEM 6. Nernst reported the following results for the distribution of acetic acid between water and CCl_4.

Concentration of acetic in CCl_4 (moles/litre)	0.292	0.725	1.41
Concentration of acetic in H_2O (moles/litre)	4.87	7.98	10.70

Assume that acetic acid has its normal molecular mass in water, calculate its molecular mass in CCl_4.

SOLUTION :

Formula used

$$K = \frac{C_{CCl_4}}{C_{H_2O}}$$

Quantities given

$C_{CCl_4} = 0.292$	0.725	1.41
$C_{H_2O} = 4.87$	7.98	10.70

Substitution of values

$$K = \frac{0.292}{4.87} = 0.05995 \qquad K = \frac{0.725}{7.98} = 0.0909 \qquad K = \frac{1.41}{10.70} = 0.1318$$

Since the values of K are not constant, acetic acid does not exist as monomer in CCl_4. Now let us apply the formula

$$K = \frac{C_{water}}{\sqrt{C_{CCl_4}}}$$

Substitution of values

$$K = \frac{4.87}{\sqrt{0.292}} = 9.0185 \qquad K = \frac{7.98}{\sqrt{0.725}} = 9.377 \qquad K = \frac{10.70}{\sqrt{1.41}} = 9.014$$

Since the value of K is constant, acetic acid exists as dimer in CCl_4 and its

molecular mass = 2 × CH_3COOH = 120

SOLVED PROBLEM 7. At 25 °C the iodine solution in water which contains 0.0516 g lit^{-1} is in equilibrium with CCl_4 solution containing 4.1280 g lit^{-1} of iodine. If at 25 °C iodine solutions contains 0.410 g lit^{-1} of iodine find out the solubility of iodine in CCl_4 solution.

SOLUTION :

(i) To calculate the distribution constant

Formula used

$$K = \frac{C_{water}}{C_{CCl_4}}$$

Quantities given

C_{water} = 0.0516 g lit^{-1} C_{CCl_4} = 4.1280 g lit^{-1}

Substitution of values

$$K = \frac{0.0516 \text{ g lit}^{-1}}{4.1280 \text{ g lit}^{-1}} = 0.0125$$

(ii) To calculate the solubility of I_2 in CCl_4

Formula used

$$\frac{Conc.\ of\ I_2\ in\ water}{Cone\ of\ I_2\ in\ CCl_4} = K$$

Quantities given

K = 0.0125 $Conc.\ of\ I_2\ in\ water$ = 0.410 g lit^{-1}

Substitution of values

$$0.0125 = \frac{0.410 \text{ g lit}^{-1}}{\text{Conc. of } I_2 \text{ in } CCl_4}$$

or $$\text{conc. of } I_2 \text{ in } CCl_4 = \frac{0.410}{0.0125} \text{ g lit}^{-1} = \mathbf{32.8\ g\ lit^{-1}}$$

SOLVED PROBLEM 8. If Henry's law constant for oxygen at 25 °C is 3.30 × 10^{-7} mm Hg, find the solubility of oxygen in 1000 g of water at 25 °C and a partial pressure of 190 mm Hg.

SOLUTION :

Formula used

$$C = k \times P$$

Quantities given

$k = 3.30 \times 10^{-7}$ mm $P = 190 \text{ mm} = \frac{190}{760} \text{ atm} = 0.25 \text{ atm}$

Substitution of values

$$C = 3.30 \times 10^{-7} \times 0.25 \text{ atm g lit}^{-1}$$
$$= \mathbf{0.825 \times 10^{-7}\ g\ lit^{-1}}$$

SOLVED PROBLEM 9. Succinic acid was shaken with a mixture of water and ether. After distribution, upon analysis the concentrations of the acid in two layers are found as follows :

In aqueous layer (moles/lit)	0.0252	0.071	0.121
In ethereal layer (moles/lit)	0.0046	0.013	0.022

If succinic acid has similar molecular mass in ether and water, determine its partition coefficient.

SOLUTION :

Formula used

$$K = \frac{C_{Water}}{C_{ether}}$$

Quantities given

C_{water}	= 0.0252	0.071	0.121
C_{ether}	= 0.0046	0.013	0.022

Substitution of values

$$K = \frac{0.0252}{0.0046} = 5.478 \qquad K = \frac{0.071}{0.013} = 5.4615 \qquad K = \frac{0.121}{0.022} = 5.50$$

Thus average value of K = **5.4798**

SOLVED PROBLEM 10. The following data have been obtained on the distribution of phenol between water and Chloroform

C_1	0.094	0.164	0.254	0.436
C_2	0.254	0.761	1.850	5.430

where C_1 is concentration in the aqueous layer and C_2 is the concentration in the Chloroform layer. What conclusions do you draw from these results regarding molecular condition of phenol in the chloroform solution ?

SOLUTION :

Formula used

$$K = \frac{C_{Water}}{\sqrt{C_{CHCl_3}}} \quad \text{(for association)}$$

Quantities given

C_{water}	0.094	0.164	0.254	0.436
C_{CHCl_3}	0.254	0.761	1.850	5.430

Substitution of values

$$K = \frac{0.094}{\sqrt{0.254}} = 0.1865 \qquad K = \frac{0.164}{\sqrt{0.761}} = 0.1880$$

$$K = \frac{0.254}{\sqrt{1.850}} = 0.1868 \qquad K = \frac{0.436}{\sqrt{5.430}} = 0.1871$$

Since the values of K are constant, phenol exists as ***dimer*** in Chloroform.

SOLVED PROBLEM 11. The distribution coefficient of iodine between water and carbon disulphide is 0.0017. One litre of aqueous solution containing one gram of iodine is shaken with 100 ml of carbon disulphide till the equilibrium is reached. Find the amount of iodine extracted by carbon disulphide.

SOLUTION :

Formula used

$$K = \frac{C_{water}}{C_{CS_2}}$$

Quantities given

$K = 0.0017 \qquad C_{water} = 1 \text{ g lit}^{-1} = \frac{1}{1000} \text{ g ml}^{-1}$

$C_{CS_2} = \frac{x}{100} \text{ g ml}^{-1}$ where x is the amt. of I_2 extracted by 100 ml of CS_2

Substitution of values

$$0.001 = \frac{\frac{1 - x}{1000}}{\frac{x}{100}}$$

or

$$0.0017 = \frac{1 - x}{1000} \times \frac{100}{x}$$

or $$\frac{1-x}{10\,x} = 0.0017$$

or $$1-x = 10x \times (0.0017)$$

$$1-x = 0.017\,x$$

or $$x = \frac{1}{1.017} = \mathbf{0.983\ g}$$

SOLVED PROBLEM 12. At 298 K, an aqueous solution of iodine containing 0.0387×10^{-3} kg dm^{-3} of solution is in equilibrium with 3.31×10^{-3} kg dm^{-3} of iodine in carbon tetrachloride. If solubility of iodine in CCl_4 is 0.0291 kg dm^{-3}, what is the solubility of iodine in water ?

SOLUTION :

Formula used

$$K = \frac{C_{water}}{C_{CCl_4}}$$

Quantities given

$C_{water} = 0.0387 \times 10^{-3}$ kg dm^{-3} $\qquad$ $C_{CCl4} = 3.31 \times 10^{-3}$ kg dm^{-3}

Substitution of values

$$K = \frac{0.0387 \times 10^{-3}\ \text{kg dm}^{-3}}{3.31 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.01169$$

Now using the formula

$$K = \frac{\textit{Solubility of } I_2 \textit{ in water}}{\textit{Solubility of } I_2 \textit{ in } CCl_4}$$

Quantities given

$K = 0.01169$ $\qquad$ *Solubility of* I_2 *in* CCl_4 = 0.0291 kg dm^{-3}

Substitution of values

$$0.01169 = \frac{\text{Solubility of } I_2 \text{ in water}}{0.0291\ \text{kg dm}^{-3}}$$

or $$\textit{Solubility of } I_2 \textit{ in water} = 0.01169 \times 0.0291\ \text{kg dm}^{-3}$$

$$= \mathbf{0.00034\ kg\ dm^{-3}}$$

SOLVED PROBLEM 13. An organic acid was dissolved in two immiscible solvents (A) and (B). At equilibrium the concentration of the acid in (A) and (B) was found to be 0.40 and 0.64 mole lit^{-1} respectively. Calculate the distribution coefficient of the organic acid, if it forms dimer in the solvent B.

SOLUTION :

Formula used

$$K = \frac{C_A}{\sqrt{C_B}}$$

Quantities given

$C_A = 0.40$ $\qquad$ $C_B = 0.64$

Substitution of values

$$K = \frac{0.40}{\sqrt{0.64}} = \frac{0.40}{0.8} = \mathbf{0.5}$$

SOLVED PROBLEM 14. An organic acid is distributed between 500 ml each of a solvent A and water. In water it is dissociated. The amount of acid in aqueous layer was 6 grams and in solvent A, it was 0.72 gram. If the distribution coefficient of the acid between the solvent A and water is 0.16, Calculate the degree of dissociation, assuming that the acid has normal molecular mass in A.

SOLUTION :

Formula used

$$K = \frac{C_A}{C_{water} \times (1-x)} \quad \text{where } x \text{ is the degree of dissociation}$$

Quantities given

$K = 0.16$ $\quad C_{water} = 6\text{ g}$ $\quad C_A = 0.72\text{ g}$

Substitution of values

$$0.16 = \frac{0.72\text{ g}}{6\text{ g} \times (1-x)}$$

$$\text{or} \quad 0.96\,(1-x) = 0.72$$

$$\text{or} \quad 0.96 - 0.96\,x = 0.72$$

$$1 - x = \frac{0.72}{0.96} = 0.75$$

$$\text{or} \quad x = \mathbf{0.25} \quad \text{or} \quad \mathbf{25\ \%}$$

SOLVED PROBLEM 15. Acetic acid was shaken with water and CCl_4 and the following concentrations in g mol lit^{-1} were found in two layers :

Water layer	5.02	7.98	10.70
CCl_4 layer	0.292	0.725	1.41

Assuming that acetic acid has single molecule in water, show that it exists as double molecule in CCl_4.

SOLUTION :

Formula used

$$K = \frac{C_{water}}{\sqrt{C_{CCl_4}}}$$

Quantities given

C_{water} =	5.02	7.98	10.70
C_{CCl_4} =	0.292	0.725	1.41

Substitution of values

$$K = \frac{5.02}{\sqrt{0.292}} = 9.2296 \qquad K = \frac{7.98}{\sqrt{0.725}} = 9.3772 \qquad K = \frac{10.70}{\sqrt{1.41}} = 9.0143$$

Since the value of K is constant, acetic acid exists as **dimer** in CCl_4.

