

Calculation of K_p : Let the total pressure at equilibrium be P .

P. Total number of moles at equilibrium

$$p_{\text{PCl}_5} = \frac{(a-x)}{(a+x)} \cdot P; p_{\text{PCl}_3} = \frac{x}{(a+x)} \cdot P; p_{\text{Cl}_2} = \frac{x}{(a+x)} \cdot P$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\frac{x}{(a+x)} \cdot P \times \frac{x}{(a+x)} \cdot P}{\frac{(a-x)}{(a+x)} \cdot P} = \frac{x^2 P}{(a-x)(a+x)}$$

(units = atm)

(a) **Effect of pressure:** In this case, $K_c = x^2 / (a-x)V$. If pressure is increased, the value of ' V ' decreases, i.e., the value of denominator decreases. To maintain constant value of K_c , x must also decrease. In other words, the dissociation of PCl_5 decreases. Thus, the increase of pressure would suppress the dissociation of PCl_5 .

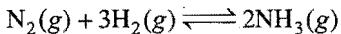
(b) **Effect of concentration:** If PCl_5 is added to the equilibrium mixture, the rate of forward reaction increases, i.e., dissociation of PCl_5 increases. In case PCl_3 or Cl_2 is added, the rate of backward reaction increases. This shall decrease the dissociation of PCl_5 .

(c) **Effect of temperature:** The dissociation of PCl_5 is an endothermic reaction. Thus, the value of equilibrium constant increases with increase of temperature. It is thus concluded that dissociation increases with the increase of temperature.

(d) **Effect of adding an inert gas:** When an inert gas is added at constant volume the equilibrium state is not disturbed. In case an inert gas is added at constant pressure, the volume increases. To maintain the constant value of K_c , x must also increase. Thus, the addition of an inert gas at constant pressure increases the degree of dissociation of PCl_5 .

Case III: Homogeneous gaseous reaction when, $\Delta n < 0$.

Synthesis of ammonia: The formation of ammonia from nitrogen and hydrogen is represented by the equation:



Let a start be made by mixing ' a ' moles of N_2 and ' b ' moles of hydrogen in a closed vessel of V litre capacity. By the time equilibrium is established ' x ' moles of nitrogen have combined with $3x$ moles of hydrogen and produced $2x$ moles of ammonia.

$$\text{At equilibrium, } [\text{N}_2] = \frac{(a-x)}{V}$$

$$[\text{H}_2] = \frac{(b-3x)}{V}$$

$$[\text{NH}_3] = \frac{2x}{V}$$

Applying law of mass action,

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

If $a = 1$ and $b = 3$, then,

$$K_c = \frac{4x^2 V^2}{27(1-x)^4}; \quad (\text{units} = \text{mol}^{-2} \text{L}^2)$$

The effect of various factors at equilibrium is discussed here.

(a) **Effect of pressure:** By increasing pressure, the volume term decreases. The value of x must increase to maintain the constant value of K_c . In other words, the formation of ammonia increases with increase of pressure.

(b) **Effect of concentration:** By increasing the concentration of either nitrogen or hydrogen in the reaction mixture, the rate of forward reaction increases, i.e., the formation of ammonia increases.

(c) **Effect of temperature:** The synthesis of ammonia is an exothermic reaction. The value of equilibrium constant decreases with increase of temperature. Thus, high temperature is not favourable for the synthesis of ammonia.

Calculation of K_p : Let the total pressure at equilibrium be P .

Total number of moles at equilibrium

$$= (a-x) + (b-3x) + 2x = (a+b-2x)$$

$$p_{\text{NH}_3} = \frac{2x}{(a+b-2x)} \times P; \quad p_{\text{N}_2} = \frac{(a-x)}{(a+b-2x)} \times P;$$

$$p_{\text{H}_2} = \frac{(b-3x)}{(a+b-2x)} \times P$$

$$K_p = \frac{[p_{\text{NH}_3}]^2}{[p_{\text{N}_2}][p_{\text{H}_2}]^3} = \frac{\left[\frac{2x}{(a+b-2x)} P\right]^2}{\left[\frac{(a-x)}{(a+b-2x)} P\right] \left[\frac{(b-3x)}{(a+b-2x)} P\right]^3}$$

$$= \frac{4x^2 (a+b-2x)^2}{(a-x)(b-3x)^3 P^2} \quad (\text{units} = \text{atm}^{-2})$$

Case IV: Homogeneous liquid system: Formation of ethyl acetate:

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.



Let a start be made by mixing ' a ' moles of an acid and ' b ' moles of an alcohol. By the time equilibrium is established, x moles of ester and ' x ' moles of water are formed, i.e., x moles of acid and x moles of alcohol have been consumed. Let V be the total volume.

At equilibrium, the active masses of reactants and products are:

$$[\text{CH}_3\text{COOH}] = \frac{(a-x)}{V}, [\text{C}_2\text{H}_5\text{OH}] = \frac{(b-x)}{V},$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = \frac{x}{V} \text{ and } [\text{H}_2\text{O}] = \frac{x}{V}$$

Applying law of mass action,

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{a-x}{V}\right) \times \left(\frac{b-x}{V}\right)}$$

$$= \frac{x^2}{(a-x)(b-x)}$$

$$\text{If } a = b = 1, \text{ then } K_c = \frac{x^2}{(1-x)^2}, \quad (K_c \text{ has no units})$$

This does not involve the volume term. Thus, K_c is not affected by the change of volume.

Case V: Heterogeneous equilibria:

Law of mass action can also be applied to the study of equilibria in which the substances are not in the same phase. Considering the decomposition of solid NaHCO_3 to produce solid Na_2CO_3 , gaseous CO_2 and H_2O .



Applying the law of mass action,

$$K'_c = \frac{[\text{Na}_2\text{CO}_3][\text{CO}_2][\text{H}_2\text{O}]}{[\text{NaHCO}_3]^2}$$

It involves two pure solids, Na_2CO_3 and NaHCO_3 . It is customary not to include the concentrations of pure solids in equilibrium expressions.

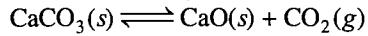
$$K'_c \frac{[\text{NaHCO}_3]^2}{[\text{Na}_2\text{CO}_3]} = [\text{CO}_2][\text{H}_2\text{O}]$$

$$\text{or } K_c = [\text{CO}_2][\text{H}_2\text{O}]$$

In terms of partial pressures we have $K_p = p_{\text{CO}_2} \times p_{\text{H}_2\text{O}}$. Similarly, in reactions in which a reactant or product occurs as a pure liquid phase, the concentration of that substance in the pure liquid is also constant. As a result, the concentrations of pure solid and pure liquid phases do not appear in the equilibrium constant expression.

Many other examples of heterogeneous equilibria are available. Such as:

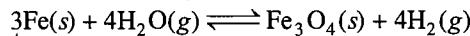
1. Decomposition of CaCO_3 ,



$$K_c = [\text{CO}_2] \text{ or } K_p = p_{\text{CO}_2}$$

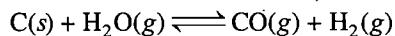
When CaCO_3 is heated in a closed vessel at a definite temperature, the pressure or concentration of CO_2 produced becomes constant irrespective of the amount of CaCO_3 taken.

2. Reaction of steam on heated iron,



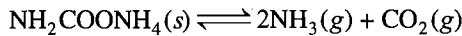
$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} \text{ or } K'_p = \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \sqrt[4]{K_p}$$

3. Reaction of steam on heated carbon,



$$K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]} \text{ or } K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

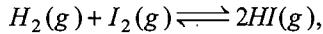
4. Dissociation of ammonium carbamate,



$$K_c = [\text{NH}_3]^2[\text{CO}_2]; \quad K_p = [P_{\text{NH}_3}]^2 \times [P_{\text{CO}_2}]$$

SOME SOLVED EXAMPLES

Example 11. For the following reaction,



If initially 25 mL of H_2 and 20 mL of I_2 are present in a container and at equilibrium 30 mL of HI is formed then calculate equilibrium constant. [AIPMT (Mains) 2009]

Solution: The given reaction is :

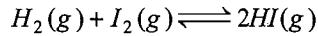
	$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$,
t_0	25 mL 20 mL 0
$t_{eq.}$	25-x 20-x 2x

Given, $2x = 30 \text{ mL} \therefore x = 15 \text{ mL}$

Equilibrium constant may be calculated as,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[30]^2}{[10][5]} = \frac{900}{15} = 60$$

Example 12. In the reaction,



the amounts of H_2 , I_2 and HI are 0.2 g, 9.2525 g and 44.8 g respectively at equilibrium at a certain temperature. Calculate the equilibrium constant of the reaction.

Solution: $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$,

Applying law of mass action,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Let the total volume be V litre, then

$$[\text{H}_2] = \frac{0.2}{2V} = \frac{0.1}{V}; [\text{I}_2] = \frac{9.2525}{254V} = \frac{0.0364}{V}$$

$$[\text{HI}] = \frac{44.8}{128V} = \frac{0.35}{V} \text{ mol L}^{-1} \text{ respectively}$$

$$\text{So, } K_c = \frac{\left(\frac{0.35}{V}\right)^2}{\frac{0.1}{V} \times \frac{0.0364}{V}} = \frac{0.35 \times 0.35}{0.1 \times 0.0364} = 33.65$$

Example 13. 0.5 mole of hydrogen and 0.5 mole of iodine react in a 10 litre evacuated vessel at 448°C ; hydrogen iodide is formed. The equilibrium constant, K_c for the reaction is 50.

(a) Calculate the number of moles of iodine which remain unreacted at equilibrium.

(b) What is the value of K_p ?

Solution: (a) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$

Initial moles $0.5 \quad 0.5 \quad 0$

No. of. moles at equilibrium $(0.5-x) \quad (0.5-x) \quad 2x$

$$K_c = \frac{4x^2}{(0.5-x)(0.5-x)} = 50$$

$$\frac{2x}{(0.5-x)} = \sqrt{50} = 7.07$$

$$2x = 0.5 \times 7.07 - 7.07x$$

$$2x + 7.07x = 0.5 \times 7.07$$

$$x = \frac{0.5 \times 7.07}{9.07} = 0.39 \text{ mole}$$

or

(b) No. of moles of I_2 at equilibrium = $(0.5 - 0.39) = 0.11$ mole

$$K_p = K_c (RT)^{\Delta n}$$

As $\Delta n = 0$, $K_p = K_c = 50$

Example 14. 25 mL of H_2 and 18 mL of I_2 vapours were heated in a sealed glass tube at 465°C and at equilibrium 30.8 mL of HI was formed. Calculate the percentage degree of dissociation of HI at 465°C.

Solution: Since, the number of moles in a gas under the same conditions of temperature and pressure are proportional to volumes (Avogadro's Law), the volumes in mL of gases may be used instead of concentrations in the case of reversible reactions in which there is no change in the number of molecules of reactants and products.

$$\text{Given, } 2x = 30.8 \text{ mL}$$

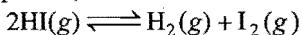
$$\text{So, } x = 15.4 \text{ mL}$$

$$\text{Vol. of } H_2 \text{ at equilibrium} = (25 - 15.4) = 9.6 \text{ mL}$$

$$\text{Vol. of } I_2 \text{ at equilibrium} = (18 - 15.4) = 2.6 \text{ mL}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(30.8)^2}{9.6 \times 2.6} = 38.0$$

Consider the equation,



Let the degree of dissociation be x

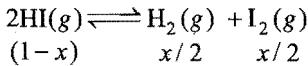
$$K'_c = \frac{x^2}{4(1-x)^2} \quad \left(K'_c = \frac{1}{K_c} = \frac{1}{38} \right)$$

$$\frac{1}{38} = \frac{x^2}{4(1-x)^2} \quad \text{or} \quad \frac{1}{6.1644} = \frac{x}{2(1-x)}$$

$$\text{or} \quad x = 0.245, \text{ i.e., } 24.5\% \text{ dissociated}$$

Example 15. 3.2 mole of HI were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation was found to be 20%. Calculate the number of moles of hydrogen iodide, hydrogen and iodine present at the equilibrium point and determine the equilibrium constant.

Solution: The dissociation of HI is represented by the equation,



Degree of dissociation, $x = 0.20$ and initial concentration of HI , $a = 3.2$ mole.

At equilibrium,

$$\text{No. of moles of } HI = a(1-x) = 3.2 \times 0.8 = 2.56$$

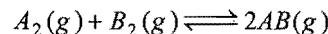
$$\text{No. of moles of } H_2 = \frac{a \cdot x}{2} = 3.2 \times 0.1 = 0.32$$

$$\text{No. of moles of } I_2 = \frac{a \cdot x}{2} = 3.2 \times 0.1 = 0.32$$

$$K_c = \frac{x^2}{4(1-x)^2} = \frac{0.2 \times 0.2}{4 \times 0.8 \times 0.8} = 0.0156$$

$$\text{Also, } K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.32 \times 0.32}{2.56 \times 2.56} = 0.0156$$

Example 16. The equilibrium constant of the reaction,



at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2 , how many moles of AB will be formed at 373 K?

Solution:

	$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$
Initial no. of moles	1
No. of moles at equilibrium	$(1-x)$
(Total volume = 3 litre)	$(2-x)$
Active masses	$\frac{(1-x)}{3} \quad \frac{(2-x)}{3} \quad \frac{2x}{3}$

Applying law of mass action,

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = \frac{4x^2}{(1-x)(2-x)}$$

$$\text{But, } \frac{4x^2}{(1-x)(2-x)} = 50$$

$$\text{or} \quad 4x^2 = (2 - 3x + x^2)50$$

$$\text{or} \quad 2x^2 = (2 - 3x + x^2)25$$

$$\text{or} \quad 23x^2 - 75x + 50 = 0$$

$$x = \frac{75 \pm \sqrt{(75)^2 - 4 \times 23 \times 50}}{2 \times 23}$$

$$x = 2.317 \text{ or } 0.934$$

The value of x cannot be more than 1, i.e., greater than the number of moles of A_2 and hence $x = 0.943$.

$$\text{No. of moles of } AB = 2x = (2 \times 0.934)$$

$$= 1.868$$

Example 17. The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\text{Mol. mass of } N_2O_4 = (28 + 64) = 92$$

$$\text{Vapour density, } D = \frac{92}{2} = 46$$

Let the degree of dissociation be x

$$\text{Given, } d = 30$$

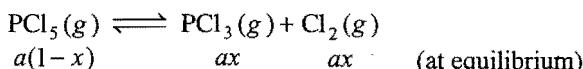
Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

$$\text{Degree of dissociation} = 53.3\%$$

Example 18. 3 g mole of phosphorus pentachloride is heated in a flask of 4 litre volume. At equilibrium it dissociates to give 40% of phosphorus trichloride and chlorine. Calculate the equilibrium constant.

Solution: Degree of dissociation = 0.4



Given, $a = 3$, $x = 0.4$ and $V = 4$.

So, at equilibrium,

$$[\text{PCl}_5] = \frac{3(1-0.4)}{4} = \frac{3 \times 0.6}{4} \text{ mol L}^{-1}$$

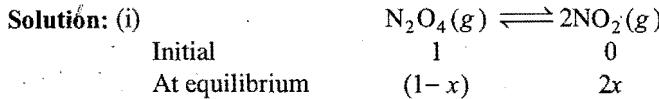
$$[\text{PCl}_3] = \frac{3 \times 0.4}{4} \text{ mol L}^{-1}$$

$$[\text{Cl}_2] = \frac{3 \times 0.4}{4} \text{ mol L}^{-1}$$

Applying law of mass action,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{3 \times 0.4 \times 3 \times 0.4}{4 \times 3 \times 0.6} = 0.2 \text{ mol L}^{-1}$$

Example 19. N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C .



$$\text{Total moles} = (1-x) + 2x = (1+x)$$

$$p_{\text{N}_2\text{O}_4} = \left(\frac{1-x}{1+x} \right) P, \quad p_{\text{NO}_2} = \frac{2x}{(1+x)} \cdot P$$

Given, $x = 0.25$ and $P = 1 \text{ atm}$

$$p_{\text{N}_2\text{O}_4} = \left(\frac{1-0.25}{1+0.25} \right) \times 1 = 0.6 \text{ atm}$$

$$p_{\text{NO}_2} = \left(\frac{2 \times 0.25}{1+0.25} \right) \times 1 = 0.4 \text{ atm}$$

$$K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ atm}$$

(ii) Let the degree of dissociation of N_2O_4 at 0.1 atm be ' α ', then,

$$p_{\text{N}_2\text{O}_4} = \left(\frac{1-\alpha}{1+\alpha} \right) \times 0.1 \text{ and } p_{\text{NO}_2} = \frac{2\alpha}{(1+\alpha)} \times 0.1$$

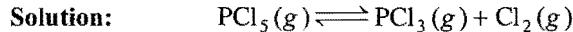
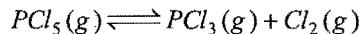
$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha} \right)^2 \times (0.1)^2}{\left(\frac{1-\alpha}{1+\alpha} \right) \times 0.1} = \frac{4\alpha^2 \times 0.1}{(1-\alpha)(1+\alpha)} = \frac{0.4\alpha^2}{(1-\alpha^2)}$$

$$\text{or } 0.267 = \frac{0.4\alpha^2}{(1-\alpha^2)} \text{ or } 0.267 = 0.667\alpha^2$$

$$\alpha = 0.632$$

Hence, dissociation of $\text{N}_2\text{O}_4 = 63.2\%$

Example 20. 1.0 mole of nitrogen and 3.0 moles of PCl_5 are placed in 100 litre vessel heated to 227°C . The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction,



Initial	3	0	0
At equilibrium	$3(1-x)$	$3x$	$3x$

(x = degree of dissociation)

$$\text{Total moles} = 3(1-x) + 3x + 3x = 3(1+x)$$

1 mole of nitrogen is present, hence actual total number of moles at equilibrium = $3(1+x) + 1$

According to gas equation,

$$PV = nRT$$

Given, $P = 2.05 \text{ atm}$, $V = 100 \text{ litres}$, $R = 0.082$

$$\text{and } T = (273 + 227) = 500 \text{ K}$$

$$\text{So, } n = \frac{2.05 \times 100}{0.082 \times 500} = 5$$

$$\text{or } 3(1+x) + 1 = 5$$

$$3x = 1 \text{ or } x = 0.333$$

$$\text{Thus, } 3(1+x) + 1 = 3 + 3 \times 0.333 + 1 = 4 + 0.999$$

$$\text{At equilibrium, } p_{\text{PCl}_5} = \frac{3(1-x)}{(3x+4)} \times 2.05$$

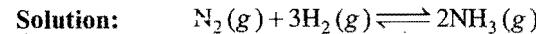
$$p_{\text{PCl}_3} = p_{\text{Cl}_2} = \frac{3x}{(3x+4)} \times 2.05$$

$$K_p = \frac{\frac{3x}{(3x+4)} \times 2.05 \times \frac{3x}{(3x+4)} \times 2.05}{\frac{3(1-x)}{(3x+4)} \times 2.05}$$

$$= \frac{9x^2 \times 2.05}{3(3x+4)(1-x)} = \frac{3 \times (0.333)^2 \times 2.05}{(4+0.999)(0.667)}$$

$$= 0.204 \text{ atm}$$

Example 21. For a gas reaction, $3\text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2\text{NH}_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere, respectively. The total pressure of the entire system is 2.8 atmosphere. What will be the value of K_p if all the concentrations are given in atmospheres?



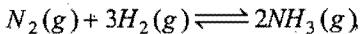
$$\begin{array}{ll} \text{Partial pressures} & 0.8 \quad 0.4 \\ \text{at equilibrium} & [2.8 - (0.8 + 0.4)] = 1.6 \end{array}$$

Applying law of mass action,

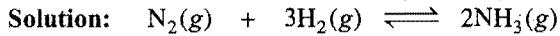
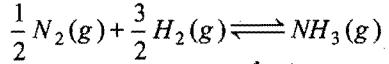
$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} = \frac{1.6 \times 1.6}{0.8 \times 0.4 \times 0.4 \times 0.4}$$

$$= 50 \text{ atm}^{-2}$$

Example 22. One mole of nitrogen and three moles of hydrogen are mixed in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction:



calculate the equilibrium constant (K_c) in concentration units. What will be the value of K for the following equilibrium?