SOLVED PROBLEM 16. A solid X is added to a mixture of benzene and water. After shaking well and allowing it to stand, 10 ml of benzene layer was found to contain 0.13 g of X, and 100 ml of water layer contained 0.22 g of X. Calculate the value of distribution coefficient.

SOLUTION :

Formula used

$$K = \frac{C_{benzene}}{C_{water}}$$

Quantities given

$$C_{benzene} = \frac{0.13}{10}\ \text{g ml}^{-1} \qquad C_{water} = \frac{0.22}{100}\ \text{g ml}^{-1}$$

Substitution of values

$$K = \frac{\dfrac{0.13}{10}\ \text{g ml}^{-1}}{\dfrac{0.22}{100}\ \text{g ml}^{-1}} = \mathbf{5.9091}$$

SOLVED PROBLEM 17. Calculate how much succinic acid would be extracted from 100 ml of water containing 5 g of acid if extracted with 50 ml of ether. Partition coefficient of succinic acid between water and ether is 5.5.

SOLUTION :

Formula used

$$K = \frac{C_{water}}{C_{ether}}$$

Quantities given

$K = 5.5$ $C_{water} = \dfrac{5\text{ g}}{100\text{ ml}}$ $C_{ether} = \dfrac{5 - x\text{ g}}{50\text{ ml}}$

Substitution of values

$$5.5 = \frac{\dfrac{5\text{ g}}{100\text{ ml}}}{\dfrac{5 - x\text{ g}}{50\text{ ml}}}$$

$$5.5 = \frac{5}{100} \times \frac{50}{5 - x}$$

$$11 \times (5 - x) = 5$$

$$55 - 11x = 5$$

$$x = \frac{55 - 5}{11} = \mathbf{4.545\ g}$$

SOLVED PROBLEM 18. The partition coefficient of a substance between benzene and water is 10.1. How much substance will be extracted from its 250 ml aqueous solution containing 2.5 g of it by using 200 ml benzene in

(i) two equal portions
(ii) a single lot

SOLUTION :

(i) In a single lot

Formula used

$$K = \frac{C_{benzene}}{C_{water}}$$

Quantities given

$K = 10.1$ $C_{Benzene} = \dfrac{x\text{ g}}{200\text{ ml}}$ $C_{water} = \dfrac{2.5 - x\text{ g}}{250\text{ ml}}$

Substitution of values

$$10.1 = \frac{\dfrac{x}{200}\ \text{g ml}^{-1}}{\dfrac{2.5 - x}{250}\ \text{g ml}^{-1}} = \frac{x}{200} \times \frac{250}{(2.5 - x)}$$

$$40.4 = \frac{5\,x}{2.5 - x}$$

or $$5\,x = 101 - 40.4\,x$$

or $$x = 2.22\text{ g}$$

(ii) In two operations of 100 ml each

Let the amount extracted be x in 1st operation

Formula used

$$K = \frac{\dfrac{x_1}{100}}{\dfrac{2.5 - x_1}{250}}$$

Quantities given

$K = 10.1$

Substitution of values

$$10.1 = \frac{\dfrac{x_1}{100}}{\dfrac{2.5 - x_1}{250}} = \frac{x_1}{100} \times \frac{250}{2.5 - x_1}$$

$$20.2 = \frac{5\,x_1}{2.5 - x_1}$$

or $$5x_1 = 50.5 - 20.2\,x_1$$

or $$x_1 = \frac{50.5}{25.2} = 2.0\text{ g}$$

Now Let the amount extracted be x_2 in 2nd operation

Formula used

$$K = \frac{\dfrac{x_2}{100}}{\dfrac{0.5 - x_2}{250}}$$

Quantities given

$K = 10.1$

Substitution of values

$$10.1 = \frac{\dfrac{x_2}{100}}{\dfrac{0.5 - x_2}{250}} = \frac{x_2}{100} \times \frac{250}{(0.5 - x_2)}$$

$$10.1 \times (1 - 2x_2) = 5\,x_2$$

$$10.1 - 20.2\,x_2 = 5\,x_2$$

or $$x_2 = \frac{10.1}{25.2} = 0.4\text{ g}$$

Total amount extracted $= x_1 + x_2 = 2\text{ g} + 0.4\text{ g} = \mathbf{2.4\ g}$

SOLVED PROBLEM 19. Experiments in the study of rate of distribution of phenol between H_2O and chloroform gave the following results :

Concentration in aqueous solution	C_1	0.094	0.103	0.254
Concentration in Chloroform	C_2	0.254	0.761	1.850

Find whether phenol exists as monomer or dimer.

SOLUTION :

In case phenol exists as monomer the value of K obtained from the following formula should be constant

Formula used

$$K = \frac{C_{water}}{C_{CHCl_3}}$$

Quantities given

C_{water} =	0.094	0.103	0.254
C_{CHCl_3} =	0.254	0.761	1.850

Substitution of values

$$K = \frac{0.094}{0.254} = 0.3700 \qquad K = \frac{0.103}{0.761} = 0.135 \qquad K = \frac{0.254}{1.850} = 0.1373$$

Since the value of K is not constant, phenol does not exists as monomer.

Now

Formula used

$$K = \frac{C_{water}}{\sqrt{C_{CHCl_3}}}$$

Substitution of values

$$K = \frac{0.094}{\sqrt{0.254}} = 0.1865 \qquad K = \frac{0.103}{\sqrt{0.761}} = 0.1868 \qquad K = \frac{0.254}{\sqrt{1.850}} = 0.1867$$

Since the value of K is constant, phenol exists as **dimer** in chloroform.

SOLVED PROBLEM 20. An organic compound is twice more soluble in ether than in water. Calculate the amount of the compound extracted when 100 ml of aqueous solution containing 1 g of compound is shaken with (i) 100 ml of ether at one time (ii) two successive quantities of 50 ml each.

SOLUTION :

(i) In a single operation

Formula used

$$K = \frac{C_{ether}}{C_{water}}$$

Let x be the amt. of compound extracted by 100 ml of ether.

Quantities given

$C_{ether} = \frac{x}{100}$ g ml^{-1} $\qquad$ $C_{water} = \frac{1 - x}{100}$ g ml^{-1} $\qquad$ $K = 2$

Substitution of values

$$2 = \frac{\frac{x}{100}\text{ g ml}^{-1}}{\frac{1-x}{100}\text{ g ml}^{-1}} = \frac{x}{1-x}$$

or $\qquad 2(1 - x) = x$

or $\qquad 3x = 2$

$$x = \mathbf{0.67\ g}$$

(ii) In double operation

Let x_1 be the amount of the compound extracted by 50 ml of ether

Formula used

$$K = \frac{C_{ether}}{C_{water}}$$

Substitution of values

$$2 = \frac{\dfrac{x}{50}\ \text{g ml}^{-1}}{\dfrac{1-x}{100}\ \text{g ml}^{-1}} = \frac{x_1}{50} \times \frac{100}{1-x_1}$$

or $$1 - x_1 = x_1$$

or $$2x_1 = 1$$

$$x_1 = 0.5$$

$$\text{Amt. of the compound left} = 1.0\text{ g} - 0.5\text{ g} = 0.5\text{ g}$$

Now in second operation let the amount extracted be x_2

Formula used

$$K = \frac{C_{ether}}{C_{water}}$$

Quantities given

$K = 2$ $\quad C_{ether} = \dfrac{x_2}{50}$ g ml^{-1} $\quad C_{water} = \dfrac{0.5}{100}$ g ml^{-1}

Substitution of values

$$2 = \frac{\dfrac{x_2}{50}\ \text{g ml}^{-1}}{\dfrac{0.5}{100}\ \text{g ml}^{-1}} = \frac{x_2}{50} \times \frac{100}{0.5}$$

$$2 = \frac{2x_2}{0.5}$$

or $$x_2 = \frac{1}{2} = 0.5$$

Total amount extracted 0.5 + 0.5 = **1 g**

SOLVED PROBLEM 21. At 298 K an aqueous solution of iodine containing 0.0516 g lit^{-1} is in equilibrium with a carbon tetrachloride (CCl_4) solution containing 4.412 g lit^{-1}. The solubility of iodine in water at 298 K is 0.34 g lit^{-1}. Find the solution of iodine in carbon tetrachloride.

SOLUTION :

(i) To calculate the value of Distribution coefficient K

Formula used

$$K = \frac{C_{CCl_4}}{C_{water}}$$

Quantities given

$C_{CCl_4} = 4.412$ g lit^{-1} $\quad C_{water} = 0.0516$ g lit^{-1}

Substitution of values

$$K = \frac{4.412 \text{ g lit}^{-1}}{0.0516 \text{ g lit}^{-1}} = 85.5$$

(ii) To calculate the solubility of iodine in CCl_4.

Formula used

$$K = \frac{\text{Solubility of Iodine in } CCl_4}{\text{Solubility of Iodine in water}}$$

Quantities given

Solubility of Iodine in water = 0.34 g lit^{-1} $K = 85.5$

Substitution of values

$$85.5 = \frac{\text{Solubility of Iodine in } CCl_4}{0.34 \text{ g lit}^{-1}}$$

or $$\text{Solubility of Iodine in } CCl_4 = 85.5 \times 0.34 \text{ g lit}^{-1}$$
$$= \mathbf{29.07 \text{ g lit}^{-1}}$$

SOLVED PROBLEM 22. The distribution constant of a certain solid X between two immiscible solvents A and B is 10 at 25 °C. If the solubility of the solid in solvent A is 4.8 mol lit^{-1}, what is the solubility in solvent B?

SOLUTION :

Formula used

$$K = \frac{\text{Solubility in solvent } A}{\text{Solubility in solvent } B}$$

Quantities given

$K = 10$ *Solubility in solvent A* = 4.8 mol lit^{-1}

Substitution of values

$$10 = \frac{4.8 \text{ mol lit}^{-1}}{\text{Solubility in solvent B}}$$

or $$\text{Solubility in solvent } B = \frac{4.8 \text{ mol lit}^{-1}}{10}$$
$$= \mathbf{0.48 \text{ mol lit}^{-1}}$$

SOLVED PROBLEM 23. An organic acid is distributed between 200 cm^3 each of a solvent *A* and water. In water it is dissociated. The amount of acid in aqueous layer was 2.4 g and in the solvent *A* layer it was 0.288 g. If the partition coefficient between the solvent *A* and water is 0.16, calculate the degree of dissociation assuming that the acid has normal molecular mass in solvent *A*.