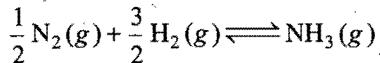
At equilibrium	$(1-x)$	$(3-3x)$	$2x(x=0.0025)$
Active masses	$\frac{(1-0.0025)}{4}$	$\frac{(3-0.0075)}{4}$	$\frac{(0.0050)}{4}$

Applying law of mass action,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{0.0050}{4}\right)^2}{\left(\frac{0.9975}{4}\right)\left(\frac{2.9925}{4}\right)^3}$$

$$= 1.49 \times 10^{-5} \text{ litre}^2 \text{ mol}^{-2}$$

K for the reaction,



is equal to $\sqrt{K_c}$.

$$K = \sqrt{K_c} = \sqrt{1.49 \times 10^{-5}}$$

$$= 3.86 \times 10^{-3} \text{ litre mol}^{-1}$$

Example 23. In an experiment one mole of acetic acid and one mole of alcohol were allowed to react until equilibrium was established. The equilibrium mixture was found to contain 2/3 mole of ester. Calculate the equilibrium constant of the reaction.

Solution:



Initial no. of moles	1	1	0	0
No. of moles at equilibrium	$\left(1 - \frac{2}{3}\right)$	$\left(1 - \frac{2}{3}\right)$	$\frac{2}{3}$	$\frac{2}{3}$
Active masses	$\frac{1}{3V}$	$\frac{1}{3V}$	$\frac{2}{3V}$	$\frac{2}{3V}$

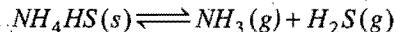
V is the total volume in litres.

Applying law of mass action,

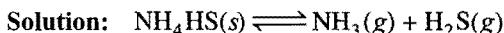
$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]}$$

$$= \frac{\frac{2}{3V} \times \frac{2}{3V}}{\frac{1}{3V} \times \frac{1}{3V}} = 4$$

Example 24. Ammonium hydrogen sulphide dissociates according to the equation:



If the observed pressure at equilibrium is 1.12 atm at 380 K, what is the equilibrium constant K_p of the reaction?

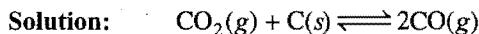


$$p_{NH_3} = p_{H_2S} = \frac{1}{2} \times 1.12 = 0.56 \text{ atm}$$

$$K_p = p_{NH_3} \times p_{H_2S} = 0.56 \times 0.56 = 0.3136$$

Example 25. A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K_p if total pressure at equilibrium is 0.8 atm.

(IIT 1993)



Initial	0.5 atm	0 atm
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At equilibrium	$(0.5-x)$ atm	$2x$ atm
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At equilibrium, the total pressure is 0.8 atm.

$$p_{\text{total}} = p_{CO_2} + p_{CO}$$

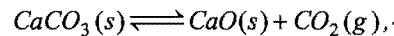
$$0.8 = (0.5-x) + 2x = 0.5 + x$$

or $x = 0.3 \text{ atm}$

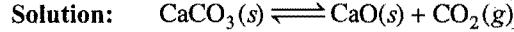
Applying law of mass action,

$$K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(2 \times 0.3)^2}{0.2} = \frac{0.36}{0.2} = 1.8 \text{ atm}$$

Example 26. A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.654 litre and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction,



is 3.9×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.



$$K_p = p_{CO_2}$$

Let the number of moles of CO_2 be formed = n

$$n = \frac{p_{CO_2} \times V}{RT} = \frac{3.9 \times 10^{-2} \times 0.654}{0.082 \times 1000}$$

$$= 3.11 \times 10^{-4} \text{ mol}$$

The amount of $CaO(s)$ formed will also be $= 3.11 \times 10^{-4}$ mol

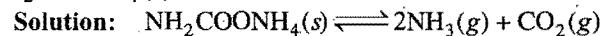
Hence, mass of CaO formed $= 3.11 \times 10^{-4} \times 56 = 0.0174 \text{ g}$

Example 27. The decomposition of ammonium carbamate at 30°C is represented as:



The equilibrium constant K_p is $2.9 \times 10^{-5} \text{ atm}^3$.

What is the total pressure of gases in equilibrium with $NH_2COONH_4(s)$ at 30°C?



At equilibrium	$(1-x)$	$2x$	x
----------------	---------	------	-----

$$K_p = (p_{NH_3})^2 \times p_{CO_2}$$

$$2.9 \times 10^{-5} = (2x)^2 \times x = 4x^3$$

$$x = \left(\frac{2.9 \times 10^{-5}}{4} \right)^{1/3} = 0.0194 \text{ atm}$$

Total pressure = $2x + x = 3x = 3 \times 0.0194 = 0.0582 \text{ atm}$

Example 28. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at 100°C , the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Calculate the equilibrium constant of this reaction.

Solution:

$\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$			
Initial	1	1	0
At equilibrium	$1-x$	$1-x$	x
	$1-0.543$	$1-0.543$	0.543

Given, $x = 0.543$.

Applying law of mass action,

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$$

Example 29. The equilibrium constant for the reaction, $\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$ is 4. What will be the composition of the equilibrium mixture when one mole of acetic acid is taken along with 4 moles of ethyl alcohol?

Solution:

$\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$			
Initial	1	4	0
At equilibrium	$1-x$	$4-x$	x

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{x^2}{(1-x)(4-x)} = 4$$

$$x^2 = 4(1-x)(4-x)$$

$$= 4[4 - 5x + x^2]$$

$$= 16 - 20x + 4x^2$$

or

$$3x^2 - 20x + 16 = 0$$

$$x = \frac{20 \pm \sqrt{400 - 192}}{6} = \frac{20 \pm 14.42}{6}$$

$$x = 0.93 \text{ or } 5.7366$$

The value 5.7366 is not possible, hence $x = 0.93$

Thus, the composition of mixture at equilibrium is

$$[\text{CH}_3\text{COOH}] = (1 - 0.93) = 0.07 \text{ mole}$$

$$[\text{C}_2\text{H}_5\text{OH}] = (4 - 0.93) = 3.07 \text{ mole}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = 0.93 \text{ mole}$$

$$[\text{H}_2\text{O}] = 0.93 \text{ mole}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. For the reaction, $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$, the value of K_c at 600°C is 0.1. When the equilibrium concentrations of both the reactants is 0.5 mol, what is the value of K_p at the same temperature? (KCET 2005)

- (a) 0.5 (b) 0.1 (c) 0.01 (d) 0.025

[Ans. (b)]

[Hint: $K_p = K_c(RT)^{\Delta n}$]

Since, $\Delta n = 0$, hence, $K_p = K_c$]

8. $A(g) + 3B(g) \rightleftharpoons 4C(g)$, initial concentration of A is equal to that of B . The equilibrium concentrations of A and C are equal. K_c of the reaction will be:

- (a) 0.08 (b) 0.8 (c) 8 (d) 80
(e) 1/8

[Ans. (c)]

[Hint: $A(g) + 3B(g) \rightleftharpoons 4C(g)$

$t = 0$	a	a	0
$t_{eq.}$	$a - x$	$a - 3x$	$4x$

$$a - x = 4x \text{ given}$$

$$a = 5x$$

$$K_c = \frac{[C]^4}{[A][B]^3} = \frac{[4x]^4}{[4x][2x]^3} = \frac{256}{32} = 8$$

9. For a hypothetical reaction:



The equilibrium constant K_c has units:

- (a) mol L^{-1} (b) $\text{mol}^{-1} \text{L}$
(c) $(\text{mol L}^{-1})^{-2}$ (d) unitless

[Ans. (a)]

[Hint: Unit of $K_c = (\text{mol L}^{-1})^{\Delta n}$

$$= (\text{mol L}^{-1})^1 = \text{mol L}^{-1}]$$

10. Starting with 1 mol of O_2 ; 2 mol of SO_2 , the equilibrium for the formation of $\text{SO}_3(g)$ was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present, the equilibrium constant will be:

$$(a) \frac{x^2 V}{(1-x)^3} \quad (b) \frac{4x^2}{(2-x)(1-x)}$$

$$(c) \frac{(1-x)^3}{2V} \quad (d) \frac{x^2}{(2-x)(1-x)}$$

[Ans. (a)]

[Hint: $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$

$t = 0$	$\frac{2}{V}$	$\frac{1}{V}$	0
$t_{eq.}$	$\frac{2-2x}{V}$	$\frac{1-x}{V}$	$\frac{2x}{V}$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{[2x/V]^2}{\left[\frac{2-2x}{V}\right]^2 \left[\frac{1-x}{V}\right]} = \frac{x^2 V}{(1-x)^3}$$

11. For the reaction, $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$, $K = 47.6$, if the initial number of moles of each reactant and product is 1 mole, then at equilibrium: [JEE (Orissa) 2006]

- (a) $[\text{I}_2] = [\text{H}_2]; [\text{I}_2] > [\text{HI}]$ (b) $[\text{I}_2] < [\text{H}_2]; [\text{I}_2] = [\text{HI}]$
(c) $[\text{I}_2] = [\text{H}_2]; [\text{I}_2] < [\text{HI}]$ (d) $[\text{I}_2] > [\text{H}_2]; [\text{I}_2] = [\text{HI}]$

[Ans. (c)]

[Hint: $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

$[\text{H}_2] = [\text{I}_2]$ will be same at equilibrium, since it is same at initial state.

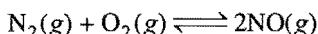
$$K_c = \frac{[\text{HI}]^2}{[\text{I}_2]^2}$$

$$K_c [I_2]^2 = [HI]^2$$

$$47.6 [I_2]^2 = [HI]^2$$

$$[I_2] < [HI]$$

12. In a closed vessel of volume V , a mol of nitrogen and b mol of oxygen are made to react to give nitric oxide, according to the reaction:



If at equilibrium, $2x$ mol of NO are obtained, then:

[BV (Pune) 2006]

$$(a) K_c = \frac{4x^2}{(a-x)(b-x)} \times \frac{1}{V}$$

$$(b) K_c = \frac{4x^2}{(a-x)(b-x)} \times V$$

$$(c) K_c = \frac{x^2}{(a-x)(b-x)} \times V$$

$$(d) K_c = \frac{4x^2}{(a-x)(b-x)}$$

[Ans. (d)]

[Hint: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$\begin{array}{cccc} t=0 & a & b & 0 \\ t_{eq.} & \frac{(a-x)}{V} & \left(\frac{b-x}{V}\right) & \frac{2x}{V} \end{array}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

13. Equivalent amounts of H_2 and I_2 are heated in a closed till equilibrium is obtained. If 80% of the hydrogen can be converted to HI, the K_c at this temperature is: (VITEEE 2007)

- (a) 64 (b) 16 (c) 0.25 (d) 4

[Ans. (a)]

[Hint: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$\begin{array}{cccc} t=0 & 1 & 1 & 0 \\ t_{eq.} & \frac{1-0.8}{V} & \frac{1-0.8}{V} & \frac{2 \times 0.8}{V} \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\frac{1.6}{V}\right]^2}{\frac{0.2}{V} \times \frac{0.2}{V}} = 64$$

14. Equimolar concentration of H_2 and I_2 are heated to equilibrium in a 2 litre flask. At equilibrium, the forward and backward rate constants are found to be equal. What percentage of initial concentration of H_2 has reacted at equilibrium? [FMAT (Kerala) 2006]

- (a) 33% (b) 66%
 (c) 50% (d) 40%

[Ans. (a)]

[Hint: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$\begin{array}{cccc} t_0 & 1 & 1 & 0 \\ t_{eq.} & \frac{1-x}{2} & \frac{1-x}{2} & \frac{2x}{2} \end{array}$$

$$K = \frac{k_f}{k_b} = 1 = \frac{[HI]^2}{[H_2][I_2]} = \frac{(x)^2}{\left(\frac{1-x}{2}\right)\left(\frac{1-x}{2}\right)}$$

$$1 = \frac{4x^2}{(1-x)^2}$$

$$1 = \frac{2x}{1-x}$$

$$x = 0.33$$

$$\% \text{ of } H_2 \text{ reacted} = 33]$$

9.8 LE CHATELIER'S PRINCIPLE

There are three main factors which can change the state of equilibrium in a reversible system. These are concentration, pressure and temperature. Le Chatelier, a French chemist, presented a qualitative principle known as Le Chatelier's principle which can describe the effect of change in concentration, pressure and temperature on any reversible system whether physical or chemical.

According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

Or

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to annul the effect of that change.

(a) Change in concentration: If an additional amount of any reactant or product is added to the system, the stress is relieved as the reaction that consumes the added substance occurs more rapidly than its reverse reaction, i.e., if any of the reactants is added, the rate of forward reaction increases and if any of the products is added, the rate of backward reaction increases.

In general, in a chemical equilibrium, increasing the concentrations of the reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of reactants.

(b) Change in pressure: If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more than before. According to Le Chatelier's principle, the equilibrium will shift in the direction in which there is decrease in number of moles, i.e., towards the direction in which there is decrease in volume.

In general, an increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller number of moles of gases and a decrease in pressure favours the opposite reaction. If there is no change in number of moles of gases in a reaction, a pressure change does not affect the equilibrium.

(c) Change in temperature: A chemical reaction (reversible) involves two opposing reactions, forward and

backward. If one reaction is endothermic, the other will be exothermic in nature. When heat energy is added by raising temperature, the system can relieve itself from the stress if the reaction which absorbs heat moves faster, i.e., **endothermic reaction is always favoured with increase of temperature.**

Conclusions:

- Increase in concentration of any substance favours the reaction in which it is used up.
- High pressure is favourable for the reaction in which there is decrease in volume.
- A rise in temperature favours the endothermic reaction.
- Role of catalyst:** Positive catalyst increases the rate of both forward and backward reactions equally; the equilibrium will be attained in less time, i.e., same amount of product will be formed in less time.

On the other hand, negative catalyst lowers the rate of both forward and backward reactions equally. Same amount of product will be formed in more time.

Catalyst does not affect equilibrium constant and heat of reaction.

Summary of Le Chatelier's Principle

Effect of inert gas addition

Condition	Effect
$\Delta V = 0, V = \text{Constant}$	$\Delta n = 0, +\text{ve or } -\text{ve}$ No effect
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n = 0$ No effect
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n > 0$ Forward shift
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n < 0$ Backward shift

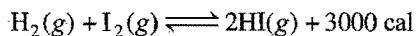
where, Δn = number of gaseous moles of product – number of gaseous moles of reactant

Effect of temperature and pressure

Nature of reaction	Effect of increased temperature	Δn ; Side with fewer mole of gas	Effect of increase in P
1. Exothermic	backward shift	0; neither	no shift
2. Exothermic	backward shift	-ve; right	forward shift
3. Endothermic	forward shift	-ve; right	forward shift
4. Endothermic	forward shift	+ve; left	backward shift
5. Exothermic	backward shift	+ve; left	backward shift
6. Exothermic	backward shift	-ve; right	forward shift
7. Endothermic	forward shift	+ve; left	backward shift
8. Endothermic	forward shift	+ve; left	backward shift

Application of Le Chatelier's Principle

(a) Formation of HI:



Effect of concentration: When concentration of H_2 or I_2 is increased at equilibrium, the system moves in a direction which decreases the concentration, i.e., the rate of forward reaction increases thereby increasing the concentration of HI.

Effect of pressure: As there is no change in the number of moles in the reaction, the equilibrium state remains unaffected by change of pressure.

Effect of temperature: By increasing temperature, the equilibrium state shifts towards the reaction which moves with

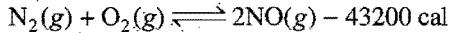
absorption of heat. The formation of HI is an exothermic reaction. Thus, the backward reaction moves faster when temperature is increased.

In short, we can say that the favourable conditions for greater yield of HI are:

- High concentrations of H_2 and I_2 and

(ii) Low temperature.

(b) Formation of nitric oxide:



Effect of concentration: When concentration of N_2 or O_2 is increased, the system moves in a direction in which N_2 or O_2 is used up, i.e., rate of forward reaction increases thereby increasing the concentration of NO.

Effect of pressure: In the formation of nitric oxide, the number of moles remains the same, i.e., no change in volume occurs. Consequently, the equilibrium state is not affected by any change in pressure.

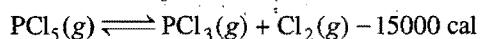
Effect of temperature: The formation of NO is endothermic in nature. If the temperature is raised, the equilibrium shifts in the direction in which heat is absorbed. The concentration of NO will, therefore, be higher at higher temperature.

Thus, favourable conditions for greater yield of nitric oxide are:

- High concentrations of N_2 and O_2 and

(ii) High temperature

(c) Dissociation of PCl_5 :



Effect of concentration: When concentration of PCl_5 is increased at equilibrium, the rate of forward reaction increases as to decrease the added concentration. Thus, more of PCl_3 and Cl_2 are formed.

Effect of pressure: The volume increases in the dissociation of PCl_5 . When pressure is increased, the system moves in the direction in which there is decrease in volume. Thus, high pressure does not favour dissociation of PCl_5 .

Effect of temperature: The dissociation of PCl_5 is an endothermic reaction. Thus, increase of temperature favours the dissociation.

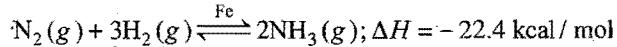
Thus, favourable conditions for dissociation of PCl_5 are:

- High concentration of PCl_5 ,

(ii) Low pressure and

(iii) High temperature.

(d) Formation of ammonia:



(i) At high pressure reaction will shift in forward direction to form more product.

(ii) When concentration of N_2 and H_2 is raised or concentration of NH_3 is lowered, then again the equilibrium shifts in forward direction to form more ammonia.

If concentration of only one reactant is raised, then again the equilibrium shifts in forward direction till the other reactant is available for reaction.

- (iii) The reaction shifts in forward direction at low temperature. But at very low temperature the rate of reaction becomes very low; thus moderate temperature is favourable for this reaction.

9.9 APPLICATION OF LE CHATELIER'S PRINCIPLE TO PHYSICAL EQUILIBRIA

(i) Solid \rightleftharpoons Liquid \rightleftharpoons Gas

When temperature is raised, the above equilibrium shifts in forward direction.

(ii) **Effect of pressure on boiling point:** When pressure is raised, condensation of vapour takes place. Thus, vapour pressure is lowered. Now more heat is required to equate vapour pressure with atmospheric pressure as a result of which boiling point increases.

(iii) **Effect of pressure on melting point:** There are two types of solids:

(a) Solids whose volume decreases on melting, e.g., ice, diamond, carborundum, magnesium nitride and quartz.

Solid (higher volume) \rightleftharpoons Liquid (lower volume)

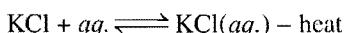
The process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solids whose volume increases on melting, e.g., Fe, Cu, Ag, Au, etc.

Solid (lower volume) \rightleftharpoons Liquid (higher volume)

In this case the process of melting become difficult at high pressure; thus melting point becomes high.

(c) **Solubility of substances:** When solid substances are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).



In such cases, solubility increases with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.

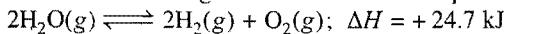


In such cases, solubility decreases with increase in temperature.

(d) **Solubility of gases in liquids:** When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

15. Consider the following reversible reaction at equilibrium:



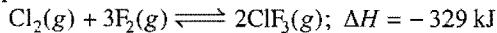
which one of the following changes in conditions will lead to maximum decomposition of $\text{H}_2\text{O(g)}$?

- (a) Increasing both temperature and pressure
- (b) Decreasing temperature and increasing pressure
- (c) Increasing temperature and decreasing pressure
- (d) Increasing temperature at constant pressure
- (e) Increasing pressure at constant temperature

[Ans. (c)]

[Hint: Reaction is endothermic and $\Delta n > 0$, hence, the formation of product will be favoured by increasing the temperature and decreasing the pressure.]