SOLUTION :

Formula used

$$K = \frac{C_1}{C_2(1-\alpha)}$$

Quantities given

$K = 0.16$

$C_1 = 0.288 \text{ g}/200 \text{ cm}^3 = 1.44 \times 10^{-3} \text{ g cm}^{-3}$

$C_2 = 2 \text{ g} / 200 \text{ cm}^3 = 1.2 \times 10^{-2} \text{ g cm}^{-3}$

Substitution of values

$$0.16 = \frac{1.44 \times 10^{-3} \text{ g cm}^{-3}}{1.2 \times 10^{-2} \text{ g cm}^{-3} (1-\alpha)}$$

or $$(1-\alpha) = \frac{1.44}{1.2 \times 0.16} = 0.75$$

or $$\alpha = \mathbf{0.25} \text{ or } \mathbf{25\ \%}$$

SOLVED PROBLEM 24. In the distribution of benzoic acid between water and benzene the following values have been obtained in equal volumes of solvents :

$C_{water\ (g)}$	1.50	1.95	2.97
$C_{Benzene\ (g)}$	24.2	41.2	97.0

What is the molecular condition of benzoic acid in benzene ?

SOLUTION :

Formula used

$$K = \frac{C_{water}}{C_{benzene}}$$

Quantities given

C_{water}	= 1.5	1.95	2.97
$C_{benzene}$	= 24.2	41.2	97.0

Substitution of values

$$K = \frac{1.5}{24.2} = 0.061983 \qquad K = \frac{1.95}{41.2} = 0.04733 \qquad K = \frac{2.97}{97.0} = 0.030619$$

Since the value of K is not constant, benzoic acid does not exist as monomer in benzene. Now

Formula used

$$K = \frac{C_{water}}{\sqrt{C_{benzene}}}$$

Substitution of values

$$K = \frac{1.5}{\sqrt{24.2}} = \frac{1.5}{4.919} = 0.3049$$

$$K = \frac{1.95}{\sqrt{41.2}} = \frac{1.95}{6.4187} = 0.3038$$

$$K = \frac{2.97}{\sqrt{97.0}} = \frac{2.97}{9.8488} = 0.30156$$

Now the value of distribution coefficient is constant. Hence benzoic acid exists as dimer in benzoic acid.

SOLVED PROBLEM 25. Succinic acid shows molecular mass in water and is associated in benzene. The following data was obtained on the distribution of succinic acid between water and benzene.

C_{water}	0.150	0.195	0.289
$C_{benzene}$	2.42	4.120	9.700

Calculate the molecular mass of succinic acid in benzene

SOLUTION :

Formula used

$$K = \frac{C_{water}}{\sqrt{C_{benzene}}}$$

Quantities given

C_{water}	= 0.150	0.195	0.289
$C_{benzene}$	= 2.42	4.120	9.70

Substitution of values

$$K = \frac{0.150}{\sqrt{2.42}} = \frac{0.150}{1.5556} = 0.0964$$

$$K = \frac{0.195}{\sqrt{4.120}} = \frac{0.195}{2.0297} = 0.0960$$

$$K = \frac{0.289}{\sqrt{9.70}} = \frac{0.289}{3.11448} = 0.09279$$

Since the value of K is almost constant, succinic acid exists as dimer in benzene.

$\therefore$ mol. mass of succinic acid in benzene $= 2 \times (C_4H_6O_4)$

$= 2 \times 118$

$= \mathbf{236}$

ADDITIONAL PRACTICE PROBLEMS

1. Iodine was shaken in a mixture of CS_2 and water. The concentrations of I_2 in two layers are as follows :

Concentration of I_2 in CS_2 (g dm^{-3})	41	66	129	174
Concentrations of I_2 in water (g dm^{-3})	0.1	0.161	0.314	0.423

Calculate the distribution constant of I_2 between CS_2 and water.

Answer. 410

2. In an experiment on distribution of I_2 with CCl_4 and H_2O following results were obtained

Concentration of I_2 in CCl_4 layer (g/100 cm^{-3})	5.1	10.2	15.2	20.3
Concentration of I_2 in water H_2O (g/100cm^{-3})	0.06	0.119	0.178	0.236

Calculate the distribution constant of I_2 between CCl_4 and water.

Answer. 85.5

3. A solid Y was added to mixture of benzene and water. After shaking well and allowing it to stand, 20 cm^3 of the benzene was found to contain 0.26 g of Y and 200 cm^3 of water layer contained 0.44 g of Y. Calculate the value of distribution constant.

Answer. 5.9

4. At 298 K an aqueous solution of iodine containing 0.0516 g dm^{-3} is in equilibrium with $CHCl_3$ solution containing 4.412 g dm^{-3}. The solubility of iodine in water at 298 K is 0.34 g dm^{-3}. Find out the solubility of iodine in $CHCl_3$.

Answer. 29.07 g dm^{-3}

5. The solubility of iodine in water is 0.35 g lit^{-1}. Calculate its solubility in carbon tetrachloride, if the distribution constant of iodine in CCl_4 and water is 88.

Answer. 30.8 g lit^{-1}

6. In an experiment on distribution of succinic acid between water and ether at 20ºC, 10 ml of ethereal layer contains 0.046 g of acid. Calculate the amount of succinic acid present in 25 ml of the aqueous solution in equilibrium with it if the distribution coefficient of succinic acid between water and ether is 5.2.

Answer. 0.598 g

7. Succinic acid shows normal molecular mass in water and abnormal in benzene. When succinic acid was distributed between water and benzene following results were obtained.

Concentration of succinic acid in Benzene (g lit^{-1})	1.50	1.95	2.89
Concentration of succinic acid in water (g lit^{-1})	24.70	41.20	96.50

Calculate the molecular mass of succinic acid in benzene.

Answer. 236

8. 100 g of an acid was dissolved in 1 litre of water. The distribution coefficient of acid between ether and water is 3. One litre of ether in one lot was used to extract acid. Calculate the amount of acid extracted.

Answer. 37.5

9. In an experiment of distribution of benzoic acid between water and benzene, following results were obtained:

Concentration in water (mol lit^{-1})	0.00579	0.00749	0.0114
Concentration in C_6H_6 (mol lit^{-1})	0.0485	0.0835	0.1950

Calculate the molecular mass of benzoic acid in benzene assuming that acid behaves normally in water.

Answer. 244

10. The distribution coefficient of an organic acid between benzene and water is 80. An aqueous solution of the acid containing 2.25 g in 100 cm^3 was extracted with (i) 10 cm^3 of benzene in one lot and (ii) twice with 5cm^3 benzene each time. Calculate the amount of acid extracted in each experiment.

Answer. (i) 2 g (ii) 2.16 g

19

The Phase Rule

CHAPTER

KEY CONCEPTS AND EQUATIONS

THE PHASE RULE

It is an important generalisation dealing with the behaviour of heterogeneous systems. With its application it is possible to predict the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium. The phase rule is

$$F = C - P + 2$$

or

$$F + P = C + 2$$

where F is the number of degrees of freedom, C is the number of components and P is the number of phases of the system. These terms are expressed in the following section.

PHASE, COMPONENT AND DEGREES OF FREEDOM

A **phase** may be defined as any homogeneous part of a system having all physical and chemical properties the same throughout.

A **component** may be defined as the least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation.

The **degree of freedom** is defined as the least number of variable factors (concentration, pressure and temperature) which must be specified so that the remaining variables are fixed automatically and the system is completely defined.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. How many phases are present in each of the following system :

(i) a drop of water placed in a stoppered bottle.

(ii) a piece of molten ice placed in a beaker covered with a watch glass

(iii) mixture of N_2, H_2 and O_2.

SOLUTION : (i) No. of phases in a drop of water in a stoppered bottle

There will be two phases *viz.* liquid water and its vapours.

(ii) No. of phases in a piece of molten ice placed in a beaker covered with watch glass

There will be two phases in a piece of molten ice placed in a beaker covered with watch glass *viz.* liquid water and its vapours.

(iii) Mixture of N_2, H_2 and O_2.

There will be only one phase in a mixture of N_2, H_2 and O_2.

SOLVED PROBLEM 2. How many components are present in the following systems ?

(a) Water $\rightleftharpoons$ water-vapour

(b) $KCl + H_2O \rightleftharpoons$ KCl hydrate

SOLUTION : (a) Water $\rightleftharpoons$ water-vapour

The system contains only one component as only one specie is chemically independent.

(b) KCl + water $\rightleftharpoons$ KCl hydrate

In this system there are only two components which are chemically indepedent.

SOLVED PROBLEM 3. Calculate the number of components in the following systems :

(i) a solution of common salt

(ii) $MgCO_{3\,(s)} \rightleftharpoons MgO_{(s)} + CO_{2\,(g)}$ (in a closed vessel)

(iii) $NH_4Cl_{(s)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}$

SOLUTION : (i) A solution of common salt

A solution of NaCl in water is a 1-phase system. Its composition can be expressed in terms of two chemical individuals – NaCl and water.

(ii) $MgCO_{3\,(s)} \rightleftharpoons MgO_{(s)} + CO_{2\,(g)}$ (in a closed vessel)

In this equilibrium the composition of all the phases can be expressed in terms of any two of three chemical substances in equilibrium. Thus the no. of components in the system is 2.

(iii) $NH_4Cl_{(s)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}$

The composition of all the phases can be expressed in terms of the same chemical substances NH_4Cl. Thus the no. of components in the system is one.

SOLVED PROBLEM 4. Calculate the number of components in the equilibrium

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

SOLUTION : In the equilibrium

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

There are three species present. We can change the number of moles of any two of these chemical species as the no. of moles of third component is calculated by the equilibrium

$$K = \frac{[PCl_3]\ [Cl_2]}{[PCl_5]}$$

Thus there are only two components in this system.

SOLVED PROBLEM 5. Calculate the number of components in the equilibrium

$$n\,H_2O \rightleftharpoons (H_2O)_n$$

SOLUTION : This system contains a number of chemical species : H_2O, $(H_2O)_2$, $(H_2O)_{3.....}$. But there is only one component because all the equilibria established in the system depend only on one chemically independent specie H_2O. Thus there is only one component in this system.

SOLVED PROBLEM 6. Calculate the number of phases (P), components (C) and degrees of freedom (F) for the system in which ammonium chloride is in equilibrium with ammonia and hydrochloric acid certain amount of hydrochloric acid initially present in the system.

SOLUTION :

In the given system no. of phases = 2

no. of components = 2

It is a two component system because the concentration of ammonia is not always equal to the concentration of HCl in the vapour phase

Applying phase rule

$$F + P = C + 2$$

or $$F + 2 = 2 + 2$$

or $$F = \mathbf{2}$$

SOLVED PROBLEM 7. The atmospheric pressure at a Hill station on particular day is 650 torr. At what temperature does water boil in the hill station on that day ? ($\Delta H_{vap} = 40.67$ kJ mol^{-1}).

SOLUTION :

Formula used

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303 \times R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Quantities given

$T_1 = 273 + 100 = 373$ K

$P_1 = 760$ torr

$R = 8.314$ J

$P_2 = 650$ torr

$\Delta H_{vap} = 40.67$ kJ mol^{-1}

Substitution of values

$$\log \frac{650}{760} = \frac{40.67 \times 10^3}{2.303 \times 8.314}\left[\frac{1}{373} - \frac{1}{T_2}\right]$$

$$\log 0.8552 = 2124.077\left[\frac{1}{373} - \frac{1}{T_2}\right]$$

or $$T_2 = 368.60 \text{ K}$$

$$= 368.60 - 273$$

$$= \mathbf{95.6\ ^{o}C}$$

ADDITIONAL PRACTICE PROBLEMS

1. Starting with pure NH_4Cl the following equilibrium is established.

$$NH_4Cl_{(g)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}$$

State the number of components in the system.

Answer. 2

2. Calculate the number of phases in a mixture of four gases enclosed in a container.

Answer. 1

3. State how many phases are present in the following systems

(i) $I_{2\,(s)} \rightleftharpoons I_{2\,(g)}$

(ii) Ice $\rightleftharpoons$ Water Water Vapour

Answer. (i) 2, (ii) 3

4. How many degrees of freedom will be present in the following systems ?

(i) $I_{2\,(s)} \rightleftharpoons I_{2\,(CCl_4)}$

(ii) Two partially miscible liquids in the absence of vapour

Answer. (i) 2. (ii) 2

5. The vapour pressure of 2,2,4-trimethylpentane at 20.7 ºC and 29.1ºC are 40 and 60 torr respectively. Calculate the enthalpy of vaporization of this compound.

Answer. 35.6 kJ mol^{-1}

6. The atmospheric pressure in a deep valley on a particular day is 120 torr. Calculate the boiling point of water in that valley on that day (Heat of vaporization = 2.260 kJ g^{-1}).

Answer. 386.45 K

7. Determine the number of phases, components and degrees of freedom in the system : Ice, water and vapour in equilibrium.

Answer. 3,1 and 0

8. How many degrees of freedom will be present in a solution of sodium sulphate in equilibrium with water vapour ?

Answer. 2

9. Calculate the number of components present in the following systems

(i) A solution of common salt

(ii) $NH_{3\,(g)}$

Answer. (i) 2, (i) 1

10. Calculate the degrees of freedom and number of components for a system of sodium chloride solution in water containing undissolved salt, in equilibrium with water vapour.

Answer. 1 and 2

20

Chemical Kinetics

CHAPTER

KEY CONCEPTS AND EQUATIONS

RATE OF A REACTION

It is defined as the change in concentration of any of reactants or products per unit time. For the reaction

$$A \longrightarrow B$$

$$\text{Rate of reaction} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

The negative sign indicates that the concentration of reactant A is decreasing with time.

UNITS OF RATE

Recation rate has the units of concentration divided by time. Concentration is expressed in moles per litre and time in seconds, minutes, hours or years. Thus,

Units of reaction rate are mole $\text{lit}^{-1}\ \text{sec}^{-1}$ or mol $\text{lit}^{-1}\ \text{min}^{-1}$

RATE LAWS

The rate of a reaction is directly proportional to the reactant concentration, each concentration being raised to some power which may be some integer or fraction. Thus, for the reactions given below, rate of reactions are also shown.

$$A \longrightarrow \text{Products} \qquad \text{Rate} \propto [A]^n \quad \text{or} \quad \text{Rate} = k\,[A]^n$$

$$2A + B \longrightarrow \text{Products} \qquad \text{Rate} \propto [A]^m[B]^n \quad \text{or} \quad \text{Rate} = k\,[A]^m[B]^n$$

where k is a constant called rate constant for the reaction and m and n are small integers or fractions.

An expression which shows how the reaction rate is related to concentration is called **rate law** or **rate equation.**

ORDER OF A REACTION

The order of a reaction is the sum of powers of concentrations in the rate law. For example, for the reaction

$$A + B \longrightarrow \text{Products}$$

the rate is $k\,[A]^m[B]^n$ and order of the reaction is $m + n$. Reaction may be classified according to order. Thus, when

$m + n = 0$ the reaction is zero order reaction

$m + n = 1$ the reaction is first order reaction

$m + n = 2$ the reaction is second order reaction

MOLECULARITY OF A REACTION

The number of reactant molecules involved in a reaction is called the molecularity of the reaction. It is always a whole number and can not have zero value. It may be different from the order of reaction.

RATE EQUATIONS FOR DIFFERENT TYPES OF REACTIONS

The rate equations for different types of reactions having different order are summarised in the Table 20.1

TABLE 20.1 : RATE EQUATIONS FOR DIFFERENT TYPES OF REACTIONS.

Reaction	Reaction Equation	Order of Reaction	Rate constant expression
$A \longrightarrow$ Products	Rate $= k[A]^0$	0	$k = \frac{x}{t}$
$B \longrightarrow$ Products	Rate $= k[A]$	1	$k = \frac{2.303}{t} \log \frac{a}{a-x}$
$A + B \longrightarrow$ Products	Rate $= k[A][B]$	2	$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$
$2A \longrightarrow$ Products	Rate $= k[A]^2$	2	$k = \frac{1}{t} \times \frac{x}{a(a-x)}$
$3A \longrightarrow$ Products	Rate $= k[A]^3$	3	$k = \frac{1}{t} \times \frac{x(2a-x)}{2a^2(a-x)^2}$

RATE CONSTANTS AND ITS UNITS

The rate constant is defined as the rate of reaction when the concentration of all reactants is untity. The units of rate constant depend upon the order of the reaction. For various types of reactions the units of rate constant are as follows :

For a zero order reaction $k = \frac{x}{t} \quad \frac{\text{mol lit}^{-1}}{\text{time}^{-1}}$ or $\text{mol lit}^{-1}\ \text{time}^{-1}$

For a 1st order reaction $k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \frac{1}{\text{time}} \times \frac{\text{mol lit}^{-1}}{\text{mol lit}^{-1}} = \text{time}^{-1}$

For a 2nd order reaction $k = \frac{1 \times x}{t\, a(a-x)} \quad \frac{1}{\text{time}} \times \frac{\text{mol lit}^{-1}}{\text{mol lit}^{-1} \times \text{mol lit}^{-1}} = \text{mol}^{-1}\ \text{lit time}^{-1}$

For a 3rd order reaction $k = \frac{x\,(2a-x)}{t\ 2a^2\,(a-x)^2} \quad \frac{\text{mol lit}^{-1} \times \text{mol lit}^{-1}}{\text{time} \times (\text{mol lit}^{-1})^4} = \text{mol}^{-2}\ \text{lit}^2\ \text{time}^{-1}$

HALF LIFE OF A REACTION

It is defined as the time required for the concentration of a reactant to decrease to half its initial value. It is represented by $t_{½}$ or $t_{0.5}$ For a first order reaction $t_{½}$ is given by

For a first order reaction $t_{½}$ *is given by*

$$t_{½} = \frac{2.303}{k} \times \log \frac{a}{a - a/2}$$

$$= \frac{2.303}{k} \times \log \frac{a}{a/2}$$

$$= \frac{2.303}{k} \times \log 2 = \frac{0.693}{k}$$

For a second order reaction $t_{½}$ is given by

$$t_{½} = \frac{1}{k}\ \frac{x}{a(a-x)} \quad \text{where } x = a/2$$

$$= \frac{1}{k} \quad \frac{a/2}{a/2\,(a - a/2)}$$

$$= \frac{2}{k\ a} \propto \frac{1}{a}$$

DETERMINATION OF ORDER OF A REACTION

(i) Using Intergrated rate equations

This is hit and trial method involving the use of different rate equations. The rate equation which gives the constant value of *k* corresponds to the correct order of the reaction. In this method different initial concentrations of reactants *a*, are taken and the concentrations left *(a – x)* after regular time intervals are measured. These values are substituted in the following equations :

for a first order reaction $k = \frac{2.303}{t} \log \frac{a}{a-x}$

for a second order reaction $k = \frac{1 \times x}{t \times a\,(a-x)}$

and for a third order reaction $k = \frac{a\,(2a-x)}{t \times 2a^2 \times (a-x)}$

(ii) Graphical Method

For a reaction A ⟶ Products, if the graph between log $\frac{a}{a-x}$ and *t* is a straight line, the reaction is of the first order. In case the graph between the $\frac{1}{a-x}$ and *t* is a straight line the reaction is second order. (Fig. 20.1 and Fig. 20.2)

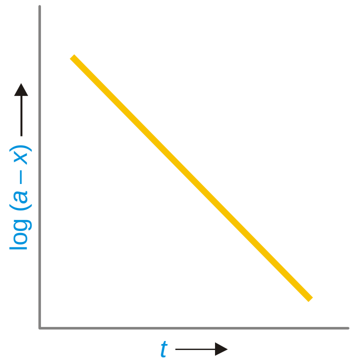


Figure 20.1

Plot of log $\frac{a}{a-x}$ vs *t* for a 1st order reaction.

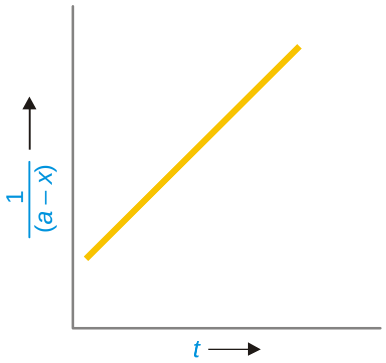


Figure 20.2

Plot of log $\frac{1}{a-x}$ vs *t* for a 2nd order reaction.

(iii) Using Half-life Period

Two separate experiments are performed by taking different initial concentrations of a reactant and the time in which the concentration is reduced to half is noted. If the half life is

(a) independent of initial concentration order of reaction = 1

(b) $\propto \frac{1}{[A]}$ order of reaction = 2

(c) $\propto \frac{1}{[A]^2}$ order of reaction = 3

(d) $\propto \frac{1}{[A]^{n-1}}$ order of reaction = $n - 1$

Also for *n*th order of reaction

$$n = 1 + \frac{\log [t_1/t_2]}{\log [A_2/A_1]}$$

where A_1 is the initial concentration and t_1, the half life period in experiment one and A_2 the initial concentration and t_2, the half life period in second experiment.

(iv) The differential Method

The rate of a reaction of *n*th order is proportional to *n*th power of concentration.

$$-\frac{dC}{dt} = kC^n$$

Two experiments with different initial concentrations are performed and the value of *n*, the order of reaction, is determined by using the formula

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_1}{dt}\right)}{\log C_1 - \log C_2}$$

EFFECT OF TEMPERATURE ON REACTION RATE

Temperature coefficient is given by

$$\text{Temperature Coefficient} = \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}} = 2 \text{ to } 3$$

Thus an increase of temperature by 10 °C increases the rate of reaction by 2 to 3 times.