16. The exothermic formation of ClF_3 is represented by the equation:



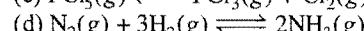
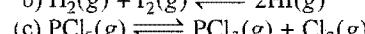
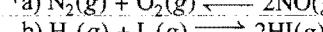
Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 and ClF_3 ? (AIIEEE 2005)

- (a) Increasing the temperature
- (b) Removing Cl_2
- (c) Increasing the volume of the container
- (d) Adding F_2

[Ans. (d)]

[Hint: Equilibrium will shift in forward direction by increasing the concentration of reactant.]

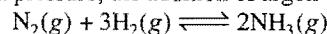
17. Which among the following reactions will be favoured at low pressure?



[Ans. (c)]

[Hint: On lowering the pressure, equilibrium favours the direction of higher volume.]

18. At constant pressure, the addition of argon to:



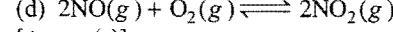
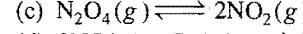
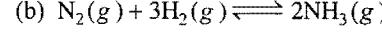
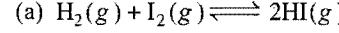
will:

- (a) shift the equilibrium in forward direction
- (b) shift the equilibrium in backward direction
- (c) not affect the equilibrium
- (d) stop the reaction

[Ans. (b)]

[Hint: If volume is not constant, the addition of inert gas favours the direction where volume is increasing.]

19. The equilibrium reaction that is not influenced by volume change at constant temperature is: (CET (J&K) 2006)



[Ans. (a)]

[Hint: When, $\Delta n = 0$, there is no effect of pressure and volume change on the equilibrium.]

20. $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)} + \text{Heat}$

What is the effect of the increase of temperature on the equilibrium of the reaction? (KCET 2003)

- (a) Equilibrium is unaltered
- (b) Reaction rate does not change
- (c) Equilibrium is shifted to the left
- (d) Equilibrium is shifted to the right

[Ans. (c)]

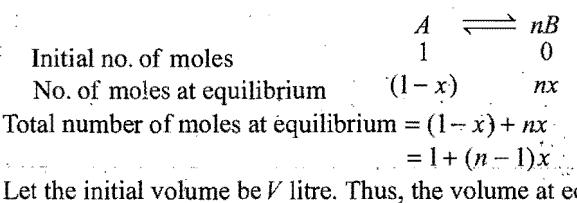
[Hint: The given reaction is exothermic, therefore, the equilibrium will shift in backward direction by the increase of temperature.]

9.10 CALCULATION OF DEGREE OF DISSOCIATION FROM DENSITY MEASUREMENTS

Degree of dissociation is defined as the fraction of one molecule dissociated. It is denoted by x or α . Its value is always less than 1. When the value becomes equal to 1, it is said that the substance is completely dissociated.

The degree of dissociation in the case of second type of reactions (reversible) is determined by measuring density of reaction mixture at equilibrium.

Consider the general reversible reaction,



Let the initial volume be V litre. Thus, the volume at equilibrium
 $= [1 + (n-1)x]V$.

Let 'd' be the observed vapour density at a particular temperature when degree of dissociation is 'x' and D be the vapour density when there is no dissociation. Again,

$$D \propto \frac{1}{V} \quad \dots (i)$$

$$\text{and} \quad d \propto \frac{1}{[1 + (n-1)x]V} \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii),

$$\frac{D}{d} = 1 + (n-1)x$$

$$\text{or} \quad \frac{D}{d} - 1 = (n-1)x$$

$$\text{or} \quad \frac{D-d}{d} = (n-1)x$$

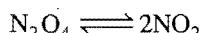
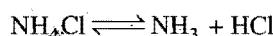
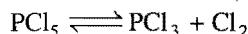
$$\text{or} \quad x = \frac{D-d}{(n-1)d} \quad \dots (iii)$$

$$x = \frac{M-m}{(n-1)m}$$

where, M = initial molecular mass

m = molecular mass at equilibrium.

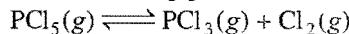
In the dissociation of PCl_5 , NH_4Cl and N_2O_4 , the value of $n = 2$.



$$\text{So, } x = \frac{D-d}{(2-1)d} = \frac{D-d}{d}$$

Calculation of Degree of Reaction using Pressure-Temperature Determination

Let us consider the following gaseous reaction:



Initial pressure and temperature are P_1 and T_1 . At equilibrium, pressure and temperature are P_2 and T_2 respectively. The volume of vessel is constant, equal to ' V '.

		n	V	T	P
$t = 0$	a	0	0	a	V
$t_{\text{eq.}}$	$a - ax$	ax	ax	$a + ax$	V
Initial state				$P_1 V = aRT_1$... (i)
Equilibrium state				$P_2 V = (a + ax)RT_2$... (ii)
Dividing equation (i) by eq. (ii), we get					
		$\frac{P_1}{P_2} = \frac{T_1}{(1+x)T_2}$			
		$(1+x) = \frac{T_1 P_2}{T_2 P_1}$			
		$x = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$			

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

21. At equilibrium:

$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 the observed molecular weight of N_2O_4 is 80 g mol⁻¹ at 350 K. The percentage dissociation of $\text{N}_2\text{O}_4(g)$ at 350 K is:

- (a) 10% (b) 15% (c) 20% (d) 18%
 (e) 13%

[Ans. (b)]

[Hint: Degree of dissociation may be calculated as,

$$\begin{aligned} x &= \frac{M-m}{(n-1)m} \quad \because n = 2 \text{ (number of gas moles produced by 1 mol reactant)} \\ &= \frac{92-80}{(2-1)80} \quad (M = 92, m = 80) \\ &= \frac{12}{80} = 0.15 \end{aligned}$$

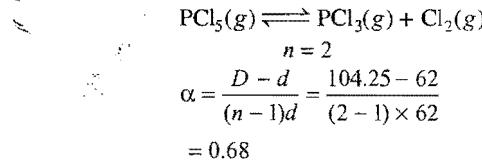
Percentage dissociation = $0.15 \times 100 = 15$]

22. The vapour density of PCl_5 is 104.25 but when heated to 230°C, its vapour density is reduced to 62. The degree of dissociation of PCl_5 at this temperature will be:

- (a) 6.8% (b) 68% (c) 46% (d) 64%

[Ans. (b)]

[Hint: The reaction is:



Percentage dissociation = $0.68 \times 100 = 68\%$]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction:



If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2 ?

Solution: $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

Initial concentration	1	1	1	1
Equilibrium concentration	$1-x$	$1-x$	$1+x$	$1+x$

Applying law of mass action,

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\frac{1+x}{1-x} = 4 \text{ or } 1+x = 4 - 4x$$

$$\text{or } 5x = 3, \text{ i.e., } x = \frac{3}{5} = 0.6$$

Conc. of NO_2 at equilibrium = $(1 - 0.6) = 0.4$ mole

Conc. of NO at equilibrium = $(1 + 0.6) = 1.6$ mole

Example 2. At $817^\circ C$, K_p for the reaction between $CO_2(g)$ and excess of hot graphite (s) is 10 atm.

(a) What are the equilibrium concentrations of the gases at $817^\circ C$ and a total pressure of 5 atm?

(b) At what total pressure does the gas contain 5% CO_2 by volume? (IIT 2000)

Solution: (a) $CO_2(g) + C(s) \rightleftharpoons 2CO(g); K_p = 10$ atm

$$\text{Given: } p_{CO(g)} + p_{CO_2(g)} = 5 \text{ atm}$$

$$\text{Let } p_{CO(g)} = x \text{ atm}$$

$$\text{So, } p_{CO_2(g)} = (5 - x) \text{ atm}$$

$$K_p = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{x^2}{(5-x)}$$

$$\text{or } 10 = \frac{x^2}{(5-x)}$$

$$\text{or } x^2 + 10x - 50 = 0$$

On solving, we get

$$x = 3.66$$

$$p_{CO(g)} = 3.66 \text{ atm}$$

or Mole fraction CO at equilibrium = 73.2% (by volume)

$$p_{CO_2(g)} = 1.34 \text{ atm}$$

or Mole fraction CO_2 at equilibrium = 26.8% (by volume)

(b) Let the total pressure be P atm

Given, % CO_2 (by volume) = 5 and % CO (by volume) = 95

$$p_{CO_2} = \frac{5}{100} \times P = 0.05P \text{ and } p_{CO} = \frac{95}{100} \times P = 0.95P$$

$$K_p = 10 = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{0.95P \times 0.95P}{0.05P} = 18.05P$$

$$\text{or } P = 0.554 \text{ atm}$$

Example 3. At 700 K , CO_2 and H_2 react to form CO and H_2O . For this process K_c is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K .

(i) Find out the amount of each gas at equilibrium state.

(ii) After equilibrium is reached another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find the composition of the mixture at the new equilibrium state.

Solution: (i) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

Initial no. of moles	0.45	0.45	0	0
of moles at equilibrium	$0.45 - x$	$0.45 - x$	x	x

Applying law of mass action,

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{x \times x}{(0.45 - x)(0.45 - x)} = \frac{x^2}{(0.45 - x)^2} = 0.11$$

So,

$$\frac{x}{(0.45 - x)} = 0.33$$

$$x = 0.11$$

At equilibrium, $[CO_2] = [H_2] = 0.34$ mole
 $[CO] = [H_2O] = 0.11$ mole

(ii) $CO_2 + H_2 \rightleftharpoons CO + H_2O$

Initial moles	0.34 + 0.34	0.34 + 0.34	0.11	0.11
	= 0.68	= 0.68		

At equilibrium $0.68 - y \quad 0.68 - y \quad 0.11 + y \quad 0.11 + y$

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{(0.11 + y)(0.11 + y)}{(0.68 - y)(0.68 - y)} = 0.11$$

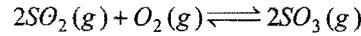
$$\text{or } \frac{0.11 + y}{0.68 - y} = 0.33$$

$$\text{or } 0.11 + y = 0.33 \times 0.68 - 0.33y$$

$$\text{or } y = 0.086$$

At equilibrium, $[CO] = [H_2O] = 0.11 + 0.086 = 0.196$ mole
 $[CO_2] = [H_2] = 0.68 - 0.086 = 0.594$ mole

Example 4. A mixture of SO_3 , SO_2 and O_2 gases is maintained in a 10 litre flask at a temperature at which the equilibrium constant for the reaction is 100:



(i) If the number of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present?

(ii) If the number of moles of SO_3 in the flask is twice the number of moles of SO_2 , how many moles of oxygen are present?

Solution: (i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

At equilibrium, let the number of moles of each of SO_2 and SO_3 be n_1 and of oxygen n_2 , i.e.,

$$[SO_2] = \frac{n_1}{10}$$

$$[O_2] = \frac{n_2}{10}$$

$$[\text{SO}_3] = \frac{n_1}{10}$$

Applying law of mass action,

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{\left(\frac{n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2 \left(\frac{n_2}{10}\right)} = 100$$

or

$$n_2 = 0.1 \text{ mole}$$

$$\text{Oxygen} = 0.1 \text{ mole}$$

(ii) Let the number of moles of SO_2 be n_1

$$\text{So, number of moles of } \text{SO}_3 = 2n_1$$

Let the number of moles of oxygen be n_2

$$K_c = \frac{\left(\frac{2n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2 \left(\frac{n_2}{10}\right)} \text{ or } 100 = \frac{40}{n_2}$$

$$n_2 = 0.4 \text{ mole}$$

$$\text{Oxygen} = 0.4 \text{ mole}$$

Example 5. At 250°C and 1 atmospheric pressure, the vapour density of PCl_5 is 57.9. Calculate (i) K_p for the reaction,



at 250°C , (ii) the percentage dissociation when pressure is doubled.

Solution: (i) Mol. mass of PCl_5 = 208.5

$$\text{Vapour density, } D = \frac{208.5}{2} = 104.25$$

$$\text{Observed vapour density, } d = 57.9$$

$$\text{Degree of dissociation, } \alpha = \frac{D - d}{d} = \frac{104.25 - 57.9}{57.9} = 0.80$$



At equilibrium	$1 - \alpha$	α	α
	$(1 - 0.80)$	0.80	0.80

$$\text{Total number of moles} = (1 + \alpha) = (1 + 0.80) = 1.80$$

$$\text{Partial pressure of } \text{PCl}_5 = \frac{0.2}{1.80} \times 1 = \frac{1}{9}$$

$$\text{Partial pressure of } \text{PCl}_3 = \frac{0.80}{1.80} \times 1 = \frac{4}{9}$$

$$\text{Partial pressure of } \text{Cl}_2 = \frac{0.80}{1.80} \times 1 = \frac{4}{9}$$

$$\text{So, } K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{4/9 \times 4/9}{1/9} = \frac{16}{9} = 1.78$$

(ii) Let the degree of dissociation be α when pressure is 2 atmospheres.

At equilibrium

$$p_{\text{PCl}_5} = \frac{(1 - \alpha)}{(1 + \alpha)} \cdot P = \frac{(1 - \alpha)}{(1 + \alpha)} \times 2$$

$$p_{\text{PCl}_3} = \frac{\alpha}{(1 + \alpha)} \cdot P = \frac{\alpha}{(1 + \alpha)} \times 2$$

$$p_{\text{Cl}_2} = \frac{\alpha}{(1 + \alpha)} \cdot P = \frac{\alpha}{(1 + \alpha)} \times 2$$

$$K_p = \frac{\frac{\alpha}{(1 + \alpha)} \times 2 \times \frac{\alpha}{(1 + \alpha)} \times 2}{\frac{(1 - \alpha)}{(1 + \alpha)} \times 2} = \frac{\alpha^2}{(1 - \alpha^2)} \times 2 = 1.78$$

$$\text{or } \frac{\alpha^2}{(1 - \alpha^2)} = 0.89$$

$$\text{or } \alpha^2 = 0.89 - 0.89\alpha^2$$

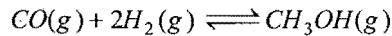
$$\text{or } 1.89\alpha^2 = 0.89$$

$$\alpha^2 = \frac{0.89}{1.89}$$

$$\alpha = 0.686$$

Thus, PCl_5 is 68.6% dissociated.

Example 6. For the reaction,



hydrogen gas is introduced into a five litre flask at 327°C , containing 0.2 mole of $\text{CO}(g)$ and a catalyst, until the pressure is 4.92 atmosphere. At this point 0.1 mole of $\text{CH}_3\text{OH}(g)$ is formed. Calculate the equilibrium constants K_p and K_c . (IIT 1998)

Solution: Let the number of moles of hydrogen introduced be m moles.

$$\text{Total moles of CO and hydrogen} = 0.2 + m$$

$$\text{Applying, } PV = nRT$$

$$P = 4.92 \text{ atm}, V = 5 \text{ litre}, R = 0.082,$$

$$T = (273 + 327) = 600 \text{ K}$$

$$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$$

$$\text{or } 0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}$$

$$\text{or } m = 0.3 \text{ mole}$$

$\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$	$0.2 - x$	$0.3 - 2x$	x	(No. of moles at equilibrium)
	0.2 - 0.1	0.3 - 0.2	0.1	
	0.1	0.1	0.1	
	$\frac{0.1}{5}$	$\frac{0.1}{5}$	$\frac{0.1}{5}$	(Active masses)

Applying law of mass action,

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{\frac{0.1}{5}}{\frac{0.1}{5} \times \left(\frac{0.1}{5}\right)^2} = 2500 \text{ mol}^{-2} \text{ L}^2$$

We know that, $K_p = K_c (RT)^{\Delta n}$, $\Delta n = -2$

$$\text{or } K_p = 2500(0.082 \times 600)^{-2}$$

$$\text{or } K_p = \frac{2500}{49.2 \times 49.2} = 1.0327 \text{ atm}^{-2}$$

Example 7. 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 this reaction.

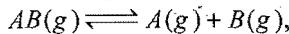
Solution: $S_8(g) \rightleftharpoons 4S_2(g)$

Initial mole	1	0
At equilibrium	$1-x$	$4x$
	$(1-0.29)$	(4×0.29)
	= 0.71	= 1.16

Applying law of mass action,

$$K_p = \frac{[p_{S_2}]^4}{[p_{S_8}]} = \frac{(1.16)^4}{0.71} = 2.5582 \text{ atm}^3$$

Example 8. For the equilibrium,

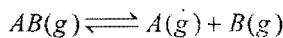


K_p is equal to four times the total pressure. Calculate the number of moles of A formed.

Solution: Let the total equilibrium pressure be = P atm

$$\text{Given, } K_p = 4P$$

Let the start be made with 1 mole of $AB(g)$ and the degree of dissociation be x .



$$\text{At equilibrium } 1-x \quad x \quad x$$

$$\text{Total moles at equilibrium} = 1-x+x+x = 1+x$$

$$\text{Thus, } p_A = \text{Partial pressure of } A = \frac{x}{1+x} \cdot P$$

$$p_B = \text{Partial pressure of } B = \frac{x}{1+x} \cdot P$$

$$p_{AB} = \text{Partial pressure of } AB = \frac{1-x}{1+x} \cdot P$$

Applying the law of mass action,

$$K_p = \frac{p_A \times p_B}{p_{AB}} = \frac{\left(\frac{x}{1+x} \cdot P\right)\left(\frac{x}{1+x} \cdot P\right)}{\left(\frac{1-x}{1+x} \cdot P\right)}$$

$$\text{So, } 4P = \frac{x^2}{1-x^2} \cdot P$$

$$\text{or } 4 - 4x^2 = x^2$$

or

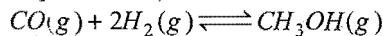
$$5x^2 = 4$$

or

$$x = \frac{2}{\sqrt{5}}$$

Hence, number of moles of A formed = $\frac{2}{\sqrt{5}}$ times initial moles of AB taken

Example 9. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 705 K along with a catalyst so that the following reaction can take place:



Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. (IIT 1993)

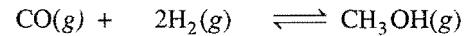
Solution: (i) Let the total number of moles of gases be n at equilibrium.

$$\text{Applying equation, } PV = nRT$$

$$\text{Given, } P = 8.5 \text{ atm; } V = 2.5 \text{ L;}$$

$$R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1} \text{ and } T = 705 \text{ K}$$

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367 \text{ mol}$$



Initial mole	0.15	$(nH_2)_0$	0
At equilibrium	$0.15 - x$	$[(nH_2)_0 - 2x]$	$x = 0.08$

Number of moles of CO at equilibrium

$$= (0.15 - 0.08) = 0.07 \text{ mole}$$

Number of moles of H_2 at equilibrium

$$= \text{total moles} - \text{moles of CO} - \text{moles of CH}_3\text{OH}$$

$$= (0.367 - 0.07 - 0.08)$$

$$= 0.217 \text{ mole}$$

Applying law of mass action,

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{\frac{0.08}{2.5}}{\frac{0.07}{2.5} \times \left(\frac{0.217}{2.5}\right)^2} = 151.6 \text{ mol}^{-2} \text{ L}^2$$

$$\text{Now, } K_p = K_c (RT)^{\Delta n} = 151.6 \times (0.0821 \times 705)^{-2}$$

$$= 0.045 \text{ atm}^{-2}$$

$$\text{(ii) Since, } [(nH_2)_0 - 2x] = 0.217$$

$$\text{or } (nH_2)_0 = 0.217 + 2 \times 0.08$$

$$= 0.377 \text{ mole}$$

$$(n_{CO})_0 = 0.15$$

$$\text{Total moles } (n_0) = 0.377 + 0.15 = 0.527$$

Hence,

$$P_0 = \frac{n_0 RT}{V} = \frac{0.527 \times 0.0821 \times 705}{2.5}$$

$$= 12.20 \text{ atm}$$

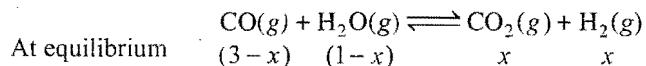
Example 10. The equilibrium constant for the reaction,



at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0 atm.

- (i) How many moles of H_2 are present at equilibrium?
(ii) Calculate the partial pressures of gases in equilibrium mixture.

Solution: (i) In the given reaction, $\Delta n = 0$, hence, $K_c = K_p$



Applying law of mass action,

$$\frac{x \times x}{(3-x)(1-x)} = 0.63$$

$$x^2 = 0.63(3 - 4x + x^2)$$

$$0.37x^2 + 2.52x - 1.89 = 0$$

or $x^2 + 6.81x - 5.1 = 0$

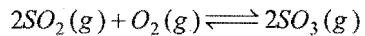
$$x = \frac{-6.81 \pm [6.81 \times 6.81 - 4 \times (-5.1)]^{1/2}}{2} = 0.68 \text{ mole} = \text{H}_2$$

(ii) Partial pressure of CO_2 = partial pressure of H_2
= mole fraction \times total pressure
 $= \frac{0.68}{4} \times 2 = 0.34 \text{ atm}$

Partial pressure of $\text{CO}(g) = \frac{(3-0.68)}{4} \times 2 = 1.16 \text{ atm}$

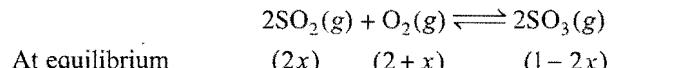
Partial pressure of $\text{H}_2\text{O}(g) = \frac{(1-0.68)}{4} \times 2 = 0.16 \text{ atm}$

Example 11. The equilibrium constant K_p for the reaction,



is 900 atm^{-1} at 800K . A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800K .

Solution: The system in the initial stage does not contain SO_2 , SO_3 will, thus, decompose to form SO_2 and O_2 until equilibrium is reached. The partial pressure of SO_3 will decrease. Let the decrease in partial pressure be $2x$.



Applying law of mass action,

$$K_p = \frac{(1-2x)^2}{(2x)^2(2+x)} \quad (2+x) \rightarrow 2$$

$$900 = \frac{(1-2x)^2}{8x^2}$$

or $\frac{1-2x}{x} = 84.85$

or $x = 0.0115 \text{ atm}$

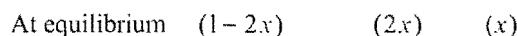
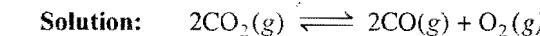
Thus, the partial pressures at equilibrium are:

$$p_{\text{SO}_2} = 2 \times 0.0115 = 0.023 \text{ atm}$$

$$p_{\text{O}_2} = 2 + 0.0115 = 2.0115 \text{ atm}$$

$$p_{\text{SO}_3} = 1 - 2 \times 0.0115 = 0.977 \text{ atm}$$

Example 12. What is the concentration of CO in equilibrium at 25°C in a sample of a gas originally containing 1.00 mol L^{-1} of CO_2 ? For the dissociation of CO_2 at 25°C , $K_c = 2.96 \times 10^{-92}$.



Applying law of mass action,

$$K_c = \frac{[\text{O}_2][\text{CO}]^2}{[\text{CO}_2]^2} = \frac{x \times (2x)^2}{(1-2x)^2} = 2.96 \times 10^{-92}$$

It can be assumed that $1-2x \approx 1.0$ as K_c is very small.

So, $4x^3 = 2.96 \times 10^{-92}$

or $x = 1.95 \times 10^{-31} \text{ mol L}^{-1}$

$$[\text{CO}] = 2x = 2 \times 1.95 \times 10^{-31}$$

$$= 3.90 \times 10^{-31} \text{ mol L}^{-1}$$

Example 13. Ammonia is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium. Calculate % of NH_3 actually decomposed.

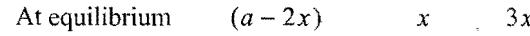
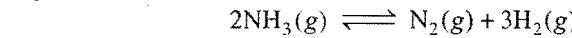
Solution: Pressure of NH_3 at $27^{\circ}\text{C} = 15 \text{ atm}$

Pressure of NH_3 at $347^{\circ}\text{C} = P \text{ atm}$

$$\frac{P}{620} = \frac{15}{300}$$

$$P = 31 \text{ atm}$$

Let a moles of ammonia be present. Total pressure at equilibrium = 50 atm



Total moles $a - 2x + x + 3x = a + 2x$

$$\frac{\text{Initial number of moles}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure}}{\text{Equilibrium pressure}}$$

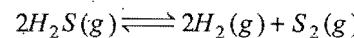
$$\frac{a}{(a+2x)} = \frac{31}{50}$$

$$x = \frac{19}{62} a$$

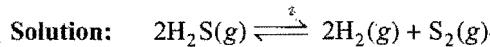
$$\text{Amount of ammonia decomposed} = 2x = 2 \times \frac{19}{62} a = \frac{19}{31} a$$

$$\% \text{ of ammonia decomposed} = \frac{19 \times a}{31 \times a} \times 100 \\ = 61.3$$

Example 14. Calculate the per cent dissociation of $\text{H}_2\text{S}(g)$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000K for the reaction,



The value of K_c is 1.0×10^{-6} .



At equilibrium	$(0.1-x)$	x	$x/2$
Molar conc.	$\frac{(0.1-x)}{0.4}$	$\frac{x}{0.4}$	$\frac{x}{0.8}$

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{\left(\frac{x}{0.4}\right)^2 \left(\frac{x}{0.8}\right)}{\left(\frac{0.1-x}{0.4}\right)^2} = 1.0 \times 10^{-6}$$

$$\text{or } \frac{x^3}{0.8(0.1-x)^2} = 1.0 \times 10^{-6}$$

as x is very small; $0.1-x \rightarrow 0.1$

$$\frac{x^3}{0.8 \times (0.1)^2} = 1.0 \times 10^{-6}$$

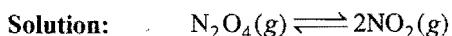
$$x^3 = 8 \times 10^{-9}$$

$$\text{or } x = 2 \times 10^{-3}$$

$$\text{So, per cent dissociation} = \frac{2 \times 10^{-3}}{0.1} \times 100 = 2.0$$

Example 15. The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 38.3 at 26.7°C . Calculate the number of moles of NO_2 in 100 grams of the mixture.

(MLNR 1993)



$$\text{At equilibrium } (1-x) \quad 2x$$

$$x \text{ (degree of dissociation)} = \frac{D-d}{(n-1)d}$$

$$\text{Given, } d = 38.3, D = \frac{\text{Mol. mass of N}_2\text{O}_4}{2} = \frac{92}{2} = 46, n = 2$$

$$\text{So, } x = \frac{46 - 38.3}{38.3} = 0.2$$

$$\text{At equilibrium, amount of N}_2\text{O}_4 = 1 - 0.2 = 0.8 \text{ mol}$$

$$\text{and amount of NO}_2 = 2 \times 0.2 = 0.4 \text{ mol}$$

$$\text{Mass of the mixture} = 0.8 \times 92 + 0.4 \times 46$$

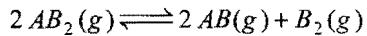
$$= 73.6 + 18.4 = 92.0 \text{ g}$$

Since, 92 gram of the mixture contains = 0.4 mol NO_2

So,

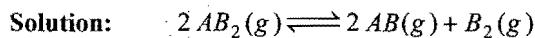
$$100 \text{ gram of the mixture contains} = \frac{0.4 \times 100}{92} = 0.43 \text{ mol NO}_2$$

Example 16. At temperature T , the compound $\text{AB}_2(\text{g})$ dissociates according to the reaction,



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 .

(IIT 1994)



$$\text{At equilibrium } (1-x) \quad x \quad x/2$$

Total moles at equilibrium = $1-x+x+x/2$

$$= \frac{2+x}{2}$$

$$P_{\text{AB}_2} = \frac{2(1-x)}{(2+x)} \cdot P; \quad P_{\text{AB}} = \frac{2x}{(2+x)} \cdot P; \quad P_{\text{B}_2} = \frac{x}{(2+x)} \cdot P;$$

$$K_p = \frac{(P_{\text{AB}})^2 (P_{\text{B}_2})}{(P_{\text{AB}_2})^2} = \frac{\left[\frac{2x}{(2+x)} P\right]^2 \left(\frac{x}{(2+x)} P\right)}{\left(\frac{2(1-x)}{(2+x)} P\right)^2} \\ = \frac{x^3 P}{(2+x)(1-x)^2}$$

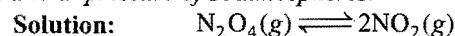
As x is very small, $(2+x) \rightarrow 2$ and $(1-x) \rightarrow 1$.

$$\text{So, } K_p = \frac{x^3 P}{2}$$

$$\text{or } x^3 = \frac{2K_p}{P}$$

$$\text{or } x = \left(\frac{2K_p}{P}\right)^{1/3}$$

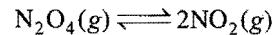
Example 17. At 25°C and one atmospheric pressure, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atmosphere, respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and at a total pressure of 10 atmospheres.



$$\text{At equilibrium } 0.7 \quad 0.3 \text{ atm}$$

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{0.3 \times 0.3}{0.7} = 0.1285 \text{ atm}$$

Let the degree of dissociation of N_2O_4 be x when total pressure is 10 atmosphere.



$$\text{At equilibrium } (1-x) \quad 2x$$

Total number of moles = $1-x+2x=1+x$

$$P_{\text{N}_2\text{O}_4} = \frac{(1-x)}{(1+x)} \times 10; \quad P_{\text{NO}_2} = \frac{2x}{(1+x)} \times 10$$

$$K_p = 0.1285 = \frac{\left(\frac{2x}{1+x}\right)^2 \times 10^2}{\left(\frac{1-x}{1+x}\right) \times 10} = \frac{40x^2}{1-x^2}$$

Since, x is very small, $(1-x^2) \rightarrow 1$

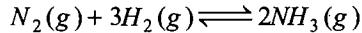
$$\text{So, } x^2 = \frac{0.1285}{40}$$

$$\text{or } x = 0.0566$$

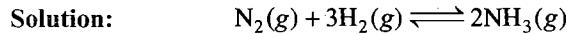
$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10 = \frac{1-0.0566}{1+0.0566} \times 10 = \frac{0.9436 \times 10}{1.0566} = 8.93 \text{ atm}$$

$$p_{NO_2} = \frac{2x}{(1+x)} \times 10 = \frac{2 \times 0.0566}{1+0.0566} \times 10 = \frac{0.1132}{1.0566} \times 10 = 1.07 \text{ atm}$$

Example 18. At 450°C , the equilibrium constant, K_p , for the reaction,



was found to be 16×10^{-5} at a pressure of 200 atm. If N_2 and H_2 are taken in 1:3 ratio what is % of NH_3 formed at this temperature?



At equilibrium $(1-x) \quad (3-3x) \quad 2x$

Total number of moles $= 1-x + 3-3x + 2x = 4-2x$

$$p_{N_2} = \frac{(1-x)}{(4-2x)} P; \quad p_{H_2} = \frac{(3-3x)}{(4-2x)} P; \quad p_{NH_3} = \frac{2x}{(4-2x)} P$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left(\frac{2x}{4-2x} P\right)^2}{\left(\frac{1-x}{4-2x} P\right) \left(\frac{3-3x}{4-2x} P\right)^3} = \frac{4x^2(4-2x)^2}{(1-x) \times 27 \times (1-x)^3 P^2}$$

$$1.6 \times 10^{-5} = \frac{16}{27} \times \frac{x^2(2-x)^2}{(1-x)^4 \times (200)^2}$$

$$\text{or } \frac{x^2(2-x)^2}{(1-x)^4} = \frac{1.6 \times 10^{-5} \times 27 \times (200)^2}{16} = \frac{16 \times 10^{-6} \times 27 \times (200)^2}{16}$$

$$\text{or } \frac{x(2-x)}{(1-x)^2} = 200 \times 10^{-3} \times \sqrt{27} = 1.039$$

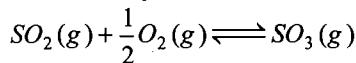
$$\text{or } x = 0.30$$

Moles of ammonia formed $= 2 \times 0.30 = 0.60$

Total moles at equilibrium $= (4-2x) = (4-2 \times 0.30) = 3.40$

$$\% \text{ of } NH_3 \text{ at equilibrium} = \frac{0.60}{3.40} \times 100 = 17.64$$

Example 19. A mixture of SO_2 and O_2 at 1 atmosphere in the ratio of 2:1 is passed through a catalyst at 1170°C for attainment of equilibrium. The exit gas is found to contain 87% SO_3 by volume. Calculate K_p for the reaction,



Solution: The volume of SO_2 and O_2 at equilibrium $= (100 - 87) = 13 \text{ mL}$

$$\text{Volume of } SO_2 = \frac{2}{3} \times 13 = 8.67 \text{ mL}$$

$$\text{Volume of oxygen} = \frac{1}{3} \times 13 = 4.33 \text{ mL}$$

$$p_{SO_3} = \frac{87}{100} \times 1 = 0.87 \text{ atm}$$

$$p_{SO_2} = \frac{8.67}{100} \times 1 = 0.0867 \text{ atm}$$

$$p_{O_2} = \frac{4.33}{100} \times 1 = 0.0433 \text{ atm}$$

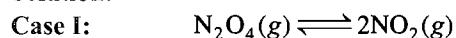
$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times (p_{O_2})^{1/2}} = \frac{0.87}{(0.0867) \times (0.0433)^{1/2}} = \frac{0.87}{(0.0867) \times 0.208} = 48.24 \text{ atm}^{-1/2}$$

Example 20. N_2O_4 dissociates as



at 55°C and one atmosphere % decomposition of N_2O_4 is 50.3%. At what pressure and same temperature, the equilibrium mixture has the ratio of $N_2O_4 : NO_2$ as 1:8?

Solution:



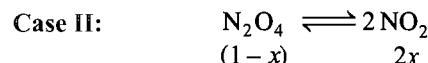
At equilibrium $(1-x) \quad 2x$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times P; \quad p_{NO_2} = \frac{2x}{(1+x)} \times P$$

$$K_p = \frac{\left(\frac{2x}{1+x} P\right)^2}{\left(\frac{1-x}{1+x} P\right)} = \frac{4x^2 P}{(1-x^2)}$$

Given, $x = 0.503$ and $P = 1$

$$K_p = 1.3548 \text{ atm}$$



$(1-x) \quad 2x$

Given, $\frac{(1-x)}{2x} = \frac{1}{8}$

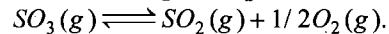
$$x = 0.8$$

Let the new pressure be P atm.

$$K_p = \frac{4x^2 P}{(1-x^2)} = \frac{4 \times 0.8 \times 0.8 \times P}{(1+0.8)(1-0.8)} = 1.3548$$

$$P = 0.19 \text{ atm}$$

Example 21. At 627°C and one atmosphere SO_3 is partially dissociated into SO_2 and O_2 by the reaction,



The density of the equilibrium mixture is 0.925 g L^{-1} . What is the degree of dissociation?

Solution: Let the molecular mass of the mixture at equilibrium be M_{mix} .

Applying the relation,

$$M_{\text{mix}} = \frac{dRT}{P} = \frac{0.925 \times 0.0821 \times 900}{1} = 68.348$$

Molecular mass of $\text{SO}_3 = 80$

$$\text{Vapour density of } \text{SO}_3, D = \frac{80}{2} = 40$$

$$\text{Vapour density of mixture, } d = \frac{68.348}{2} = 34.174$$

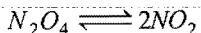
Let the degree of dissociation be x .

$$x = \frac{D-d}{(n-1)d} = \frac{40-34.174}{\left(\frac{3}{2}-1\right) \times 34.174} = \frac{5.826 \times 2}{34.174} = 0.34$$

or $x = 34\%$ dissociated

i.e., SO_3 is 34% dissociated.

Example 22. Density of equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 384 K is 1.84 g dm^{-3} . Calculate the equilibrium constant of the reaction.



Solution: We know that,

$$Pm = dRT$$

$$1 \times m = 1.84 \times 0.0821 \times 384$$

$$m = 29 \times 2$$

Vapour density (d) at equilibrium = 29

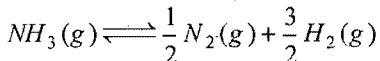
Initial vapour density = $M/2 = 92/2 = 46$

$$x = \frac{D-d}{(n-1)d} = \frac{46-29}{29} = 0.586$$



$t=0$	1	0	
$t_{eq.}$	$1-x$	$2x$	(Total moles = $1+x$)
	$\frac{1-x}{1+x} \times P$	$\frac{2x}{1+x} \times P$	
	$K_p = \frac{4x^2 P}{1-x^2} = \frac{4 \times (0.586)^2 \times 1}{1-(0.586)^2} = 2.09 \text{ atm}$		

Example 23. For the reaction,



show that degree of dissociation of NH_3 is given as:

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{p}{K_p} \right]^{-1/2}$$

where, 'p' is equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C, calculate K_c .

Solution:

$\text{NH}_3(g)$	\rightleftharpoons	$\frac{1}{2}\text{N}_2$	$+$	$\frac{3}{2}\text{H}_2(g)$	Total moles
$t=0$		1		0	1
$t_{eq.}$		$1-\alpha$		$\alpha/2$	$3\alpha/2$
p_i		$\left(\frac{1-\alpha}{1+\alpha}\right)p$		$\left(\frac{\alpha}{2(1+\alpha)}\right)p$	$\left(\frac{3\alpha}{2(1+\alpha)}\right)p$ ($P_i \rightarrow$ partial pressure)

$$K_p = \frac{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}{[\text{NH}_3]}$$

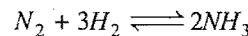
$$= \left[\frac{\alpha}{2(1+\alpha)} p \right]^{1/2} \left[\frac{3\alpha}{2(1+\alpha)} p \right]^{3/2} = \frac{p\alpha^2 \sqrt{27}}{4(1-\alpha^2)}$$

$$\text{Solving for } \alpha, \text{ we get } \alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{p}{K_p} \right]^{-1/2}$$

K_c can be calculated by using $K_p = K_c (RT)^{\Delta n}$

$$K_p = 78.1; T = 673 \text{ K}; \Delta n = 1$$

Example 24. The equilibrium constant K_p for the reaction,



is 1.64×10^{-4} at 400°C and 0.144×10^{-4} at 500°C. Calculate the mean heat of formation of 1 mole of NH_3 from its elements in this temperature range.

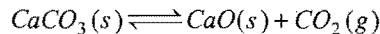
Solution: We know that, $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\log \frac{0.144}{1.64} = \frac{\Delta H}{2.303 \times 1.987 \times 10^{-3}} \left(\frac{1}{673} - \frac{1}{773} \right)$$

$$\Delta H = -25.14 \text{ kcal for 2 mole}$$

$$= -12.57 \text{ kcal mol}^{-1}$$

Example 25. When limestone is heated, quicklime is formed according to the equation,



The experiment was carried out in the temperature range 800–900°C. Equilibrium constant K_p follows the relation,

$$\log K_p = 7.282 - \frac{8500}{T}$$

where, T is temperature in Kelvin. At what temperature the decomposition will give $\text{CO}_2(g)$ at 1 atm?

Solution: $K_p = p_{\text{CO}_2} = 1$

$$\log K_p = 7.282 - \frac{8500}{T}$$

$$\log 1 = 7.282 - \frac{8500}{T}$$

$$T = \frac{8500}{7.282} = 1167.26 \text{ K}$$

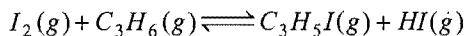
$$= 894.26^\circ\text{C}$$

Example 26. Equilibrium constant for the reaction of iodine with propane according to the following equation was determined.

Some results obtained at 545 K were as given ahead:

Initial Pressures (mm Hg)			Equilibrium Pressures (mm)	
I ₂	C ₃ H ₆	HI	HI	C ₃ H ₅ I
23.9	505.8	0	1.80	1.80
16.1	355.3	1.62	2.27	0.645

Calculate equilibrium constant according to the following equation,



Solution: Ist experiment:

I ₂ (g)	+	C ₃ H ₆ (g)	\rightleftharpoons	C ₃ H ₅ I(g)	+	HI(g)
t = 0	23.9	505.8		0	0	
t _{eq.}	(23.9 - 1.8)	(505.8 - 1.8)		1.80	1.80	

$$K_p = \frac{P_{C_3H_5I} \times P_{HI}}{P_{I_2} \times P_{C_3H_6}} = \frac{1.8 \times 1.8}{22.1 \times 504} = 2.9 \times 10^{-4}$$

Similarly, solve for second experiment.