ARRHENIUS EQUATION

The relation between the rate constant, *k*, for a reaction and the temperature is given by

$$k = A\,e^{-E_a/RT}$$

where E_a is the activation energy, *R* the gas constant and *T*, the absolute temperature.

Taking logarithms we have

$$\log k = -\frac{E_a}{RT} + \log A$$

If k_1 and k_2 are the values of rate constant at temperatures T_1 and T_2 we have

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. In the first order reaction

$$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$$

the initial pressure of A is 84 mm and the total pressure at the end of 6 minutes is 110 mm. Calculate the half life of the reaction.

SOLUTION :

The reaction is

	$A_{(g)} \longrightarrow$	$B_{(g)}$	$+\ C_{(g)}$
Initial pressure	84 mm	0	0
Pressure after 6 minutes	$(84 - x)$ mm	x mm	x mm

After 6 minutes the total pressure $= 84 - x + x + x \text{ mm} = 84 + x$

$$= 110 \text{ mm}$$

or $\quad 84 + x = 110$ mm

or $\quad x = 26$ mm

(i) To calculate the value of rate constant

Formula used

$$k = \frac{2.303}{t}\log\frac{a}{a - x}$$

Quantities given

$t = 6$ minutes $a = 84$ mm $a - x = 84 - 26$ mm $= 58$ mm

Substitution of values

$$k = \frac{2.303}{6\,\text{min}} \log \frac{84\,\text{mm}}{58\,\text{mm}}$$

$$= \frac{2.303}{6\,\text{min}} \log 1.4482$$

$$= 0.3838 \times 0.1608\,\text{min}^{-1}$$

$$= 0.0617\,\text{min}^{-1}$$

(ii) To calculate half life period

Formula used

$$t_{½} = \frac{0.693}{k}$$

Substitution of values

$$t_{1/2} = \frac{0.693}{0.0617\,\text{min}^{-1}} = \mathbf{11.23\ min}$$

SOLVED PROBLEM 2. The rate constant for a reaction at 20 ºC is half of the rate constant at 30 ºC. Calculate the energy of activation of the reaction. [R = 1.987 cal K^{-1} mol^{-1}]

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

Quantities given

$\frac{k_2}{k_1} = 2$ $R = 1.987$ cal K^{-1} mol^{-1}

$T_1 = 20 + 273 = 293$ K $T_2 = 273 + 30 = 303$ K

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987\,\text{cal K}^{-1}\text{mol}^{-1}}\left[\frac{303\,\text{K} - 293\,\text{K}}{303\,\text{K} \times 293\,\text{K}}\right]$$

or

$$E_a = \frac{2.303 \times 1.987 \times 0.3010 \times 303 \times 293}{10}$$

$$= 12228.36\ \text{cal}$$

$$= \mathbf{12.22836\ kcal}$$

SOLVED PROBLEM 3. In a first order reaction, half of the reactant is decomposed in 1000 sec. How long will it be until 1/3 of the reactant is left ?

SOLUTION :

(i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{½}}$$

Quantities given

$$t_{½} = 1000\ \text{sec}$$

Substitution of values

$$k = \frac{0.693}{1000\ \text{sec}} = 0.000693\ \text{sec}^{-1}$$

(ii) To calculate time when 1/3 of the reactant is left

Formula used

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

Quantities given

$a = 1$ $x = 2/3$ $a - x = 1/3$ $k = 0.000693\ \text{sec}^{-1}$

Substitution of values

$$t = \frac{2.303}{0.000693\ \text{sec}^{-1}} \log \frac{1}{1/3}$$
$$= 3323.23 \times \log\ 3\quad \text{sec}$$
$$= 3323.23 \times 0.4771\ \text{sec}$$
$$= \mathbf{1585.51\ sec}$$

SOLVED PROBLEM 4. A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?

SOLUTION :

(i) To calculate the value of rate constant

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$a = 100$ $x = 15$ $a - x = 85$ $t = 20$ minutes

Substitution of values

$$k = \frac{2.303}{20\ \text{min}} \log \frac{100}{85}$$
$$= 0.11515 \times \log 1.17647\ \text{min}^{-1}$$
$$= 0.11515 \times 0.07058\ \text{min}^{-1}$$
$$= 8.127 \times 10^{-3}\ \text{min}^{-1}$$

(ii) To calculate the time when reaction is 60% complete.

Formula used

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$k = 8.127 \times 10^{-3}\ \text{min}^{-1}$ $a = 100$ $a - x = 40$

Substitution of values

$$t = \frac{2.303}{8.127 \times 10^{-3}\ \text{min}^{-1}} \log \frac{100}{40}$$
$$= 283.376 \times \log 2.5\ \text{min}$$
$$= 283.376 \times 0.3979\ \text{min}$$
$$= \mathbf{112.76\ min}$$

SOLVED PROBLEM 5. 50% of H_2O_2 decomposes in 10 minutes in an experiment. Find out its velocity coefficient if the reaction is first order.

SOLUTION :

Formula used

$$k = \frac{0.693}{t_{½}}$$

Quantities given

$$t_{½} = 10\ \text{min}$$

Substitution of value

$$k = \frac{0.693}{10\ \text{min}} = \mathbf{0.0693\ min^{-1}}$$

SOLVED PROBLEM 6. If a first order reaction is half completed in 100 seconds, calculate the time required for 99% of the reaction to be completed.

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 100 \text{ sec}$$

Substitiution of values

$$k = \frac{0.693}{100 \text{ sec}} = 0.00693 \text{ sec}^{-1}$$

(ii) To calculate the time for 99% of the reaction to be completed

Formula used

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$k = 0.00693 \text{ sec}^{-1}$ $a = 100$ $x = 99$ $a - x = 1$

Substitution of values

$$t = \frac{2.303}{0.00693 \text{ sec}^{-1}} \log \frac{100}{1}$$

$$= 332.32 \times \log 100 \text{ sec}$$

$$= 332.32 \times 2 \text{ sec} = \mathbf{664.64 \text{ sec}}$$

SOLVED PROBLEM 7. 50% of a first order reaction is completed in 23 minutes. Calculate the time required to complete 90% of the reaction.

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 23 \text{ minutes}$$

Substitiution of values

$$k = \frac{0.693}{23 \text{ min}} = 0.03013 \text{ min}^{-1}$$

(ii) To calculate the time required to complete 90% of reaction

Formula used

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$k = 0.03013 \text{ min}^{-1}$ $a = 100$ $x = 90$ $a - x = 10$

Substitution of values

$$t = \frac{2.303}{0.03013 \text{ min}^{-1}} \log \frac{100}{10}$$

$$= 76.44 \text{ min} \times \log 10$$

$$= \mathbf{76.44 \text{ min}} \qquad [\because \log 10 = 1]$$

SOLVED PROBLEM 8. From the following show that the decomposition of hydrogen peroxide in aqueous solution is a first order reaction.

Time (min)	0	15	30
V	25.4	9.83	3.81

where V is the volume of $KMnO_4$ required in ml to decompose a definite volume of hydrogen peroxide.

SOLUTION :

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$t = 15\text{ min}$ $\quad a = 25.4$ $\quad a - x = 9.83$

and $t = 30\text{ min}$ $\quad a = 25.4$ $\quad a - x = 3.81$

Substitution of values

$$k = \frac{2.303}{15\,\text{min}} \log \frac{25.4}{9.83} \qquad k = \frac{2.303}{30\,\text{min}} \log \frac{25.4}{3.81}$$

$$= 0.1535\text{min}^{-1} \times \log 2.5839 \qquad k = 0.07676\text{ min}^{-1} \times \log 6.6666$$

$$= 0.1535\text{min}^{-1} \times 0.41227 \qquad = 0.07676\text{ min}^{-1} \times 0.8239$$

$$= 0.06328 \qquad = 0.06324$$

Since the value of k is constant, the reaction is of first order.

SOLVED PROBLEM 9. 75% of a reaction of the first order was completed in 32 minutes. When was it half completed ?

SOLUTION :

(i) To calculate the value of rate constant

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$t = 32\text{ min}$ $\quad a = 100$ $\quad x = 75$ $\quad a - x = 25$

Substitution of values

$$k = \frac{2.303}{32\,\text{min}} \log \frac{100}{25}$$

$$= 0.0171969 \times \log 4$$

$$= 0.71967 \times 0.6021$$

$$= \mathbf{0.0433\ min^{-1}}$$

(ii) To calculate half life period

Formula used

$$t_{½} = \frac{0.693}{k}$$

Substitution of values

$$t_{½} = \frac{0.693}{0.0433\,\text{min}^{-1}} = \mathbf{16.0\ min}$$

SOLVED PROBLEM 10. In a gaseous reaction, the time for half change ($t_{½}$) for various partial pressures (P) was as follows :

P (mm)	500	600	800	1000
$t_{1/2}$ (min)	268	223	168	134

Calculate the order of the reaction.

SOLUTION :

Since the value of $t_{½}$ is varying with the initial pressure, the reaction can not be of first order.

Formula given

$$k = \frac{1}{t_{½}(a)} \text{ for a second order reaction}$$

Quantities given

$t_{½} =$	268	223	168	134 minutes
$a =$	500	600	800	1000 mm

Substitution of values

$$k = \frac{1}{268 \times 500} = 7.462 \times 10^{-6}$$

$$k = \frac{1}{223 \times 600} = 7.473 \times 10^{-6}$$

$$k = \frac{1}{168 \times 800} = 7.440 \times 10^{-6}$$

$$k = \frac{1}{134 \times 1000} = 7.460 \times 10^{-6}$$

Since the value of k is constant, the reaction is of second order.

SOLVED PROBLEM 11. For a certain reaction the rate constant $k = 2.46 \times 10^{-5}$ at 273 K and 1.63×10^{-3} at 303 K. Calculate the energy of activation for the reaction.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1\, T_2} \right]$$

Quantities given

$k_1 = 2.46 \times 10^{-5}$ $\quad T_1 = 273\text{ K}$ $\quad R = 1.987\text{ cal K}^{-1}\text{ mol}^{-1}$

$k_2 = 1.63 \times 10^{-3}$ $\quad T_2 = 303\text{ K}$

Substitiution of values

$$\log \frac{1.63 \times 10^{-3}}{2.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 1.987\text{ cal K}^{-1}\text{mol}^{-1}} \times \left[\frac{303\text{ K} - 273\text{ K}}{303\text{ K} \times 273\text{ K}} \right]$$

$$E_a = \frac{1.8212 \times 2.303 \times 1.987 \times 303 \times 273}{30}$$

$$= \mathbf{22979\text{ cal}}$$

SOLVED PROBLEM 12. The half life for a first order reaction is 2.5×10^3 sec. How long will it take for 1/5th of the reactant to be left behind ?