Example 27. At 817°C K_p for the reaction between CO₂ and excess hot graphite to form 2CO(g) is 10.

- What is the analysis (mole fraction) of the gases at equilibrium at 817°C and a total pressure of 4 atm? What is the partial pressure of CO₂ at equilibrium?
- At what total pressure will the gas mixture have 6% CO₂ by volume?

Solution: (i) CO₂(g) + C(s) \rightleftharpoons 2CO(g)

t = 0	1	0
t _{eq.}	1 - α	2α
P _{eq.}	$\left(\frac{1-\alpha}{1+\alpha}\right)p$	$\left(\frac{2\alpha}{1+\alpha}\right)p$

$$K_p = \frac{4\alpha^2 p}{1-\alpha^2}; 10 = \frac{4\alpha^2 4}{1-\alpha^2}$$

On solving, we get α = 0.62

$$x_{CO_2} = \frac{1-\alpha}{1+\alpha} = \frac{1-0.62}{1+0.62} = 0.2345 = 23.45\% \text{ (by volume)}$$

$$x_{CO} = 0.7655 = 76.55\% \text{ (by volume)}$$

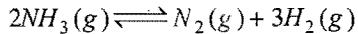
$$P_{CO_2} = (0.2345 \times 4.0) \text{ atm} = 0.938 \text{ atm}$$

(ii) Let the total pressure be P atm.

$$K_p = 10 = \frac{[P_{CO}]^2}{P_{CO_2}} = \frac{0.94 \times P \times 0.94 \times P}{0.06 \times P}$$

$$P = 0.68 \text{ atm}$$

Example 28. Ammonia under a pressure of 20 atm at 127°C is heated to 327°C in a closed vessel. Under these conditions NH₃ is partially decomposed to N₂ and H₂ according to the equation:



After decomposition at constant volume in a vessel the pressure increases to 45 atm. What is the percentage of ammonia dissociated?

Solution:

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

n	P	V	T
a	20	V	400
a - aα	aα/2	3aα/2	a + aα
			40

$$V = \frac{nRT}{P} = \frac{a \times R \times 400}{20} \quad \dots(1)$$

$$V = \frac{nRT}{P} = \frac{a(1+\alpha) \times R \times 600}{45} \quad \dots(2)$$

$$\text{On dividing, we get } 1 = \frac{400 \times 45}{(1+\alpha)20 \times 600}$$

$$\alpha = 0.5$$

Percentage dissociation of NH₃ = 50

Example 29. When 3.06 g of solid NH₄HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

- Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH₄HS is introduced into the flask?

(IIT 1990)

Solution: NH₄HS(s) \rightleftharpoons NH₃(g) + H₂S(g)

$$\text{Moles of NH}_4\text{HS} = \frac{3.06}{51} = 0.06$$

Degree of dissociation = 0.3

At equilibrium,

$$[\text{NH}_3(\text{g})] = \frac{0.3 \times 0.06}{2}; [\text{H}_2\text{S}(\text{g})] = \frac{0.3}{2} \times 0.06$$

$$K_c = [\text{NH}_3(\text{g})][\text{H}_2\text{S}(\text{g})] = \frac{0.3 \times 0.06 \times 0.3 \times 0.06}{2 \times 2}$$

$$= 8.1 \times 10^{-5}$$

Now applying,

$$K_p = K_c (RT)^{\Delta n} = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$$

$$= 0.049$$

Since, NH₄HS is solid, so it causes no change in equilibrium.

Example 30. At 540 K, 0.10 mole of PCl₅ are heated in a 8 litre flask. The pressure of equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

(IIT 1990)

Solution: PCl₅ \rightleftharpoons PCl₃ + Cl₂

At equilibrium (mole) (0.1 - x) x x

Total number of moles, n = (0.1 - x) + x + x = (0.1 + x)

$$PV = nRT$$

$$1 \times 8 = (0.1 + x) \times 0.082 \times 540$$

$$x = 0.08$$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{x^2}{(0.1-x) \times 8}$$

$$= \frac{0.08 \times 0.08}{(0.1-0.08)8} = 4 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_p = K_c (RT)^{\Delta n} = K_c RT (\Delta n = +1)$$

$$= 4 \times 10^{-2} \times 0.082 \times 540 = 1.77 \text{ atm}$$

Example 31. At 817°C , K_p for the reaction between $\text{CO}_2(g)$ and excess hot graphite(s) is 10 atm.

(a) What are the equilibrium concentrations of gases at 817°C and a total pressure of 5 atm?

(b) At what total pressure, the gas contains 5% CO_2 by volume? (IIT 2000)

Solution: (a) $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g)$

At equilibrium $(5-x)$ atm x atm

$$K_p = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{x^2}{(5-x)}$$

$$10 = \frac{x^2}{5-x}$$

$$x^2 = 50 - 10x$$

$$x^2 + 10x - 50 = 0$$

$$x = \frac{-10 \pm \sqrt{100 + 200}}{2} = 3.66$$

i.e., $p_{\text{CO}} = 3.66$ atm; $p_{\text{CO}_2} = 1.34$ atm

$$\text{Concentration of CO} = \frac{p}{RT} = \frac{3.66}{0.0821 \times 1090} = 0.041 \text{ mol litre}^{-1}$$

$$\text{Concentration of CO}_2 = \frac{p}{RT} = \frac{1.34}{0.0821 \times 1090} = 0.015 \text{ mol litre}^{-1}$$

(b) $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g)$

$$t=0 \quad 1 \quad 0 \quad 0$$

$$t_{\text{eq.}} \quad 1-\alpha \quad 2\alpha \quad$$

$$p_i = \frac{1-\alpha}{1+\alpha} p \quad \frac{2\alpha}{1+\alpha} p$$

$$K_p = \frac{\left[\frac{2\alpha}{1+\alpha} p \right]^2}{\left[\frac{1-\alpha}{1+\alpha} p \right]} = \frac{4\alpha^2 p}{1-\alpha^2} \quad \dots (\text{i})$$

$$\frac{5}{100} = \frac{1-\alpha}{1+\alpha}$$

$$\alpha = 0.95$$

$$\therefore \text{From eq. (i), } 10 = \frac{4 \times (0.95)^2}{1 - (0.95)^2} \times p$$

$$p = 0.27 \text{ atm}$$

Example 32. The value of K_p is $1 \times 10^{-3} \text{ atm}^{-1}$ at 25°C for the reaction $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$. A flask contains NO at 0.02 atm and at 25°C . Calculate the mole of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mole of gas produces 1 atm pressure at 25°C . (Ignore probable association of NO to N_2O_2). (IIT 2001)

Solution: $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$

$t=0$	0.02	0	0
$t_{\text{eq.}}$	$\frac{0.02 \times 99}{100}$	p	$\frac{0.02 \times 1}{100}$
	0.0198	p	0.0002

$$K_p = \frac{[p_{\text{NOCl}}]^2}{[p_{\text{NO}}]^2 [p_{\text{Cl}_2}]} = \frac{(0.02 \times 0.01)^2}{(0.99 \times 0.02)^2 \times p} = 10^{-3}$$

$$p = 0.102 \text{ atm}$$

$$PV = nRT$$

$$0.102 \times V = n \times R \times T \quad \dots (\text{i})$$

$$1 \times V = 0.2 \times R \times T \quad \dots (\text{ii})$$

From eqs. (i) and (ii), $n = 0.0204$ (no. of moles of Cl_2 at equilibrium)

Pressure of Cl_2 involved in reaction

$$= \frac{1}{2} \times \text{pressure of NOCl}$$

$$= \frac{1}{2} \times \frac{0.02}{100} = 0.0001 \text{ atm}$$

$$PV = nRT$$

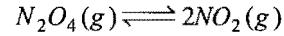
$$0.0001 \times V = n \times RT \quad \dots (\text{iii})$$

From eqs. (ii) and (iii), $n = 2 \times 10^{-5}$ (moles of Cl_2 involved in reaction)

Initial moles of Cl_2 taken = $0.0204 + 2 \times 10^{-5}$

$$= 0.02042$$

Example 33. In the following equilibrium,



when 5 moles of each is taken and the temperature is kept at 298 K , the total pressure was found to be 20 bar.

Given : $\Delta G_f^\circ \text{N}_2\text{O}_4 = 100 \text{ kJ}$, $\Delta G_f^\circ \text{NO}_2 = 50 \text{ kJ}$

(a) Find ΔG of the reaction at 298 K .

(b) Find the direction of the reaction. (IIT 2004)

Solution: Reaction Quotient = $\frac{[p_{\text{NO}_2}]^2}{p_{\text{N}_2\text{O}_4}} = \frac{100}{10} = 10$

$$\Delta G_{\text{reaction}}^\circ = 2\Delta G_f^\circ \text{NO}_2 - \Delta G_f^\circ \text{N}_2\text{O}_4$$

$$= 2 \times 50 - 100 = 0$$

We know that, $\Delta G = \Delta G^\circ - 2.303 RT \log Q_p$

$$= 0 - 2.303 \times 8.314 \times 298 \log 10$$

$$= -5705.8 \text{ J} = -5.705 \text{ kJ}$$

Negative value shows that reaction will be in forward direction..

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Irreversible and reversible reactions: Chemical reactions can be classified as irreversible and reversible reactions. The reactions which move in one direction only are called **irreversible reactions**. In these reactions products do not react to produce original reactants. In such reactions an arrow (\rightarrow) is placed between reactants and products. The chemical reactions which take place in both directions under similar conditions are called **reversible reactions**. In such reactions products also react with each other to produce reactants again. The sign (\rightleftharpoons) is placed between reactants and products.

2. Chemical equilibrium: Chemical equilibrium is the most important characteristic property of reversible reactions. It is the state at which both forward and backward reactions occur at the same speed.

At equilibrium state,

$$\text{Rate of forward reaction} = \text{Rate of backward reaction}$$

At equilibrium state, the concentrations of the reactants and products do not change with time. The following are the characteristics of the equilibrium state:

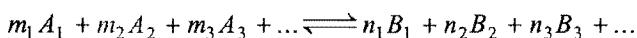
- (i) It can be achieved only if the reversible reaction is carried out in a closed space.
- (ii) It is characterised by constancy of certain properties such as concentration, pressure, density, colour, etc.
- (iii) It can be attained from either side of the reaction.
- (iv) It can be attained in lesser time by use of a catalyst.
- (v) It is dynamic in nature, i.e., reaction does not stop, but both the forward and backward reactions move with the same speed.
- (vi) Change of pressure, concentration or temperature favours one of the reaction and thus shifts the equilibrium point in one direction.

Reversible chemical reactions are classified into two types:

- (i) **Heterogeneous reactions:** The reversible reactions in which more than one-phase is present.
- (ii) **Homogeneous reactions:** The reversible reactions in which only one-phase is present. These are further classified into three types:

- (a) When there is no change in the number of molecules, i.e., $\Delta n = 0$.
- (b) When there is an increase in the number of molecules, i.e., $\Delta n = +ve$.
- (c) When there is a decrease in the number of molecules, i.e., $\Delta n = -ve$.

3. Law of chemical equilibrium (Application of law of mass action): Consider the general homogeneous reversible reaction in which equilibrium has been attained at a certain temperature.



$$\text{Rate of forward reaction} = \text{Rate of backward reaction}$$

$$k_f [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots = k_b [B_1]^{n_1} [B_2]^{n_2} [B_3]^{n_3} \dots$$

$$\text{or } \frac{\{(B_1)^{n_1} (B_2)^{n_2} (B_3)^{n_3} \dots\}}{\{(A_1)^{m_1} (A_2)^{m_2} (A_3)^{m_3} \dots\}} = \frac{k_f}{k_b} = K_c$$

The equilibrium constant, K_c , at a given temperature, is the ratio of rate constants of forward and backward reactions. It is also defined as the ratio between the molar concentrations of the products to the molar concentrations of the reactants with each concentration term raised to the power equal to stoichiometric coefficient in the balanced chemical equation.

The value of equilibrium constant is independent of the following factors;

- (i) Initial concentration of reactants.
- (ii) The direction from which equilibrium has been attained.
- (iii) The presence of a catalyst.
- (iv) The presence of inert materials.

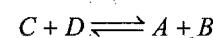
The value of equilibrium constant depends upon the following factors:

- (i) **The mode of representation of the reaction:** Consider the reversible reaction,

$$A + B \rightleftharpoons C + D$$

$$K_c = \frac{[C][D]}{[A][B]}$$

The products are made the reactants, i.e., the reaction is reversed:



$$K'_c = \frac{[A][B]}{[C][D]}$$

$$\text{So, } K'_c = \frac{1}{K_c}$$

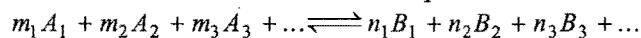
- (ii) **Stoichiometric representation of a chemical equation:** The value of equilibrium constant will be numerically different if the reaction can be written with the help of two or more stoichiometric equations.

$$\text{i.e., } 2\text{NO}_2(g) \rightleftharpoons \text{N}_2(g) + 2\text{O}_2(g); \quad K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2}$$

$$\text{or } \text{NO}_2(g) \rightleftharpoons (1/2)\text{N}_2(g) + \text{O}_2(g); \quad K'_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]}{[\text{NO}_2]}$$

$$\text{Thus, } K'_c = \sqrt{K_c}$$

- (iii) **Use of partial pressures:** When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature.



$$K_p = \frac{(p_{B_1})^{n_1} (p_{B_2})^{n_2} (p_{B_3})^{n_3} \dots}{(p_{A_1})^{m_1} (p_{A_2})^{m_2} (p_{A_3})^{m_3} \dots}$$

$$K_p = K_c (RT)^{\Delta n}$$

where, Δn = total number of molecules of products – total number of molecules of reactants.

When, $\Delta n = 0, K_p = K_c;$
 and $\Delta n = +ve, K_p > K_c;$
 $\Delta n = -ve, K_p < K_c;$

(iv) **Temperature:** The value of equilibrium constant changes with temperature. The values of equilibrium constants at two different temperatures are related by the following equation:

$$\log K_2 - \log K_1 = -\frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad T_2 > T_1$$

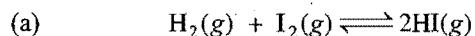
When, $\Delta H = 0, i.e.,$ heat of reaction at constant volume is zero,

When, $\Delta H = +ve, i.e.,$ endothermic reaction,
 $K_2 > K_1$
 and when, $\Delta H = -ve, i.e.,$ exothermic reaction
 $K_2 < K_1$

Units of equilibrium constant: Partial pressures are measured in terms of atmospheres. Therefore, units of K_p will be (atm) $^{\Delta n}$. Since, concentrations are measured in terms of moles per litre, the units of K_c are (mol L $^{-1}$) $^{\Delta n}$.

K_p and K_c will be pure numbers when, $\Delta n = 0$.

4. Equilibrium expressions for some reactions:

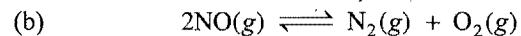


Initially	a	b	0
At equilibrium	$(a-x)$	$(b-x)$	$(2x)$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

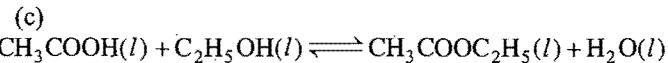
$$K_p = \frac{[p_{HI}]^2}{p_{H_2} \times p_{I_2}} = \frac{\frac{(2x)^2}{(a-x)(b-x)} P^2}{\left(\frac{a-x}{a+b} \cdot P\right) \left(\frac{b-x}{a+b} \cdot P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So, $K_c = K_p$



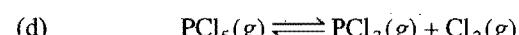
Initially	a	0	0
At equilibrium	$(a-x)$	$x/2$	$x/2$

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2}$$



Initially	a	b	0	0
At equil.	$(a-x)$	$(b-x)$	x	x

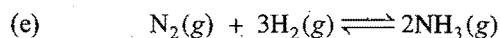
$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(a-x)(b-x)}$$



Initially	a	0	0
At equilibrium	$(a-x)$	x	x
Active masses	$\frac{(a-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(a-x)}{V}} = \frac{x^2}{(a-x)V}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{x}{a+x} \cdot P\right) \times \left(\frac{x}{a+x} \cdot P\right)}{\left(\frac{a-x}{a+x} \cdot P\right)} = \frac{x^2 P}{(a+x)(a-x)}$$



Initially	a	b	0
At equilibrium	$(a-x)$	$(b-3x)$	$2x$
Active masses	$\left(\frac{a-x}{V}\right)$	$\left(\frac{b-3x}{V}\right)$	$\left(\frac{2x}{V}\right)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left[\frac{2x}{(a+b-2x)} P\right]^2}{\left[\frac{(a-x)}{(a+b-2x)} P\right] \left[\frac{(b-3x)}{(a+b-2x)} P\right]^3} = \frac{4x^2 (a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

5. Activation energies for the forward and backward reactions: Both forward and backward reactions follow the same path and from the same activated complex. However, the activation energies of both reactions are different.

$$\Delta E = E_a(f) - E_a(b)$$

For exothermic reaction, $E_a(f) < E_a(b), i.e., \Delta E = -ve$

For endothermic reaction, $E_a(f) > E_a(b), i.e., \Delta E = +ve$

Threshold energy = Energy of reactants + Activation energy of forward reaction

Threshold energy = Energy of products + Activation energy of backward reaction

6. Standard free energy change of a reaction and its equilibrium constant are related to each other at temperature T by the following relation:

$$\Delta G^\circ = -2.303RT \log K_p$$

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

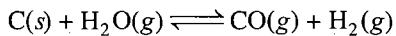
When, $\Delta G^\circ = -ve$, the value of equilibrium constant will be large positive quantity and when ΔG° is positive, the value of K is less than 1, i.e., low concentration of products at equilibrium state.

7. Degree of dissociation from density measurements: Degree of dissociation in the case of reversible reactions in which there is increase in the number of molecules can be determined by

measuring density of the reaction mixture at equilibrium. Let d be the observed density at a particular temperature when degree of dissociation is x and D be the vapour density when there is no dissociation.

$$x = \frac{D - d}{(n - 1)d}; \text{ where, } n \text{ is the number of molecules of products.}$$

8. Heterogeneous equilibria: Law of mass action can also be applied to the heterogeneous system. In such systems the concentrations of pure solids and liquids are not considered in equilibrium expressions.



$$K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \quad \text{or} \quad K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$$

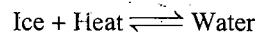
i.e., concentration of $\text{C}(s)$ is not taken into account.

9. Le Chatelier's principle: It is a qualitative principle which can describe the effect of change in concentration, pressure and temperature on the reversible system whether physical or chemical. It is stated as "If the system at equilibrium is subjected to a change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to annul the effect of that change." The following conclusions have been derived from this principle:

- (i) Increase in concentration of any substance favours the reaction in which it is used up.
- (ii) High pressure is favourable for the reaction in which there is decrease in volume.
- (iii) A rise in temperature favours the endothermic reaction.

Applications of Le Chatelier's Principle

- (i) **Ice water system (melting of ice):**

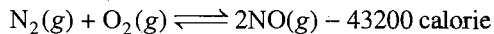


It is an endothermic process and there is decrease in volume. Thus, the favourable conditions for melting of ice are:

- (a) High temperature and (b) High pressure.

(ii) Solubility of gases in liquids: When a gas dissolves in a liquid, there is decrease in volume. Thus, increase in pressure will favour the dissolution of a gas in liquid.

- (iii) **Formation of nitric oxide:**



In this chemical reaction, there is no change in the number of molecules and heat is absorbed (endothermic). Thus, favourable conditions for greater yields of NO are:

- (a) High concentrations of N_2 and O_2 ,
- (b) High temperature and
- (c) No effect of pressure and catalyst.

(iv) $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) + 22400 \text{ calorie}$: The reaction involves decrease in number of molecules and evolution of heat (exothermic). The favourable conditions are:

- (a) High concentrations of N_2 and H_2 ,
- (b) High pressure and
- (c) Low temperature.