SOLUTION :

(i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 2.5 \times 10^3\text{ sec.}$$

Substitution of value

$$k = \frac{0.693}{2.5 \times 10^3\text{ sec.}} = 2.772 \times 10^{-4}\text{ sec}^{-1}$$

(ii) To calculate the time for 1/5th of the reaction to be left behind

Formula used

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

Quantities given

$a = 100$ $\quad a - x = \frac{1}{5} \times 100 = 20$ $\quad k = 2.772 \times 10^{-4}\text{ sec}^{-1}$

Substitution of values

$$t = \frac{2.303}{2.772 \times 10^{-4}\text{ sec}^{-1}} \times \log \frac{100}{20}$$

$$= 8308.08 \times \log 5\text{ sec}$$

$$= 8308.08 \times 0.6990\text{ sec}$$

$$= \mathbf{5807.34\ \ sec}$$

SOLVED PROBLEM 13. It was found that a solution of cane sugar in water hydolysed to a extent of 25% in one hour. Calculate the time that would be taken for the sugar to be 50% hydrolysed assuming the reaction is of the first order.

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$a = 100$ $\quad$ $x = 25$ $\quad$ $a - x = 75$ $\quad$ $t = 60$ min

Substitution of values

$$\begin{aligned} k &= \frac{2.303}{60\,\text{min}} \log \frac{100}{75} \\ &= 0.03838\ \text{min}^{-1} \times \log\ 4/3 \\ &= 0.038383\ \text{min}^{-1} \times \log 1.3333 \\ &= 4.794 \times 10^{-3}\ \text{min}^{-1} \end{aligned}$$

(ii) To calculate the half time period

Formula used

$$t_{½} = \frac{0.693}{k}$$

Substitution of value

$$\begin{aligned} t_{½} &= \frac{0.693}{4.794 \times 10^{-3}\ \text{min}^{-1}} \\ &= \mathbf{144.5\ min} \end{aligned}$$

SOLVED PROBLEM 14. Calculate the activation energy of a reaction whose rate constant gets double for 10 ºC rise in temperature.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$\frac{k_2}{k_1} = 2$ $\quad$ $R = 1.987$ cal K^{-1} mol^{-1} $\quad$ $T_1 = 27 + 273 = 300$ K

$T_2 = 372 + 273 = 310$ K

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987\ \text{cal K}^{-1}\text{mol}^{-1}} \left[\frac{310 - 300}{300 \times 310} \right]$$

or

$$\begin{aligned} E_a &= \frac{0.3010 \times 2.303 \times 1.987 \times 300 \times 310}{10} \\ &= \mathbf{12809.77\ cal} \end{aligned}$$

SOLVED PROBLEM 15. For a certain reaction the values of the rate constants at 25 °C and 65 °C were found to be 3.46×10^{-5} and 4.86×10^{-3} respectively. Calculate the energy of activation for the reaction.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1\, T_2} \right]$$

Quantities given

$k_2 = 4.86 \times 10^{-3}$ $\quad$ $T_1 = 25 + 273 = 298$ K $\quad$ $R = 1.987$ cal^{-1} K^{-1} mol^{-1}

$k_1 = 3.46 \times 10^{-5}$ $\quad$ $T_2 = 65 + 273 = 338$ K

Substitution of values

$$\log \frac{4.86 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 1.987\ \text{cal K}^{-1}\text{mol}^{-1}} \left[\frac{338\ \text{K} - 298\ \text{K}}{338\ \text{K} \times 298\ \text{K}} \right]$$

or

$$E_a = \frac{2.14845 \times 2.303 \times 1.987 \times 338 \times 298}{40}$$

$$= \mathbf{24757.12\ cal}$$

SOLVED PROBLEM 16. Calculate the half life period for the first order reaction whose rate constant is 1.052×10^{-3} $\sec^{-1}$.

SOLUTION :

Formula used

$$t_{½} = \frac{0.693}{k}$$

Quantities given

$$k = 1.052 \times 10^{-3}\ \sec^{-1}$$

Substitution of values

$$t = \frac{0.693}{1.052 \times 10^{-3}\ \sec^{-1}} = \mathbf{659\ sec}$$

SOLVED PROBLEM 17. The rate constant for the first order reaction at 45 °C is twice that at 35 °C. Find the energy of activation of the reaction.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Quantities given

$\frac{k_2}{k_1} = 2$ $\quad R = 1.987$ cal K^{-1} mol^{-1} $\quad T_1 = 45 + 273 = 318$ K

$T_2 = 35 + 273 = 308$ K

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987\ \text{cal}\ K^{-1} mol^{-1}}\left[\frac{318\ K - 308\ K}{318\ K \times 308\ K}\right]$$

or

$$E_a = \frac{0.3010 \times 2.303 \times 1.987 \times 318 \times 308}{10}$$

$$= 13490.75\ \text{cal}$$

$$= \mathbf{13.49075\ kcal}$$

SOLVED PROBLEM 18. In the reaction

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

equimolar mixture of gas at 336 mm Hg initial pressure was changed in 108 seconds. When the initial pressure was 288 mm it was half changed in 148 seconds. Determine the order of the reaction.

SOLUTION :

Formula used

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1}$$

Quantities given

$t_2 = 108$ sec $\quad A_1 = 288$ mm $\quad t_1 = 148$ sec $\quad A_2 = 336$ mm

Substitution of values

$$\frac{108\ \sec}{148\ \sec} = \left(\frac{288\ mm}{336\ mm}\right)^{n-1}$$

Taking logarithms

$$\log \frac{108}{148} = n - 1 \times \log \frac{288}{336}$$

or $$n - 1 = \frac{\log (108/148)}{\log (288/336)}$$

or $$n = 1 + \left(\frac{-0.1368}{-0.0669}\right)$$

$$= 1 + 2$$

$$= \mathbf{3}$$

SOLVED PROBLEM 19. If a unimolecular reaction is one quarter completed in 100 minutes, what is the specific rate constant k ? $\left(k = \frac{2.303}{t} \log \frac{a}{a - x}\right)$

SOLUTION :

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Quantities given

$a = 100$ $x = 25$ $a - x = 75$ $t = 100$ minutes

Substitution of values

$$k = \frac{2.303}{100 \text{ min}} \log \frac{100}{75}$$

$$= \frac{2.303}{100} \text{min}^{-1} \times \log 1.333$$

$$= 0.02303 \text{ min}^{-1} \times 0.1249$$

$$= \mathbf{2.8764 \times 10^{-3} \ min^{-1}}$$

SOLVED PROBLEM 20. Saponification of ethyl acetate was carried out by NaOH using equal concentration of the two at 310 K. At regular intervals 20 ml samples of reaction mixture were titrated against the standard acid and the following results were obtained :

Time (min)	0	4.89	10.07	22.63
Vol. of acid used (ml)	47.65	38.92	32.62	22.58

Show that the reaction is of second order.

SOLUTION :

Formula used

$$k = \frac{1}{t} \times \frac{x}{a(a - x)}$$

Quantities given

$t = 4.89$ min	10.07	22.63 min	$a = 47.65$
$x = 8.73$	15.030	25.070	
$a - x = 38.92$	32.62	22.58	

Substitution of values

$$k = \frac{1 \times 8.73}{4.89 \text{ min} \times 47.65 \times 38.92} = \mathbf{0.000960 \ min^{-1}}$$

$$k = \frac{1 \times 15.030}{10.07 \text{ min} \times 47.65 \times 32.62} = \mathbf{0.000960 \ min^{-1}}$$

and $$k = \frac{1}{22.63 \text{ min}} \times \frac{25.070}{47.65 \times 22.58} = \mathbf{0.000986 \ min^{-1}}$$

Since the value of k is constant, the reaction is of first order.

SOLVED PROBLEM 21. If the initial cocentration of both the reactants following a second order reation kinetics are the same, then how long will it take for the 70% completion of the reaction, if 30% of the reaction is completed in 12 minutes.

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{1}{t} \times \frac{x}{a\,(a-x)}$$

Quantities given

$t = 12\ \text{min}$

$x = 30$

$a = 100$

Substitution of values

$$k = \frac{1}{12\ \text{min}} \times \frac{30}{100 \times 70}$$
$$= 3.5714 \times 10^{-4}$$

(ii) To calculate the time for 70% completion of reaction

Formula used

$$t = \frac{1}{k} \times \frac{x}{a\,(a-x)}$$

Quantities given

$x = 70$

$a = 100$

$k = 3.5714 \times 10^{-4}\ \text{min}^{-1}$

Substitution of values

$$t = \frac{1}{3.7514 \times 10^{-4} \text{min}^{-1}} \times \frac{70}{100 \times 30}$$
$$= \mathbf{62.199\ min}$$

SOLVED PROBLEM 22. The specific reaction rate for the decomposition of N_2O_5 vapour is found to be 3.46×10^{-5} at 298 K and 4.87×10^{-3} at 338 K. Determine the activation energy of the reaction.

SOLUTION :

Formula given

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_2\ T_1}\right]$$

Quantities given

$k_2 = 4.87 \times 10^{-3}$

$k_1 = 3.46 \times 10^{-5}$

$T_2 = 338\ \text{K}$

$T_1 = 298\ \text{K}$

$R = 8.314\ \text{J K}^{-1}$

Substituting of values

$$\log \frac{4.87 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314\ \text{J}}\left[\frac{338\ \text{K} - 298\ \text{K}}{338\ \text{K} \times 298\ \text{K}}\right]$$

or

$$2.1484 = \frac{E_a}{2.303 \times 8.314\ \text{J}}\left[\frac{40\ \text{K}}{338\ \text{K} \times 298\ \text{K}}\right]$$

or

$$E_a = \frac{2.1484 \times 2.303 \times 8.314\ \text{J} \times 338 \times 298}{40}$$
$$= 103583.86\ \text{J}$$
$$= \mathbf{103.58386\ kJ}$$

SOLVED PROBLEM 23. Compound A decomposes to form B and C and reaction is first order. At 25 ºC the rate constant for the reaction is $0.45\ \text{sec}^{-1}$. What is the half life of A at 25 ºC ?

SOLUTION :

Formula used

$$t_{½} = \frac{0.693}{k}$$

Quantity given

$$k = 0.45\ \text{sec}^{-1}$$

Substitution of value

$$t_{½} = \frac{0.693}{0.45\ \text{sec}^{-1}}$$

$$= \mathbf{1.54\ sec}$$

SOLVED PROBLEM 24. For the first order reaction the half life period is 30 minutes. What is the time taken for 75% of the completion of the reaction ?

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{½}}$$

Quantity given

$$t_{½} = 30\ \text{min}$$

Substitution of value

$$k = \frac{0.693}{30\ \text{min}} = 0.0231\ \text{min}^{-1}$$

(ii) To calculate the time for 75% of completion of reaction

Formula used

$$k = \frac{2.303}{0.231\ \text{min}} \log \frac{a}{a-x}$$

Quantities given

$k = 0.231$ min $\quad a = 100 \quad x = 75$

Substitution of values

$$t = \frac{2.303}{0.231\ \text{min}^{-1}} \log \frac{100}{100-75}$$

$$= \frac{2.303}{0.231}\ \text{min} \times \log 4$$

$$= \frac{2.303}{0.231}\ \text{min} \times 0.6021$$

$$= \mathbf{60\ min}$$

SOLVED PROBLEM 25. Calculate the activation energy of a reaction whose rate constant doubles when the temperature is raised from 22 ºC to 32 ºC.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_2\ T_1} \right]$$

Quantities given

$\frac{k_2}{k_1} = 2 \quad R = 1.987\ \text{cal K}^{-1}\ \text{mol}^{-1} \quad T_2 = 32 + 273 = 305\ \text{K}$

$T_1 = 22 + 273 = 295\ \text{K}$

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1}\text{mol}^{-1}} \times \left[\frac{305\text{ K} - 295\text{ K}}{305\text{ K} \times 295\text{ K}}\right]$$

$$= \frac{0.3010 \times 2.303 \times 1.987 \times 305 \times 295}{10} \text{ cal}$$

or $$= 123931.1 \text{ cal}$$

$$= \mathbf{12.3931\ kcal}$$

SOLVED PROBLEM 26. The specific reaction rate of a chemical rate of a chemical reaction at 273 K and 303 K are 2.45 × 10^{-5} sec^{-1} and 16.2 × 10^{-4} sec^{-1} respectively. Calculate the energy of activation ($R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$)

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_2\ T_1}\right]$$

Quantities given

$k_2 = 16.2 \times 10^{-4} \text{ sec}^{-1}$ $T_2 = 303\text{ K}$ $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$

$k_1 = 2.45 \times 10^{-5} \text{ sec}^{-1}$ $T_1 = 273\text{ K}$

Substitution of values

$$\log \frac{16.2 \times 10^{-4}\text{sec}^{-1}}{2.45 \times 10^{-5}\text{sec}^{-1}} = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1}}\left[\frac{303\text{ K} - 273\text{ K}}{303\text{ K} \times 273\text{ K}}\right]$$

or $$E_a = \frac{1.8203 \times 2.303 \times 8.314 \times 303 \times 273}{30}$$

$$= 96101.67 \text{ J}$$

$$= \mathbf{96.10167\ kJ}$$

SOLVED PROBLEM 27. In the Asshenius equation for a certain reaction, the value of A and E_a (activation energy) are 4 × 10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes ?

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{½}}$$

Quantities given

$$t_{½} = 10 \text{ min}$$

Substitution of values

$$k = \frac{0.693}{10 \times 60 \text{ sec}} = 1.155 \times 10^{-3} \text{ sec}^{-1}$$

(ii) To calculate the temperature

Formula used

$$k = Ae^{-E_a/RT}$$

or $$\log k = \frac{E_a}{2.303\,R\,T} + \log A$$

Quantities given

$k_2 = 1.55 \times 10^{-3}\ \text{sec}^{-1}$ $\quad A = 4 \times 10^{13}\ \text{sec}^{-1}$ $\quad E_a = 98.6\ \text{kJ mol}^{-1}$

$R = 8.314 \times 10^{-3}\ \text{kJ mol}^{-1}$

Substitution of values

$$\log 1.55 \times 10^{-3} = \log(4 \times 10^{13}) - \frac{98.6\ \text{kJ}}{2.303 \times 8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1} \times T}$$

$$-2.9374 = 13.6021 - \frac{5.1496 \times 10^3}{T}$$

$$T = \frac{5.1496 \times 10^3}{13.6021 + 2.9374}$$

$$= \mathbf{311.35\ K}$$

SOLVED PROBLEM 28. The catalyst decomposition of N_2O by gold at 900 ºC and at initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(a) What is the order of the reaction ?

(b) How much of it will decompose in 100 minutes at initial pressure of 600 mm ?

SOLUTION :(i) To calculate the order of reaction

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad \text{for 1st order reaction}$$

Quantities given

$a = 100$ $\quad x = 50$ and 73 $\quad t = 53$ mts and 100 mts

$a - x = 100 - 50$ and $100 - 73 = 27$

Substitution of values

$$k = \frac{2.303}{53} \log \frac{100}{50} \quad \text{and} \quad k = \frac{2.303}{100} \log \frac{100}{27}$$

$$k = 0.013864\ \text{min}^{-1} \qquad k = 0.013095\ \text{min}^{-1}$$

Since k is constant the reaction is of **first** order

(ii) To calculate the amount decomposed in 100 minutes at initial pressure of 600 mm

Formula used

$$\%\ \textit{decomposition} = \frac{\textit{Initial pressure} \times \%\ \textit{decomposed}}{100}$$

[∵ It is independent of initial conc. for 1st order reaction]

Quantities given

Initial pressure = 600 $\quad$ *% decomposed* = 73

Substitution of values

$$\text{Amount of } N_2O \text{ decomposed} = \frac{600\ \text{mm} \times 73}{100}$$

$$= \mathbf{438\ \ mm}$$

SOLVED PROBLEM 29 The decomposition of N_2O_5 according to the equation :

$$2\,N_2O_{5\,(g)} \longrightarrow 4\,NO_{2\,(g)} + O_{2\,(g)}$$

is a first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

SOLUTION :

The reaction is

$$\begin{array}{llcll} & 2\,N_2O_{5\,(g)} & \longrightarrow & 4\,NO_{2\,(g)} & +\ O_{2\,(g)} \\ \text{After 30 mts} & 2-x & & 2\,x & x/2 \end{array}$$

$$\text{The initial pressure of } N_2O_5 = \frac{\text{No. of moles of } N_2O_5}{\text{Total no. of moles}}$$

$$= \frac{2.303}{50} \times 58.4\,\text{mm} = 233.8\,\text{mm}$$

Let the amt. of N_2O_5 decomposed after 30 mt. be $= x$

then pressure due to $N_2O_5 = 233.8 - x$ mm

pressure due to $NO_2 = 2\,x$

and pressure due to $O_2 = x/2$

Total pressure after 30 minutes $= 233.8 - x + 2\,x + x/2 = 284.5$ mm (given)

$233.8 + 3\,x/2 = 284.5$ mm

or
$$x = \frac{(284.5 - 233.4) \times 2}{3} = 33.8\,\text{mm}$$

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$t = 30$ minutes $\quad a = 233.8$ mm $\quad x = 33.8$ mm $\quad a - x = 233.8 - 200\text{mm} = 33.8$ mm

Substitution of values

$$k = \frac{2.303}{30} \log \frac{233.8\,\text{mm}}{200\,\text{mm}}$$

$$= 0.7676\ \text{min}^{-1} \times \log 1.169$$

$$= 0.07676\ \text{min}^{-1} \times 0.0678$$

$$= 0.005204\ \text{min}^{-1}$$

$$= \mathbf{5.204 \times 10^{-3}\,min^{-1}}$$

SOLVED PROBLEM 30. What will be initial rate of reaction, if its rate constant is 10^{-3} min^{-1} and the concentration of the reactant is 0.2 mol dm^{-3} ? How much of the reactant will be converted into the products after 200 minutes ?

Solution : (i) To calculate the initial rate

Formula used

$$\textit{Rate of reaction} = k\,[\,A\,]$$

Quantities given

$k = 10^{-3}$ min^{-1} $\quad [A] = 0.2$ mol dm^{-3}

Substitution of values

$$\textit{Rate of reaction} = 10^{-3}\,\text{min}^{-1} \times 0.2\ \text{mol dm}^{-3} = \mathbf{2 \times 10^{-4}\,dm^{-3}\,min^{-1}}$$

(ii) To calculate the % decomposition after 200 minutes

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

or
$$\log \frac{a}{a-x} = \frac{k\,t}{2.303}$$

Quantities given

$k = 10^{-3}\,\text{min}^{-1}$ $\qquad$ $t = 200\,\text{min}$

Substitution of values

$$\log \frac{a}{a-x} = \frac{10^{-3}\,\text{min}^{-1} \times 200\,\text{min}}{2.303}$$
$$= 8.684 \times 10^{-2}$$

or
$$\frac{a}{a-x} = \text{Antilog}\,(8.684 \times 10^{-2})$$
$$\frac{a}{a-x} = 1.22$$

or
$$a = 1.22\,a - 1.22\,x$$
$$122\,x = 0.22\,a$$

or
$$x = \frac{0.22\,a}{1.22}$$
$$\%\ \text{Decomposition} = \frac{2303}{t} \times 100 = \mathbf{18\%}$$

SOLVED PROBLEM 31. The gas phase decomposition of dimethylether follows first order kinetics :

$$CH_3-O-CH_{3\,(g)} \longrightarrow CH_{4\,(g)} + H_{2\,(g)} + CO_{(g)}$$

The reaction is carried out in a constant volume container at 500 °C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a presure of 0.40 atm. What is the total pressure of the system after 12 minutes assuming ideal gas behavior ?

SOLUTION : (i) To calculate the initial concentration of CH_3-O-CH_3

The reaction is

	$CH-O-CH_{3\,(g)}$	$\longrightarrow$	$CH_{4\,(g)}$	$+\ H_{2\,(g)}$	$+\ CO_{(g)}$
Initial conc.	a		0	0	0
After 12 min	$a - x$		x	x	x

$$\text{Total Initial Conc., } a\text{, of } CH_3OCH_3 = \frac{n}{V}$$

Formula used

$$PV = n\,R\,T$$

or
$$\frac{n}{V} = \frac{P}{R\,T}$$

Quantities given

$P = 0.4\,\text{atm}$ $\qquad$ $R = 0.082\,\text{atm lit K}^{-1}\,\text{mol}^{-1}$ $\qquad$ $T = 500 + 273 = 773\,\text{K}$

Substitution of values

$$a = \frac{n}{V} = \frac{0.4\,\text{atm}}{0.082\,\text{atm lit K}^{-1}\,\text{mol}^{-1} \times 773\,\text{K}}$$
$$= 6.31 \times 10^{-3}\,\text{mol lit}^{-1}$$

(ii) To calculate of CH_3-O-CH_3 decomposed after 12 minutes

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$k = \frac{0.693}{t_{½}} = \frac{0.693}{14.5\text{min}} = 4.779 \times 10^{-2} \qquad t = 12 \text{ min} \qquad a = 6.31 \times 10^{-3} \text{mol lit}^{-1}$$