To speed up the rate of reaction at low temperature, a suitable catalyst is always employed.

Questions

1. Match List I (Equations) with List II (Type of Processes) and select the correct option:

**List-I
(Equations)**
**List-II
(Type of Processes)**

- | | |
|-------------------------------------|-----------------------------------|
| (a) $K_p > Q$ | (i) Non-spontaneous |
| (b) $\Delta G^\circ < RT \log_e Q$ | (ii) Equilibrium |
| (c) $K_p = Q$ | (iii) Spontaneous and endothermic |
| (d) $T > \frac{\Delta H}{\Delta S}$ | (iv) Spontaneous |

- (A) a = (i); b = (ii); c = (iii); d = (iv)
 (B) a = (iii); b = (iv); c = (ii); d = (i)
 (C) a = (iv); b = (i); c = (ii); d = (iii)

(D) a = (ii); b = (i); c = (iv); d = (iii) [CBSE (PMT) 2010]

[Hint: When $K_p > Q$; rate of forward reaction > rate of backward reaction, i.e., process is spontaneous.

When $\Delta G^\circ < RT \log_e Q$, ΔG° is positive, thus reaction is non spontaneous.

When $K_p = Q$, reaction is at equilibrium.

When $T\Delta S > \Delta H$, ΔG will be negative only when $\Delta H = +ve$, thus is spontaneous and endothermic.]

2. Matrix-Matching Problems (For IIT Aspirants):

- [A] Match the Column-I with Column-II:

Column-I
Column-II

- | | |
|--|--|
| (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ | (p) Unaffected by inert gas addition |
| (b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ | (q) Forward shift by rise in pressure and backward shift by inert gas addition |
| (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ | (r) Unaffected by increase in pressure |
| (d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ | (s) Backward shift by rise in pressure and forward shift by inert gas addition |

- [B] Match the reactions in the Column-I with the units of equilibrium constant in Column-II:

Column-I
Column-II

- | | |
|--|-------------------------|
| (a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ | (p) mol L ⁻¹ |
| (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ | (q) Unitless |

- (c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (r) atm
 (d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (s) $(atm)^{-2}$

- [C] Match the reactions of the Column-I with the factors in Column-II:

Column-I
Column-II

- | | |
|--|--|
| (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ | (p) Forward shift by rise in pressure
(Exothermic) |
| (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ | (q) Unaffected by change in pressure
(Exothermic) |
| (c) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ | (r) Forward shift by rise in temperature
(Endothermic) |
| (d) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ | (s) Forward shift by lowering the temperature
(Endothermic) |

- [D] Match the reactions of the Column-I with the relations in Column-II:

Column-I
Column-II

- | | |
|--|--------------------------|
| (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ | (p) $K_p = K_c(RT)$ |
| (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ | (q) $K_p = K_c(RT)^2$ |
| (c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ | (r) $K_p = K_c(RT)^{-2}$ |
| (d) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ | (s) $K_p = K_c$ |

- [E] Match the List-I with List-II:

List-I
List-II

- | | |
|----------------|---|
| (a) $Q = K$ | (p) Reaction is nearer to completion |
| (b) $Q < K$ | (q) Reaction is not at equilibrium |
| (c) $Q > K$ | (r) Reaction is fast in forward direction |
| (d) $K \ggg 1$ | (s) Reaction at equilibrium |

- [F] Match the List-I with List-II:

List-I
List-II
(Reaction)
 (K_p/K_c)

- | | |
|--|-------------------|
| (a) $A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$ | (p) $(RT)^{-2}$ |
| (b) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ | (q) $(RT)^0$ |
| (c) $A(s) + \frac{3}{2}B_2(g) \rightleftharpoons AB_3(g)$ | (r) $(RT)^{1/2}$ |
| (d) $AB_2(g) \rightleftharpoons AB(g) + \frac{1}{2}B_2(g)$ | (s) $(RT)^{-1/2}$ |

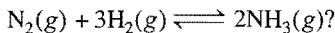
Answers

1. (C) (a = iv); (b = i); (c = ii); (d = iii)
 2. [A] (a-p, r); (b-p, r); (c-q); (d-s)
 [B] (a-p, r); (b-p, r); (c-q); (d-s)
 [C] (a-p, s); (b-p, s); (c-q, r); (d-p, r)

- [D] (a-s); (b-r); (c-p); (d-q)
 [E] (a-s); (b-q, r); (c-q); (d-p)
 [F] (a-p); (b-q); (c-s); (d-r)

PRACTICE PROBLEMS

1. K_c for the reaction, $\text{NH}_3(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g)$, at 298 K is 5.2×10^{-5} . What is the value of K_c at 298 K for the reaction,



[Hint: K'_c for reaction $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3$ is $\frac{1}{K_c}$, i.e., $\frac{1}{5.2 \times 10^{-5}}$

K_c for the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$, will be $= (K'_c)^2$
 $= \left[\frac{1}{5.2 \times 10^{-5}} \right]^2 = 3.7 \times 10^8$]

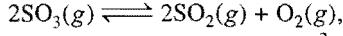
2. The value of K_p for the reaction,



is 0.035 atm at 400°C, when the partial pressures are expressed in atmosphere. Calculate the value of K_c for the same reaction.

[Ans. $6.342 \times 10^{-4} \text{ mol L}^{-1}$]

3. For the reaction,



the equilibrium constant $K_c = 2.52 \times 10^{-2}$ at 27°C; calculate K_p . (Given, $R = 0.082 \text{ litre-atm deg}^{-1} \text{ mol}^{-1}$)

[Ans. 61.99×10^{-2}]

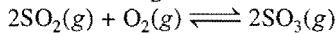
4. If K_p for the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$, is $1.64 \times 10^{-4} \text{ atm}^{-2}$ at 400°C. What will be the equilibrium constant at 500°C, if heat of reaction in this temperature range is -105185.8 joule ?

[Ans. $1.44 \times 10^{-5} \text{ atm}$]

5. For the reaction, $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$, $K_p = 0.157 \text{ atm}$ at 300 K. Calculate the value of K_c for the same reaction at the same temperature.

[Ans. $6.38 \times 10^{-3} \text{ mol L}^{-1}$]

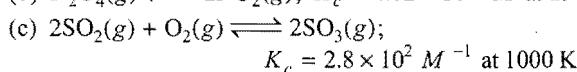
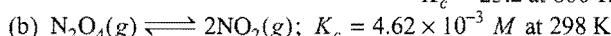
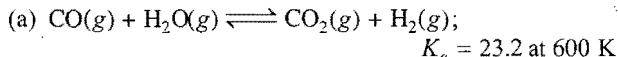
6. For the reaction, $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$, the value of K_c is 1.7×10^{12} at 300 K. Calculate the equilibrium constants for the following reactions at 300 K:



and $\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g)$

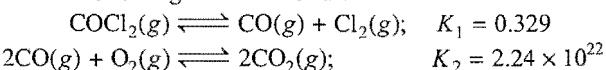
[Ans. $2.89 \times 10^{24}, 5.88 \times 10^{-13}$]

7. Determine K_p for the following reactions:



[Ans. (a) 23.2 (b) 11.45 kPa (c) 0.0337 kPa]

8. From the following data at 1000 K:



Calculate the equilibrium constant for the following reaction:

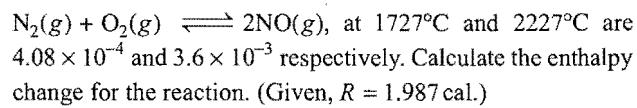


[Ans. 2.43×10^{21}]

9. For the reaction, $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$, K_p is $32 \text{ (atm)}^{-1/2}$ at 800 K and ΔH for the reaction is $-187.9 \text{ kJ mol}^{-1}$. Calculate its value at 900 K, if it is assumed that ΔH remains constant over this range of temperature.

[Ans. $1.387 \text{ atm}^{-1/2}$]

10. The equilibrium constants for the reaction,



[Ans. 43273 cal]

11. Calculate the equilibrium constant (K_p) for the reaction, $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)$, at 1300 K from the following data: $\text{C}(s) + 2\text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + 2\text{H}_2(g); K_p(1300 \text{ K}) = 3.9 \text{ atm}$

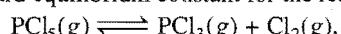


$K_p(1300 \text{ K}) = 0.7 \text{ atm}$

[Ans. 1.91 atm]

[Hint: $\frac{[\text{CO}]^2}{[\text{CO}_2]} = K_{p(\text{net})} = \frac{[\text{CO}]^2[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{CO}_2]^2} \times \frac{[\text{H}_2]^2[\text{CO}_2]}{[\text{H}_2\text{O}]^2} = (0.7)^2 \times 3.9$]

12. The standard equilibrium constant for the reaction,



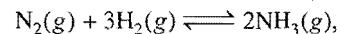
is 1.8×10^{-7} at 298 K. Calculate its ΔG° value.

[Ans. 38.49 kJ mol⁻¹]

13. For the equilibrium, $\text{Ag}_2\text{CO}_3(s) \rightleftharpoons \text{Ag}_2\text{O}(s) + \text{CO}_2(g)$, equilibrium constants are 3.98×10^{-4} and 1.41×10^{-2} respectively at 350 K and 400 K. Calculate the standard enthalpy of decomposition.

[Ans. 83.06 kJ/mol]

14. The equilibrium constant for the reaction,



- at 715 K is 6.0×10^{-2} . If in a particular reaction, there are 0.25 mol L^{-1} of H_2 and 0.06 mol L^{-1} of NH_3 present, calculate the concentration of N_2 at equilibrium.
[Ans. $[\text{N}_2] = 3.84 \text{ mol L}^{-1}$
- 15.** One mole of H_2O and one mole of CO were heated in a 10 litre closed vessel at 1260 K. At equilibrium, 40% of water was found to react in the equation,

$$\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$$
Calculate the equilibrium constant of the reaction.
[Ans. 0.44]
[Hint: $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$

$$(1 - 0.4) \quad (1 - 0.4) \quad 0.4 \quad 0.4$$

(at equilibrium)]
- 16.** Two moles of PCl_5 were introduced in a 2 litre flask and heated at 600 K to attain equilibrium. PCl_5 was found to be 40% dissociated into PCl_3 and Cl_2 . Calculate the value of K_c .
[Ans. $K_c = 0.267 \text{ mole L}^{-1}$]
- 17.** 0.1 mole of PCl_5 is heated in a litre vessel at 533 K. Determine the concentration of various species present at equilibrium, if the equilibrium constant for the dissociation of PCl_5 at 533 K is 0.414.
[Ans. $[\text{PCl}_5] = 0.0531 \text{ mol L}^{-1}$; $[\text{PCl}_3] = 0.0469 \text{ mol L}^{-1}$; $[\text{Cl}_2] = 0.0469 \text{ mol L}^{-1}$]
- 18.** At 1000 K, the equilibrium constant, K_c , for the reaction,

$$\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$$
is equal to 3.04. If 1 mole of CO and 1 mole of Cl_2 are introduced into a 1 litre box at 1000 K, what will be the final concentration of COCl_2 at equilibrium?
[Ans. $[\text{COCl}_2] = 0.568 \text{ mol L}^{-1}$]
- 19.** Given, that $K_c = 13.7$ at 546 K for

$$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$
, calculate what pressure will develop in a 10 litre box at equilibrium at 546 K when 1.00 mole of PCl_5 is injected into the empty box?
[Ans. $P = 8.93 \text{ atm}$]
[Hint: First determine degree of dissociation, then evaluate the total pressure by applying, $P = \frac{n}{V} RT$ where, $n = 1 + \alpha$.]
- 20.** In the following reaction,

$$2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$$
the amounts of H_2 , I_2 and HI are 7.8 g, 203.2 g and 1638.4 g respectively at equilibrium at a certain temperature. Calculate the equilibrium constant of the reaction.
[Ans. 0.019]
- 21.** Concentrations of two reactants A and B are 0.8 mol L^{-1} each. On mixing the two, the reaction sets in at a slow rate to form C and D.

$$A + B \rightleftharpoons C + D$$
At equilibrium, concentration of C was found to be 0.60 mol L^{-1} . Calculate the equilibrium constant.
[Ans. $K_c = 9$]
- 22.** 15 moles of hydrogen reacting with 5.2 moles of iodine form 10 g mole of hydrogen iodide. Calculate the equilibrium constant of the reaction.
[Ans. $K_c = 50$]
- 23.** In the dissociation of HI, it is found that 20% of the acid is dissociated when equilibrium is reached. Calculate the value of K_p for the equilibrium,

$$2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$$
[Ans. $K_p = 1.56 \times 10^{-2}$]
- 24.** The equilibrium constant of the reaction,

$$A + B \rightleftharpoons C + D$$
is unity. What per cent of A will be transformed if three moles of A are mixed with 5 moles of B?
[Ans. 62.5%]
[Hint: At equilibrium,

$$\frac{A}{(3-x)} + \frac{B}{(5-x)} \rightleftharpoons \frac{C}{x} + \frac{D}{x}$$
Find the value of x . % of A transformed = $\frac{x}{3} \times 100$]
- 25.** 2 moles of A and 3 moles of B are mixed and the reaction is carried at 400°C according to the equation,

$$A + B \rightleftharpoons 2C$$
the equilibrium constant of the reaction is 4. Find the concentration of C at equilibrium.
[Ans. 2.4 mole]
- 26.** A combination of hydrogen and iodine is carried out by heating 60 mL of hydrogen and 42 mL of iodine in a closed vessel. At equilibrium 28 mL of hydroiodic acid is present in the vessel. Calculate the degree of dissociation of HI.
[Hint: $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
At equilibrium (60 - 14) (42 - 14) 28 mL

$$K_c = \frac{28 \times 28}{46 \times 28} = \frac{14}{23}$$

$$2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$$

$$1-x \quad \frac{x}{2} \quad \frac{x}{2}$$
 (x is the degree of dissociation)

$$K'_c = \frac{x/2 \times x/2}{(1-x)^2} = \frac{x^2}{(1-x)^2} = \frac{14}{23}$$

or
$$\frac{x}{2(1-x)} = \frac{23}{14} = 1.2817$$

$$x = 0.72$$
]
- 27.** One mole of H_2 , 2 moles of I_2 and 3 moles of HI are injected in a one litre flask. What will be the concentration of H_2 , I_2 and HI at equilibrium when K_c is 45.9?
[Ans. $[\text{H}_2] = 0.316 \text{ mol L}^{-1}$, $[\text{I}_2] = 1.316 \text{ mol L}^{-1}$, $[\text{HI}] = 4.368 \text{ mol L}^{-1}$]
[Hint: $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
At equilibrium $(1-x) \quad (2-x) \quad (3+2x)$

$$K_c = \frac{(3+2x)^2}{(1-x)(2-x)} = 45.9$$
- On solving, $x = 0.684 \text{ mole}$]
- 28.** Four moles of hydrogen iodide were taken in a 10 litre flask kept at 800 K. When equilibrium was attained, the mixture was found to contain 0.42 mole of iodine. Calculate the equilibrium constant for dissociation of HI.
[Ans. $K_c = 1.76 \times 10^{-2}$]
- 29.** The equilibrium constant, K_c , for the reaction,

$$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$$
is 56.8 at 800 K. When the mixture was analysed, it was found

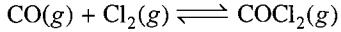
to contain 0.316 mol/L HI at 800 K. What are the concentrations of H₂ and I₂ at equilibrium? (Assume that initial concentrations of H₂ and I₂ were the same.)

[Ans. [H₂] = [I₂] = 0.0419 mol L⁻¹]

30. At same temperature and under a pressure of 4 atm, PCl₅ is 10% dissociation. Calculate the pressure at which PCl₅ will be 20% dissociated, temperature remaining same. (IIT 1996)

[Ans. 0.96 atm]

31. The reaction of the formation of phosgene gas from CO and Cl₂ is as follows:



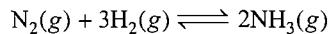
In an experiment, starting with equimolecular CO and Cl₂ in a 250 mL flask, the equilibrium mixture on analysis is found to contain 0.05 mole CO, 0.05 mole Cl₂ and 0.15 mole COCl₂. Calculate the equilibrium constant of the reaction.

[Ans. K_c = 15 mol⁻¹ L]

32. At 35°C and 1 atmospheric pressure, N₂O₄ is 27.2% dissociated into NO₂. What is the value of K_p under these conditions?

[Ans. K_p = 0.3195 atm]

33. Nitrogen and hydrogen are added to a 5 litre flask under pressure. The flask was sealed and heated. The equilibrium mixture contained 19.0 g of ammonia, 0.16 g of hydrogen and 3.4 g of nitrogen. Calculate the equilibrium constant, K_c, of the reaction:



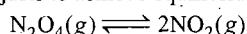
[Ans. K_c = 5.02 × 10⁵ mol⁻² L²]

34. An equilibrium mixture at 300 K contains N₂O₄ and NO₂ at 0.28 and 1.1 atm pressures respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases. (IIT 1991)

[Hint: N₂O₄(g) ⇌ 2NO₂(g)]

$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(1.1)^2}{0.28} = 4.32 \text{ atm}$$

When the volume is doubled, the pressure becomes half and the system again adjusts to achieve equilibrium.



$$\left(\frac{0.28}{2} - x\right) \left(\frac{1.1}{2} + 2x\right)$$

$$(0.14 - x)(0.55 + 2x)$$

$$K_p = \frac{(0.55 + 2x)^2}{(0.14 - x)} = 4.32$$

$$x = 0.045$$

$$P_{\text{N}_2\text{O}_4} = (0.14 - 0.045) = 0.095 \text{ atm}$$

$$P_{\text{NO}_2} = (0.55 + 2 \times 0.045) = 0.64 \text{ atm}$$

35. At 21.5°C and a total pressure of 0.0787 atm, N₂O₄ is 48.3% dissociated into NO₂. At what total pressure will the per cent dissociation be 10.0%?

[Ans. 2.37 atm]

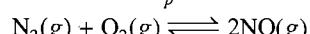
[Hint: First calculate the value of K_p and then evaluate the pressure by applying,

$$K_p = \frac{\left(\frac{0.2}{1.1}\right)^2 P^2}{\left(\frac{0.9}{1.1}\right) P} = 0.0959$$

36. At 3000 K, chlorine gas dissociates into chlorine atoms in an equilibrium reaction for which K = 0.37. What is the concentration of chlorine atoms in a vessel that originally contained 1.0 mol L⁻¹ of molecular chlorine?

[Ans. [Cl] = 0.54 mol L⁻¹]

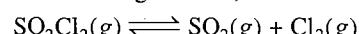
37. The equilibrium constant K_p for the reaction,



at 1500°C is 120. If N₂ and O₂ at an initial pressure of 0.25 atm each are maintained at 1500°C till equilibrium is established, calculate the partial pressure of N₂, O₂ and NO in the equilibrium mixture.

[Ans. P_{N₂} = P_{O₂} = 0.04; P_{NO} = 0.42 atm]

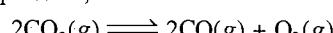
38. Find K_p for the following reaction,



If sulphuryl chloride decomposes to the extent of 91.2% at 102°C and total pressure 1 atmosphere.

[Ans. K_p = 4.94 atm]

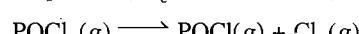
39. If carbon dioxide is 2% dissociated at 1800°C and 1 atmospheric pressure,



Calculate K_p for the reaction.

[Ans. K_p = 4.12 × 10⁻⁶ atm]

40. At a certain temperature, K_c for the reaction,



is 0.30. If 0.6 mole of POCl₃ is placed in a closed vessel of 3.0 litre capacity at this temperature, what percentage of it will be dissociated when equilibrium is established?

[Ans. 68.5%]

41. A reaction carried out by 1 mole of N₂ and 3 moles of H₂ shows at equilibrium the mole fraction of NH₃ as 0.012 at 500°C and total pressure 10 atmosphere; calculate K_p. Also report the pressure at which mole percentage of NH₃ in equilibrium mixture increased to 10.4.

[Ans. K_p = 1.431 × 10⁻⁵ atm⁻²; P = 105.41 atm]

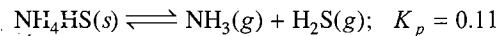
42. The degree of dissociation of N₂O₄ into NO₂ at one atmosphere and 40°C is 0.310. Calculate its K_p at 40°C. Also report degree of dissociation at 10 atmospheric pressure at the same temperature.

[Ans. K_p = 0.425 atm; degree of dissociation = 0.1025]

43. The vapour density of PCl₅ at 200°C and 252°C are 70.2 and 57.2 respectively at one atmosphere. Calculate its value of dissociation constant at these temperatures.

[Ans. K_p = 0.307, 1.19]

44. Some solid NH₄HS is placed in a flask containing 0.5 atm of NH₃. What would be the pressures of NH₃ and H₂S when equilibrium is reached?

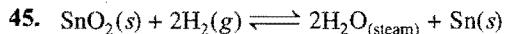


[Ans. NH₃ = 0.83 atm; H₂S = 0.33 atm] (MLNR 1994)

[Hint: NH₄HS(s) ⇌ NH₃(g) + H₂S(g)]

At equilibrium x + 0.5 x

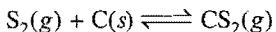
$$K_p = (x + 0.5)x = 0.11$$



For the above reaction find K_p , if at 900 K, the equilibrium mixture contains 45% H_2 by volume.

[Ans. $K_p = 1.5$]

46. The equilibrium constant for the reaction is 9.40 at 900°C.



Calculate the pressure of two gases at equilibrium, when 1.42 atm of S_2 and excess of $\text{C}(s)$ come to equilibrium.

[Ans. $p_{\text{CS}_2} = 1.28 \text{ atm}$; $p_{\text{S}_2} = 0.14 \text{ atm}$]

47. For the reaction,



$K_p = 1.16 \text{ atm}$ at 800°C. If 20.0 g of CaCO_3 were kept in a 10 litre container and heated up to 800°C, what percentage of CaCO_3 would remain unreacted at equilibrium?

[Ans. 34%]

[Hint: $K_p = p_{\text{CO}_2} = 1.16 \text{ atm}$

$$n = \frac{p_{\text{CO}_2} \times V}{RT} = \frac{1.16 \times 10}{0.0821 \times 1073} = 0.132 \text{ mol}$$

$$\text{Initial amount of CaCO}_3 = \frac{20.0}{100} = 0.2 \text{ mol}$$

$$\begin{aligned} \text{Unreacted CaCO}_3 &= 0.2 - 0.132 \\ &= 0.068 \text{ mol} \end{aligned}$$

$$\% \text{ unreacted CaCO}_3 = \frac{0.068}{0.2} \times 100 = 34\%]$$

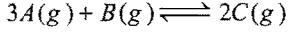
48. In the reaction, $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_p .

[Ans. $K_p = 16 \text{ atm}$]

49. A mixture of 0.373 atm of $\text{NO}(g)$ and 0.310 atm of $\text{Cl}_2(g)$ is prepared at 500°C. The reaction, $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}$, occurs. The total pressure at equilibrium is 0.544 atm. Determine K_p of the reaction.

[Ans. $K_p = 50.08 \text{ atm}^{-1}$]

50. For the reaction,



at a given temperature, K_c is 9.0. What must be the volume of a flask if the mixture of 2.0 moles each of A , B and C is obtained at equilibrium?

[Ans. $V = 6 \text{ litre}$]

51. 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 HBr at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of bromine is heated to 700 K. (IIT 1995)

[Hint: $\text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2\text{HBr}(g)$

Initial 0.6 0.2

Since, equilibrium constant is very high the reaction will be complete and bromine is consumed.

Thus, 0.2 mole of Br_2 and 0.2 mole of H_2 will be consumed to produce 0.4 mole of HBr . This can be calculated by applying law of mass action.

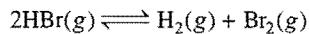
$$\frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = K \text{ or } \frac{4x^2}{(0.6-x)(0.2-x)} = 5 \times 10^8$$

$$x = 0.6 \text{ or } 0.2$$

The value of x cannot be more than 0.2 as Br_2 is a limiting reactant. Thus, when reaction is complete,

$$\text{H}_2 = (0.6 - 0.2) = 0.4 \text{ mol}; \text{Br}_2 = 0; \text{HBr} = 0.4 \text{ mol}$$

At this point some HBr will dissociate.



$$\text{At equilibrium } (0.4 - 2x) \quad (0.4 + x) \quad (x)$$

$$\frac{(0.4 + x) \times x}{(0.4 - 2x)} = \frac{1}{5 \times 10^8}$$

$$\text{or } \frac{0.4x}{0.4} = 2 \times 10^{-10} \text{ (since, } x \text{ is very small)}$$

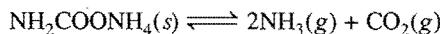
$$\text{or } x = 2 \times 10^{-10}$$

$$[\text{Br}_2] = 2 \times 10^{-10} \text{ mol}; [\text{H}_2] = 0.4 \text{ mol}; [\text{HBr}] = 0.4 \text{ mol}$$

52. One mole of H_2 , two moles of I_2 and three moles of HI are injected in a 1 litre flask. What will be the concentration of H_2 , I_2 and HI at equilibrium at 490°C? The equilibrium constant for the reaction at 490°C is 45.9.

[Ans. $[\text{H}_2] = 0.316$; $[\text{I}_2] = 1.316$; $[\text{HI}] = 4.36 \text{ mol}$]

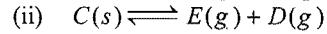
53. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows:



At equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original total pressure.

[Ans. $\frac{3}{2}$]

54. Two solid compounds A and C dissociate into gaseous product at temperature T as follows:



At 20°C, pressure over excess solid A is 50 atm and over excess solid C is 68 atm. Find the total pressure over the solid mixture.

[Ans. 84.38 atm]

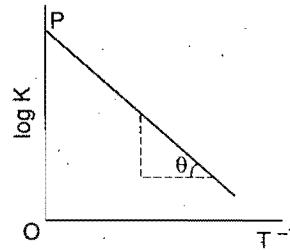
55. Variation of equilibrium constant K with temperature T is given by van't Hoff equation,

$$\log K = \log A - \frac{\Delta H^\circ}{2.303 RT}$$

A graph between $\log K$ and T^{-1} was a straight line as shown in the figure and having $\theta = \tan^{-1}(0.5)$ and $OP = 10$. Calculate:

(a) ΔH° (standard heat of reaction) when $T = 298 \text{ K}$,

(b) A (pre-exponential factor),



(c) Equilibrium constant K at 298 K,

(d) K at 798 K, if ΔH° is independent of temperature.

[Ans. (a) 9.574 J mol^{-1} ; (b) $A = 10^{10}$; (c) 9.96×10^9 ; (d) 9.98×10^9]

Hint: (a) $\log K = \log A - \frac{\Delta H^\circ}{2.303RT}$

It is equation of straight line of the type $y = c + mx$

$$\text{Slope } 'm' = \tan \theta = \frac{\Delta H^\circ}{2.303R}$$

$$0.5 = \frac{\Delta H^\circ}{2.303 \times 8.314}$$

$$\Delta H^\circ = 9.574 \text{ J mol}^{-1}$$

(b) Intercept 'c' = $\log A = 10$

$$\therefore A = 10^{10}$$

$$(c) \log K = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

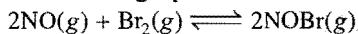
$$K = 9.96 \times 10^9$$

$$(d) \log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log \frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{798} \right)$$

On solving, $K_2 = 9.98 \times 10^9$

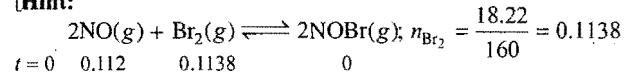
56. When 0.112 mole of NO and 18.22 g of bromine are placed in a 1.00 L reaction vessel and sealed, the mixture is heated to 350 K and the following equilibrium is established:



If the equilibrium concentration of nitrosyl bromide is 0.0824 M, what is K_c ?

[Ans. 106.74]

Hint:



$$t=0 \quad 0.112 \quad 0.1138 \quad 0$$

$$t_{eq.} \quad \left[\frac{0.112 - 2x}{1} \right] \left[\frac{0.1138 - x}{1} \right] \frac{2x}{1}$$

$$2x = 0.0824$$

$$\therefore [\text{NO}] = 0.112 - 2x$$

$$= 0.112 - 0.0824 = 0.0296 \text{ M}$$

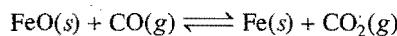
$$[\text{Br}_2] = 0.1138 - \frac{0.0824}{2} = 0.0726 \text{ M}$$

$$K_c = \frac{[\text{NOBr}]^2}{[\text{NO}]^2 [\text{Br}_2]} = \frac{[0.0824]^2}{[0.0296]^2 [0.0726]} = 106.74$$

57. Solid ammonium carbamate is put into a closed container and allowed to come to equilibrium with the gaseous products at 35°C, the total pressure is found to be 0.30 atmospheres. What is the value of K_p for this reaction at 35°C?

[Ans. 4×10^{-3}]

58. K_p for the equilibrium of,



at 1000°C is 0.403, if $\text{CO}(g)$, at a pressure of 1.0 atm and excess of $\text{FeO}(s)$ are placed in a container at 1000°C. What are the pressures of $\text{CO}(g)$ and $\text{CO}_2(g)$ when the equilibrium is attained?

[Ans. $p_{\text{CO}} = 0.713 \text{ atm}; p_{\text{CO}_2} = 0.287 \text{ atm}$]

59. A mixture of 1.0 mole of sulphur and 0.2 mole of hydrogen is heated at 90°C in a one litre flask. The equilibrium constant for the formation of hydrogen sulphide, $\text{H}_2(g) + \text{S}(s) \rightleftharpoons \text{H}_2\text{S}(g)$ is 6.8×10^{-2} . Calculate the partial pressure of H_2S at equilibrium.

[Ans. $p_{\text{H}_2\text{S}} = 0.397 \text{ atm}$]

Hint: First determine the initial pressure of H_2 by applying

$$P_0 = \frac{n}{V} \cdot RT = 5.953 \text{ atm}$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

- A reversible reaction is one which:
 - proceeds in one direction
 - proceeds in both directions
 - proceeds spontaneously
 - all the statements are wrong
 - An example of reversible reaction is:
 - $\text{Pb}(\text{NO}_3)_2 + 2\text{NaI} = \text{PbI}_2 + 2\text{NaNO}_3$
 - $\text{AgNO}_3 + \text{HCl} = \text{AgCl} + \text{HNO}_3$
 - $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$
 - $\text{KNO}_3 + \text{NaCl} = \text{KCl} + \text{NaNO}_3$
 - Which one of the following is not a reversible reaction?
 - $2\text{HI}(g) = \text{H}_2(g) + \text{I}_2(g)$
 - $\text{PCl}_5(g) = \text{PCl}_3(g) + \text{Cl}_2(g)$
 - $2\text{KClO}_3(s) = 2\text{KCl}(s) + 3\text{O}_2(g)$
 - $\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$
 - Which one is not correct for a reversible reaction?
 - The reaction is never completed
- The reactants are present in the initial stage but after that the reactants and products are always present in the reaction mixture
 - At equilibrium only products are present
 - When the reaction is carried out in closed space, it attains equilibrium state after suitable time
 - The law of mass action was proposed by:
 - Guldberg and Waage
 - Le Chatelier and Braun
 - Kossel and Lewis
 - van't Hoff
 - The rate at which a substance reacts, depends on its:
 - active mass
 - molecular mass
 - equivalent mass
 - total volume
 - Active mass is defined as:
 - number of g equivalent per unit volume
 - number of g mol per litre
 - amount of substance in gram per unit volume
 - number of g mole in 100 litre
 - 8.50 g of NH_3 is present in 250 mL volume. Its active mass is:
 - 1.0 M L^{-1}
 - 0.5 M L^{-1}
 - 1.5 M L^{-1}
 - 2.0 M L^{-1}

9. Theory of 'active mass' indicates that the rate of a chemical reaction is directly proportional to the: [PET (MP) 1990]
 (a) equilibrium constant (b) properties of reactants
 (c) volume of apparatus (d) concentration of reactants
10. The state of equilibrium refers to: [PMT (Pb.) 1993]
 (a) state of rest (b) dynamic state
 (c) stationary state (d) state of inertness
11. In a reversible chemical reaction equilibrium is said to have been established when the:
 (a) concentrations of reactants and products are equal
 (b) opposing reactions cease
 (c) speeds of opposing reactions become equal
 (d) temperatures of opposing reactions are equal
12. A chemical reaction, $A \rightleftharpoons B$, is said to be in equilibrium when:
 (a) rate of forward reaction is equal to rate of backward reaction
 (b) conversion of A to B is only 50% complete
 (c) complete conversion of A to B has taken place
 (d) only 25% conversion of A to B has taken place
13. The reaction between barium chloride and sodium sulphate goes to completion because:
 (a) barium sulphate is almost insoluble
 (b) the solubility of barium chloride decreases
 (c) lattice energy of barium sulphate is very high
 (d) the reaction is irreversible in nature
14. What is the equilibrium constant expression for the reaction, $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$?
 (Jamia Millia Islamia Engg. Ent. 2007; UPSEE 2007)
 (a) $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$ (b) $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]}$
 (c) $K_c = [O_2]^5$ (d) $K_c = \frac{1}{[O_2]^5}$
15. Equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, is correctly given by the expression:
 (a) $K_c = \frac{[H_2][I_2]}{[HI]}$ (b) $K_c = \frac{[HI]^2}{[H_2][I_2]}$
 (c) $K_c = \frac{[HI]}{[H_2][I_2]}$ (d) $K_c = \frac{[2HI]}{[H_2][I_2]}$
16. Equilibrium constant for the reaction, $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$, is correctly given by the expression:
 (a) $K = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$ (b) $K = \frac{[2NOCl]}{[2NO][Cl_2]}$
 (c) $K = \frac{[NO]^2 + [Cl_2]}{[NOCl]}$ (d) $K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$
17. For the system, $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is: [JEE (WB) 2007]
 (a) $\frac{[A]^3[B]^2}{[C]}$ (b) $\frac{[C]}{[A]^3[B]^2}$ (c) $\frac{[A]^2[B]^3}{[C]}$ (d) $\frac{[C]}{[A][B]}$
18. The equilibrium constants of the reactions,
 $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$
 and $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- are K_1 and K_2 respectively. The relationship between K_1 and K_2 is:
 (a) $K_1 = K_2$ (b) $K_2^2 = K_1$
 (c) $K_1^2 = K_2$ (d) $K_2 = \sqrt{K_1}$
19. The equilibrium constant for the given reaction is 100.
 $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$
- What is the equilibrium constant for the reaction given below:
 $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$
 (EAMCET 2009)
 (a) 10 (b) 1
 (c) 0.1 (d) 0.01
20. For the reaction, $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$, $K_c = 1.8 \times 10^{-6}$ at $185^\circ C$. The value of K_c at $185^\circ C$ for the reaction:
 $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ is: [MLNR 1993]
 (a) 0.9×10^6 (b) 1.95×10^{-3}
 (c) 1.95×10^3 (d) 7.5×10^2
21. The equilibrium constant for the synthesis of HI at $490^\circ C$ is 50.0. The value of K for the dissociation of HI will be:
 (IIT 1990)
 (a) 0.02 (b) 50.0 (c) 0.50 (d) 0.20
22. Consider the following equilibrium,
 $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g);$
 $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
- What is the relation between K_1 and K_2 ? [PET (MP) 1993]
 (a) $K_1 = \frac{1}{K_2}$ (b) $K_1 = \frac{1}{\sqrt{K_2}}$ (c) $K_1 = K_2$ (d) $K_1 = \frac{1}{K_2^2}$
23. For the reaction $AB(g) \rightleftharpoons A(g) + B(g)$, AB is 33%, dissociated at a total pressure of P . Therefore, P is related to K_p by one of the following option: [AMU (Med.) 2010]
 (a) $P = K_p$ (b) $P = 3K_p$
 (c) $P = 4K_p$ (d) $P = 8K_p$
- [Hint: $AB(g) \rightleftharpoons A(g) + B(g)$
- | | | | |
|----------|-------------------|---------------|---------------|
| t_0 | 1 | 0 | 0 |
| t_{eq} | $1 - \frac{1}{3}$ | $\frac{1}{3}$ | $\frac{1}{3}$ |
- $$p_{AB} = \frac{2/3}{4/3} \times p = \frac{p}{2};$$
- $$p_A = p_B = \frac{1/3}{4/3} \times p = \frac{p}{4}$$
- $$K_p = \frac{\frac{p}{2} \times \frac{p}{4}}{\frac{p}{8}} = \frac{p}{8}$$
- $$p = 8K_p]$$
24. For a system, $A + 2B \rightleftharpoons C$, the equilibrium concentrations are $[A] = 0.06$, $[B] = 0.12$ and $[C] = 0.216$. The K_c for the reaction is:
 (a) 125 (b) 415
 (c) 4×10^{-3} (d) 250

25. The equilibrium concentrations of x , y and yx_2 are 4, 2 and 2 respectively for the equilibrium $2x + y \rightleftharpoons yx_2$. The value of equilibrium constant, K_c is: (EAMCET 1990)

(a) 0.625 (b) 6.25 (c) 0.0625 (d) 62.5

26. 4 mole of A are mixed with 4 mole of B when 2 mole of C are formed at equilibrium, according to the reaction,



the equilibrium constant is:

(a) $\sqrt{2}$ (b) 2 (c) 1 (d) 4

27. If the equilibrium constant of the reaction $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ is 0.25, the equilibrium constant of $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$, under similar conditions, will be:

(a) 4.0 (b) 3.0 (c) 2.0 (d) 1.0

28. HI was heated in a sealed tube at 400°C till the equilibrium was reached. HI was found to be 22% decomposed. The equilibrium constant for dissociation is:

(a) 1.99 (b) 0.0199 (c) 0.0796 (d) 0.282

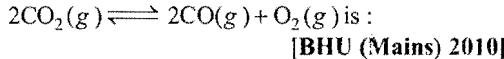
29. For a reversible reaction if the concentrations of the reactants are doubled at a definite temperature, then equilibrium constant will: (CPMT 1990; MLNR 1992)

(a) also be doubled (b) be halved
(c) become one-fourth (d) remain the same

30. In a reversible gaseous system, molar concentrations (active masses) of reactants and products are proportional to:

(a) partial pressure
(b) total pressure
(c) amounts of reactants and products
(d) none of the above

31. At 3000 K , the equilibrium partial pressure of CO_2 , CO and O_2 are 0.6, 0.4 and 0.2 atmospheres respectively. K_p for the reaction,



(a) 0.088 (b) 0.0533 (c) 0.133 (d) 0.177

32. Equilibrium constant depends on:

(a) the actual quantities of reactants and products
(b) the presence of a catalyst
(c) temperature
(d) the presence of inert material

33. For the reaction, $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$, the equilibrium constant, K_p , changes with:

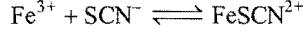
(a) total pressure
(b) catalyst
(c) the amounts of H_2 and I_2 taken
(d) temperature

34. $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$

The equilibrium constant of the above reaction is 6.4 at 300 K . If 0.25 mole each of H_2 and I_2 are added to the system, the equilibrium constant will be: (CET Karnataka 2009)

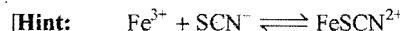
(a) 0.8 (b) 3.2 (c) 1.6 (d) 6.4

35. 3.1 mol of FeCl_3 and 3.2 mol of NH_4SCN are added to one litre of water. At equilibrium, 3.0 mol of FeSCN^{2+} are formed. The equilibrium constant K_c of the reaction:



will be:

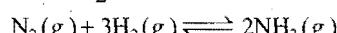
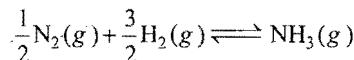
(a) 6.66×10^{-3} (b) 0.30
(c) 3.30 (d) 150



t_0	3.1	3.2	0
t_{eq}	0.1	0.2	3
	1	1	1

$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = \frac{3}{0.1 \times 0.2} = 150$$