Substitution of values

$$4.779 \times 10^{-2} \text{min}^{-1} = \frac{2.303}{t} \times \log \frac{a}{a-x}$$

or $$\log \frac{a}{a-x} = \frac{4.779 \times 10^{-2} \times 12}{2.303}$$

$$= 0.2490$$

or $$\frac{a}{a-x} = \text{antilog}\ (0.2490)$$

$$= 1.7742$$

or $$a - x = \frac{a}{1.7742}$$

$$= \frac{6.31 \times 10^{-3}}{1.7742} \text{ mol lit}^{-1} \qquad [\because a = 6.31 \times 10^{-3} \text{mol lit}^{-1}]$$

$$= 3.556 \times 10^{-3} \text{ mol lit}^{-1}$$

or $$x = 6.31 \times 10^{-3} - 3.556 \times 10^{-3} \text{mol lit}^{-1}$$

$$= 2.754 \times 10^{-3} \text{ mol lit}^{-1}$$

$$\text{Total no. of moles after 12 minutes} = a - x + x + x + x$$

$$= a + 2x$$

$$= 6.31 \times 10^{-3} + 2 \times 2.754 \times 10^{-3} \text{mol lit}^{-1}$$

$$= 11.818 \times 10^{-3} \text{mol lit}^{-1}$$

(iii) To calculate total pressure of the system after 12 minutes

Formula used

$$P = \frac{n}{V} RT$$

Quantities given

$$\frac{n}{V} = 11.818 \times 10^{-3} \text{mol lit}^{-1} \qquad R = 0.082 \text{ atm lit K}^{-1} \text{mol}^{-1} \qquad T = 773 \text{ K}$$

Substitution of values

$$P = 11.818 \times 10^{-3} \text{mol lit}^{-1} \times 0.082 \text{ atm lit K}^{-1} \text{mol}^{-1} \times 773 \text{ K}$$

$$= \mathbf{0.709 \text{ atm}}$$

SOLVED PROBLEM 32. The half life period of first order decomposition of nitramide is 2.1 hour at 15 °C

$$NH_2NO_{2\,(aq)} \longrightarrow N_2O_{(g)} + H_2O_{(l)}$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate

(a) time for NH_2NO_2 to decompose 99%; and

(b) volume of dry N_2O produced at this point measured at STP.

SOLUTION : (i) To calculate time for 99% decomposition

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \text{or} \qquad t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$a = 100$ $\quad x = 99$ $\quad a - x = 1$ $\quad k = \dfrac{0.693}{t_{½}} = \dfrac{0.693}{2.1\text{ hr}} = 0.33\text{ hr}^{-1}$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{0.33\text{ hr}^{-1}} \log \frac{100}{1} \\ &= 6.978\text{ hr} \times 2 \\ &= \mathbf{13.956\ hr} \end{aligned}$$

(ii) To calculate the volume of dry N_2O produced at STP

$$\begin{aligned} 1\text{ mole of } NH_2NO_2 &= 1\text{ mol of } N_2O \\ 62\text{ g mol}^{-1} &= 22.4\text{ lit at STP} \\ 6.2\text{ g} &= \frac{22.4 \times 6.2}{62} \\ &= 2.24\text{ lit} \end{aligned}$$

volume of N_2O produced at STP when % decomposition is 99%

$$\begin{aligned} &= \frac{2.24 \times 99}{100}\text{ lit} \\ &= \mathbf{2.2176\ lit} \end{aligned}$$

SOLVED PROBLEM 33. At 380 ºC the half period for the first order decomposition of H_2O_2 is 360 minutes. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450ºC.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2\,T_1}\right]$$

Quantities given

$k_1 = \dfrac{0.693}{t_{½}} = \dfrac{0.693}{360\text{ min}} = 1.925 \times 10^{-3}\text{ min}^{-1}$ $\qquad T_1 = 380 + 273 = 653\text{ K}$

$E_a = 200\text{ kJ mol–1}$ $\qquad R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$ $\qquad T_2 = 450 + 273 = 723\text{ K}$

Substitution of values

$$\log \frac{16.2 \times 10^{-3}\text{ sec}^{-1}}{2.45 \times 10^{-5}\text{ sec}^{-1}} = \frac{200\text{ kJ mol}^{-1}}{2.303 \times 8.314\text{ J K}^{-1}\text{mol}^{-1}}\left[\frac{723\text{ K} - 653\text{ K}}{723\text{ K} \times 653\text{ K}}\right]$$

or $$= \frac{10.445 \times 70}{723 \times 653}$$

$$= 0.01549$$

or $$\frac{k_2}{1.925 \times 10^{-3}} = \text{Antilog}\,(0.00154) = 1.003573$$

or $$k_2 = 1.925 \times 10^{-3}\text{ min}^{-1} \times 1.003573 = 1.931878 \times 10^{-3}\text{ min}^{-1}$$

(ii) To calculate time required for 75% decomposition of H_2O_2 at 450 ºC

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Quantities given

$k = 1.931878 \times 10^{-3}\ \text{min}^{-1}$ $\qquad a = 100 \qquad x = 75 \qquad a - x = 100 - 75 = 25$

Substitution of values

$$t = \frac{2.303}{1.931878 \times 10^{-3}\ \text{min}^{-1}} \log \frac{100}{25}$$

$$= \mathbf{717.76\ mm}$$

ADDITIONAL PRACTICE PROBLEMS

1. The rate of formation of a dimer in a second order dimerisation reaction is 5.8×10^{-3} mol lit^{-1} at 0.10 mol monomer concentration. Calculate the value of rate constant.

Answer. 5.8×10^{-3} mol lit^{-1} sec^{-1}

2. The half life of the reaction

$$N_2O_5 \longrightarrow 2\ NO_2 + ½\ O_2$$

is 2.4 hours at 30 ºC.

(a) Starting with 100 g of N_2O_5 how many grams will remain after a period of 9.6 hours ?

(b) What time would be required to reduce 5×10 moles of N_2O_5 to 10^8 molecules ?

Answer. (a) 6.25 g (b) 21.52 hrs

3. A reaction that is first order with respect to the reactant A has a rate constant of 6 min^{-1}. If we start [A] = 5.0 mol lit^{-1} when would [A] reach the value of 0.05 mol lit^{-1} ?

Answer. 0.7676 min

4. A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion.

Answer. 144.27 min

5. The rate constant of a first order reaction becomes 6 times when the temperature is increased from 350 K to 410 K, Calculate the energy of activation for the reaction (R = 8.314 J K^{-1} mol^{-1})

Answer. 35.656 k J

6. The reaction

$$C_2H_5I \longrightarrow C_2H_4 + HI$$

is of first order and its rate contants are 3.20×10^{-4} at 600 K and 1.60×10^{-2} sec^{-1}at 1200 K. Calculate the energy of activation for the reaction. (R = 8.314 J K^{-1} mol^{-1})

Answer. 39.07 kJ

7. Find the two third life $t_{2/3}$ of a first order reaction in which $k = 5.48 \times 10^{-14}$ sec^{-1}.

Answer. 20×10^{13} sec

8. For a certain reaction, it takes 5 minutes for the initial concentration of 0.5 mol lit^{-1} to become 0.25 mol lit^{-1} and another 5 minutes to became 0.125 mol lit^{-1}. (a) What is the order of the reaction ? (b) What is the rate constant of the reaction ?

Answer. (a) One (b) 0.136 min^{-1}

9. For the inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{glucose}}{C_2H_{16}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

the second order rate constant is 2.12×10^{-4} lit mol^{-1} sec^{-1} at 27 ºC. The activation energy of the reaction is

1.07×10^5 mol^{-1}. What is the rate constant of the reaction at 37 ºC ?

Answer. 8.457×10^{-4} lit mol^{-1} sec^{-1}

10. The following reaction is first order with a rate constant of 4.80×10^{-4} sec^{-1} at 45 ºC.

$$2\,N_2O_{5\,(g)} \longrightarrow 4\,NO_2 + \tfrac{1}{2}\,O_{2\,(g)}$$

(a) If the initial concentration is 1.65×10^{-2} mol lit^{-1}, calculate the concentration after 13.75 minutes.

(b) How long would it take for the concentration of N_2O_5 to decrease to 1.0×10^{-2} mol lit^{-1} from its initial value ?

Answer. 0.0111 mol lit^{-1} ; (b) 17.4 min

11. Sulphuryl chloride, SO_2Cl_2, decomposes in a first order reaction according to the equation

$$SO_2Cl_{2\,(g)} \longrightarrow SO_{2\,(g)} + Cl_{2\,(g)}$$

The value of rate constant at 32 ºC is 2.2×10^{-5} sec^{-1}. Calculate (a) half life period of SO_2Cl_2 at this temperature and (b) How long would it take for 75% of SO_2Cl_2 to decompose ?

Answer. (a) 3.15×10^4 sec ; (b) 17.5 hours

12. The rate constant for the formation of hydrogen iodide according to the equation

$$H_{2\,(g)} + I_{2\,(g)} \longrightarrow 2\,HI_{(g)}$$

is 2.7×10^{-4} lit mol^{-1} sec^{-1} at 600 K and 3.5×10^{-3} lit mol^{-1} lit mol^{-1} sec^{-1} at 650 K. Calculate the energy of activation for the reaction .

Answer. 1.66×10^5 J mol^{-1}

13. The rate of a particular reaction becomes three times when the temperature is increased from 298 K to 308 K. Calculate the energy of activation for the reaction.

Answer. 83.8 kJ mol^{-1}

14. A first order reaction takes 100 minutes for the completion of 60 percent of reaction Find the time when 90 percent of the reaction will be completed.

Answer. 251.2 min

15. The reaction $N_2 + O_5 \longrightarrow 2\,NO_2 + \tfrac{1}{2}\,O_2$

is of first in N_2O_5. Its rate constant is 6.2×10^{-6} sec^{-1}. If in the beginning $[N_2O_5]$ is 15 mol lit^{-1}, calculate the rate of reaction in the beginning.

Answer. 9.3×10^{-5} mol lit^{-1} sec^{-1}

16. If the half life of a first order in A is 2 min, how long will it take A to reach 25% of its initial concentration.

Answer. 4 min

17. Calculate the half life of a first order reaction where the specific rate constant is (a) 200 sec^{-1} (b) 2 min^{-1}.

Answer. (a) 0.00346 sec^{-1} ; (b) 0.3465 min^{-1}

18. A first order reaction is found to have a rate constant $k = 7.39 \times 10^{-5}$ sec^{-1}. Calculate $t_{0.5\%}$ and $t_{0.80\%}$.

Answer. 21783.4 sec and 18763.68 sec

19. An acid solution of sucrose was hydrolysed to the extent of 54% after 67 minutes. Assuming the reaction to be of first order, calculate the time taken for 80% hydrolysis.

Answer. 124.4 min

20. A second order reaction in which both the reactants have the same concentration is 25% complete in 10 minutes. How long will it take for the reaction to go to 90% completion ?

Answer. 2700 min