36. K_p and K'_p are the equilibrium constants of the two reactions, given below:



Therefore, K_p and K'_p are related by [AMU (PMT) 2009]

(a) $K_p = K'^{\frac{1}{2}}_p$ (b) $K_p = \sqrt{K'_p}$
(c) $K_p = 2K'_p$ (d) $K_p = K'_p$

37. In which of the following equilibrium K_c and K_p are not equal? [CBSE (PMT) 2010]

(a) $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$
(b) $\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g)$
(c) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
(d) $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g)$

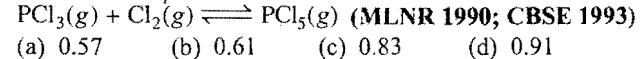
38. Select the correct statement from the following:

(a) equilibrium constant changes with addition of a catalyst
(b) catalyst increases the rate of forward reaction
(c) the ratio of mixture at equilibrium does not change by catalyst
(d) catalysts are active only in solution

39. In which of the following, the reaction proceeds towards completion? [MLNR 1990]

(a) $K = 1$ (b) $K = 10^{-2}$
(c) $K = 10$ (d) $K = 10^3$

40. For the following reaction at 250°C , the value of K_c is 26, then the value of K_p at the same temperature will be:



(a) 0.57 (b) 0.61 (c) 0.83 (d) 0.91

41. In the reaction, $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$, the amounts of PCl_5 , PCl_3 and Cl_2 are 2 mole each at equilibrium and the total pressure is 3 atmospheres. The equilibrium constant, K_p , is: (IIT 1991)

(a) 1 atm (b) 2 atm (c) 3 atm (d) 1.5 atm

42. In which of the following K_p is less than K_c ?

(a) $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
(b) $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$
(c) $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
(d) $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$

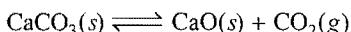
43. For a reversible reaction, the rate constants for the forward and backward reactions are 2.38×10^{-4} and 8.15×10^{-5} respectively. The equilibrium constant for the reaction is:

(a) 0.342 (b) 2.92
(c) 0.292 (d) 3.42

44. The equilibrium constant in a reversible reaction at a given temperature:

- (a) depends on the initial concentration of the reactants
 (b) depends on the concentration of products at equilibrium
 (c) it is not characteristic of the reaction
 (d) does not depend on initial concentrations
45. 1.0 g mole of ethyl alcohol and 1.0 g mole of acetic acid are mixed. At equilibrium 0.666 g mole of the ester is present. The value of equilibrium constant is: [PET (MP) 1993]
 (a) $\frac{1}{4}$ (b) $\frac{1}{2}$ (c) 2 (d) 4
46. The equilibrium constant of the reaction,
 $\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$
 is 4. If one mole of each of acetic acid and ethyl alcohol are heated in presence of a little concentrated H_2SO_4 , at equilibrium the amount of ester present is: [PET (MP) 1992]
 (a) 1 mole (b) 2 mole
 (c) $\frac{2}{3}$ mole (d) $\frac{1}{2}$ mole
47. If different quantities of ethanol and acetic acid are used in the following reversible reaction,
 $\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$
 the equilibrium constant will have values which will be?
 (a) Different in all cases
 (b) Same in all cases
 (c) Higher in cases where higher concentration of ethanol is used
 (d) Higher in cases where higher concentration of acetic acid is used
48. The reaction,
 $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$
 is begun with concentration of A and B both at initial value of 1M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression : [CBSE (PMT) 2010]
 (a) $[(0.75)^3(0.25)] / [(1.00)^2(1.00)]$
 (b) $[(0.75)^3(0.25)] / [(0.50)^2(0.75)]$
 (c) $[(0.75)^3(0.25)] / [(0.50)^2(0.25)]$
 (d) $[(0.75)^3(0.25)] / [(0.75)^2(0.25)]$
- Hint:** $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$
- | | | | | |
|----------|------|------|------|------|
| t_0 | 1 | 1 | 0 | 0 |
| t_{eq} | 0.50 | 0.75 | 0.75 | 0.25 |
- $$K = \frac{[C]^3[D]}{[A]^2[B]} = \frac{(0.75)^3(0.25)}{(0.50)^2(0.75)}$$
49. The decomposition of N_2O_4 to NO_2 is carried at 280 K in chloroform. When equilibrium has been established, 0.2 mole of N_2O_4 and 2×10^{-3} mole of NO_2 are present in 2 litre solution. The equilibrium constant for the reaction, $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$, is:
 (a) 1×10^{-2} (b) 2×10^{-3}
 (c) 1×10^{-5} (d) 2×10^{-5}
50. The unit of equilibrium constant, K_c , for the reaction $A + B \rightleftharpoons C$ would be:
 (a) mol^{-1}L (b) mol L^{-1} (c) mol L (d) no unit
51. For which of the following reactions does the equilibrium constant depend on the units of concentration?
 (a) $\text{NO}(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g)$
 (b) $\text{C}_2\text{H}_5\text{OH}(l) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$
 (c) $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$
 (d) $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$
52. The units of K_p in the following reaction are:
 $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
 (a) atm (b) atm^{-2} (c) atm^2 (d) atm^{-1}
53. The equilibrium of formation of phosgene is represented as:
 $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$
 The reaction is carried out in a 500 mL flask. At equilibrium 0.3 mole of phosgene, 0.1 mole of CO and 0.1 mole of Cl_2 are present. The equilibrium constant of the reaction is:
 (a) 30 (b) 15 (c) .5 (d) 3
54. In an equilibrium reaction, for which $\Delta G^\circ = 0$, the equilibrium constant K should be equal to:
 (a) zero (b) 10 (c) 1 (d) 2
55. The equilibrium constant K_p for the homogeneous gaseous reaction is 10^{-3} . The standard Gibbs free energy change ΔG° for the reaction at 27°C (using $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) is:
 (a) zero (b) -1.8 kcal
 (c) -4.154 kcal (d) +4.154 kcal
56. At 500 K, the equilibrium constant for reaction $cis\text{-C}_2\text{H}_2\text{Cl}_2 \rightleftharpoons trans\text{-C}_2\text{H}_2\text{Cl}_2$ is 0.6. At the same temperature, the equilibrium constant for the reaction $trans\text{-C}_2\text{H}_2\text{Cl}_2 \rightleftharpoons cis\text{-C}_2\text{H}_2\text{Cl}_2$, will be:
 (a) 1.67 (b) 0.6 (c) 1.76 (d) 1.64
57. Which one of the following oxides is most stable? The equilibrium constants are given at the same temperature:
 (a) $2\text{N}_2\text{O}_5(g) \rightleftharpoons 2\text{N}_2(g) + 5\text{O}_2(g); K = 1.2 \times 10^{34}$
 (b) $2\text{N}_2\text{O}(g) \rightleftharpoons 2\text{N}_2(g) + \text{O}_2(g); K = 3.5 \times 10^{35}$
 (c) $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g); K = 2.2 \times 10^{30}$
 (d) $2\text{NO}_2(g) \rightleftharpoons \text{N}_2(g) + 2\text{O}_2(g); K = 6.71 \times 10^{16}$
58. In a chemical equilibrium, $K_c = K_p$ when: [CEE (Bihar) 1992]
 (a) the number of molecules entering into a reaction is more than the number of molecules produced
 (b) the number of molecules entering into the reaction is equal to the number of molecules produced
 (c) the number of molecules entering into the reaction is less than the number of molecules produced
 (d) none of the above
59. In a general reaction, $A + B \rightleftharpoons AB$, which value of equilibrium constant most favours the production of AB ?
 (a) 9.0×10^{-3} (b) 3.5×10^{-3}
 (c) 4.0×10^{-7} (d) 4.0×10^{-12}
60. During thermal dissociation of a gas, the vapour density:
 (a) remains the same
 (b) increases
 (c) decreases
 (d) increases in some cases and decreases in others

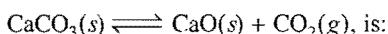
61. The vapour density of fully dissociated NH_4Cl would be:
 (a) less than half of the vapour density of pure NH_4Cl
 (b) double of the vapour density of pure NH_4Cl
 (c) half of the vapour density of pure NH_4Cl
 (d) one-third of the vapour density of pure NH_4Cl
62. In the dissociation of $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$, the degree of dissociation will be affected by:
 (a) increase of temperature (b) addition of an inert gas
 (c) addition of H_2 and I_2 (d) increase of pressure
63. In lime kilns, the following reversible reaction,



proceeds to completion because of: (CPMT 1990)

- (a) high temperature
 (b) CO_2 escapes
 (c) low temperature
 (d) molecular mass of CaO is less than that of CaCO_3

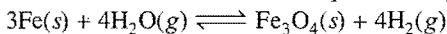
64. The equilibrium constant for the reaction,



- (a) $K_c = \frac{1}{[\text{CO}_2]}$ (b) $K_c = [\text{CO}_2]$
 (c) $K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$ (d) $K_c = \frac{[\text{CaCO}_3]}{[\text{CaO}][\text{CO}_2]}$

65. For the reaction, $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)$, the partial pressure of CO_2 and CO are 2.0 and 4.0 atm, respectively, at equilibrium. The K_p of the reaction is: (IIT 1992)
 (a) 0.5 (b) 4.0
 (c) 32.0 (d) 8.0

66. Iron fillings and water were placed in a 5 litre vessel and sealed. The tank was heated to 1000°C. Upon analysis the tank was found to contain 1.1 g of hydrogen and 42.5 g of water vapour. If the reaction in the tank is represented by,



- the value of equilibrium constant, K_c , is:
 (a) 30 (b) 0.03
 (c) 3 (d) 0.003

67. Ammonium hydrogen sulphide is contained in a closed vessel at 313 K when total pressure at equilibrium is found to be 0.8 atm. The value of K_p for the reaction, $\text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)$ is:
 (a) 0.16 (b) 1.6 (c) 0.016 (d) 16

68. Variation of K with temperature as given by van't Hoff equation can be written as:

- (a) $\log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$
 (b) $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$
 (c) $\log \frac{K_2}{K_1} = -\frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$

- (d) none of the above

69. When any system in equilibrium is subjected to a change in pressure, concentration or temperature, the equilibrium is shifted in the direction which tends to undo the effect of the change. This statement is known as:

- (a) First law of thermodynamics
 (b) Le Chatelier's principle
 (c) Hess's law
 (d) Ostwald's law
70. Le Chatelier's principle is applicable to:
 (a) only homogeneous chemical reversible reactions
 (b) only heterogeneous chemical reversible reactions
 (c) only physical equilibria
 (d) all systems, chemical or physical, in equilibrium
71. In the melting of ice, which one of the conditions will be more favourable?
 (a) High temperature and high pressure
 (b) Low temperature and low pressure
 (c) Low temperature and high pressure
 (d) High temperature and low pressure
72. Solubility of a gas in liquid increases on:
 (a) addition of a catalyst (b) decreasing of pressure
 (c) increasing of pressure (d) increasing of temperature
73. When KOH is dissolved in water, heat is evolved. If the temperature is raised, the solubility of KOH:
 (a) increases (b) decreases
 (c) remains the same (d) cannot be predicted
74. The yield of product in the reaction,

$$A_2(g) + 2B(g) \rightleftharpoons C(g) + Q \text{ kJ}$$

 would be higher at:
 (a) low temperature and high pressure
 (b) high temperature and high pressure
 (c) low temperature and low pressure
 (d) high temperature and low pressure
75. Manufacture of ammonia from the elements is represented by,

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) + 22.4 \text{ kcal}$$

 The maximum yield of ammonia will be obtained when the process is made to take place:
 (a) at low pressure and high temperature
 (b) at low pressure and low temperature
 (c) at high pressure and high temperature
 (d) at high pressure and low temperature
76. In the reaction, $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) + X \text{ cal}$, most favourable conditions of temperature and pressure for greater yield of SO_3 are:
 (a) low temperature and low pressure
 (b) high temperature and low pressure
 (c) high temperature and high pressure
 (d) low temperature and high pressure
77. What is the direction of a reversible reaction when one of the products of the reaction is removed?
 (a) The reaction moves towards right hand side
 (b) The reaction moves towards left hand side
 (c) The reaction moves equally on both the sides
 (d) The reaction stops
78. In the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$, $\Delta H = -93.6 \text{ kJ}$, the yield of ammonia does not increase when:
 (a) pressure is increased
 (b) pressure is decreased
 (c) temperature is lowered
 (d) volume of the reaction vessel is decreased

79. A cylinder provided with a piston has some PCl_5 which is in equilibrium with PCl_3 and Cl_2 . The system is compressed with the help of piston. Indicate the correct statement:
- some more PCl_5 will decompose
 - the system remains unaffected
 - PCl_3 and Cl_2 will combine to form PCl_5
 - explosion occurs
80. In the manufacture of nitric oxide, the forward reaction is favoured by:
- high pressure
 - low pressure
 - high temperature
 - low temperature
81. The reaction,
 $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightleftharpoons \text{C}_2\text{H}_6(g); \Delta H = -32.7 \text{ kcal}$
is carried out in a vessel. The equilibrium concentration of C_2H_4 can be increased by:
- increasing the temperature
 - decreasing the pressure
 - removing some hydrogen
 - all of these
82. In an exothermic reaction, a 10°C rise in temperature will:
[PMT (Bangalore) 1993]
- decrease the value of equilibrium constant
 - double the value of equilibrium constant
 - not produce any change in equilibrium constant
 - produce some increase in equilibrium constant
83. If K_p for a reaction,
 $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$
is 0.05 atm at 1000 K, its K_c in terms of R will be:
- $20000 R$
 - $0.02 R$
 - $5 \times 10^{-5} R$
 - $\frac{5 \times 10^{-5}}{R}$
84. Consider the reaction, $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ in closed container at equilibrium. What would be the effect of addition of CaCO_3 on the equilibrium concentration of CO_2 ?
(AIIMS 1991)
- Increases
 - Decreases
 - Remains unaffected
 - Data is not sufficient to predict it
85. XY_2 dissociates as:
 $XY_2(g) \rightleftharpoons XY(g) + Y(g)$
Initial pressure of XY_2 is 600 mm Hg. The total pressure at equilibrium is 800 mm Hg. Assuming volume of system to remain constant, the value of K_p is:
(BHU 1992)
- 50
 - 100
 - 200
 - 400
- Hint:** $XY_2(g) \rightleftharpoons XY(g) + Y(g)$
- $$\begin{array}{ccc} 600-x & x & x \\ 600+x & = & 800 \text{ or } x = 200 \end{array}$$
86. Which of the following reactions will be favoured at low pressure?
- $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
 - $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
 - $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
 - $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$
87. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the:
(MLNR 1990)

- (a) amount of solid to decrease
(b) amount of liquid to decrease
(c) temperature to rise
(d) temperature to fall
88. For the reaction:
 $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$
two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium:
- $[A] = [B]$
 - $[A] < [B]$
 - $[B] = [C]$
 - $[A] > [B]$
89. In a vessel containing SO_3 , SO_2 and O_2 at equilibrium, some helium gas is introduced so that total pressure increases while temperature and volume remain the same. According to Le Chatelier's principle, the dissociation of SO_3 :
(MLNR 1991)
- increases
 - decreases
 - remains unaltered
 - changes unpredictably
90. The equilibrium, $\text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statements is correct?
- Concentrations of SO_2Cl_2 , SO_2 and Cl_2 do not change
 - More Cl_2 is formed
 - Concentration of SO_2 is reduced
 - More SO_2Cl_2 is formed
91. The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2 . The % dissociation of N_2O_4 is:
 - 40
 - 57
 - 67
 - 87
92. K_p/K_c for the reaction, $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{CO}_2(g)$ is:
 - RT
 - $\frac{1}{\sqrt{RT}}$
 - \sqrt{RT}
 - 1
93. For the reactions,
 $A \rightleftharpoons B, K_c = 1; B \rightleftharpoons C, K_c = 3; C \rightleftharpoons D, K_c = 5$
 K_c for the reaction $A \rightleftharpoons D$ is:
 - 15
 - 5
 - 3
 - 1

Hint: $\frac{[B]}{[A]} = 1; \frac{[C]}{[B]} = 3; \frac{[D]}{[C]} = 5$,

Multiplying all the three, $\frac{[D]}{[A]} = 1 \times 3 \times 5$

94. The equilibrium constant of the reaction,
 $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ is 50. If the volume of the container is reduced to one half of its original value, the equilibrium constant will be:
 - 25
 - 50
 - 75
 - 100

95. $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$
The above equilibrium when subjected to pressure:
[PMT (Raj.) 1992]

 - remains unaffected
 - proceeds in the backward direction
 - proceeds in the forward direction
 - none of the above

96. Reaction, $A + B \longrightarrow C + D + 38$ kcal has activation energy 20 kcal. Activation energy for the reaction, $C + D \longrightarrow A + B$ is: [PMT (Pb.) 1993]
- 20 kcal
 - 20 kcal
 - 18 kcal
 - 58 kcal
97. The equilibrium constant for the reaction, $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightleftharpoons \text{CaSO}_4 \cdot 3\text{H}_2\text{O}(s) + 2\text{H}_2\text{O}(g)$, is equal to:
- $$\text{(a)} \frac{[\text{CaSO}_4 \cdot 3\text{H}_2\text{O}][\text{H}_2\text{O}]^2}{[\text{CaSO}_4 \cdot 5\text{H}_2\text{O}]} \quad \text{(b)} \frac{[\text{CaSO}_4 \cdot 3\text{H}_2\text{O}]}{[\text{CaSO}_4 \cdot 5\text{H}_2\text{O}]}$$
- $[\text{H}_2\text{O}]^2$
 - $[\text{H}_2\text{O}]$
98. One mole of $\text{N}_2\text{O}_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $\text{N}_2\text{O}_4(g)$ decomposes to $\text{NO}_2(g)$. The resultant pressure is:
- 1.2 atm
 - 2.4 atm
 - 2.0 atm
 - 1.0 atm
99. The equilibrium constant for the reaction, $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ is 4.0×10^{-4} at 2000 K. In the presence of a catalyst the equilibrium is attained ten times faster. Therefore, the equilibrium constant in presence of the catalyst at 2000 K is: [MLNR 1994]
- 4×10^{-4}
 - 40×10^{-4}
 - 4×10^{-2}
 - difficult to compute without more data
100. The equilibrium constant for a reaction, $A + B \rightleftharpoons C + D$ is 1×10^{-2} at 298 K and is 2 at 273 K. The chemical process resulting in the formation of C and D is:
- exothermic
 - endothermic
 - unpredictable
 - there is no relationship between ΔH and K
101. The equilibrium constant for the reaction, $A + B \rightleftharpoons C + D$ is 2.85 at room temperature and 1.4×10^{-2} at 698 K. This shows that forward reaction is:
- exothermic
 - endothermic
 - unpredictable
 - there is no relationship between ΔH and K
102. If E_f and E_r are the activation energies of forward and backward reactions and the reaction is known to be exothermic, then:
- $E_f > E_r$
 - $E_f < E_r$
 - $E_f = E_r$
 - no relation can be given between E_f and E_r
103. K_p for a reaction at 25°C is 10 atm. The activation energy for forward and reverse reactions are 12 and 20 kJ/mol respectively. The K_c for the reaction at 40°C will be:
- $4.33 \times 10^{-1} M$
 - $3.33 \times 10^{-2} M$
 - $3.33 \times 10^{-1} M$
 - $4.33 \times 10^{-2} M$
104. Concentration of pure solid and liquid is not included in the expression of equilibrium constant because:
- solid and liquid concentrations are independent of their quantities
 - solid and liquids react slowly
 - solid and liquids at equilibrium do not interact with gaseous phase
 - the molecules of solids and liquids cannot migrate to the gaseous phase
105. For an equilibrium reaction involving gases, the forward reaction is first order while the reverse reaction is second order. The units of K_p for forward equilibrium is:
- atm
 - atm^2
 - atm^{-1}
 - atm^{-2}
106. At temperature T , a compound $AB_2(g)$ dissociates according to the reaction:
- $$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$
- with a degree of dissociation ' x ' which is small as compared to unity. The expression for K_p , in terms of ' x ' and total pressure ' P ' is
- $$\text{(a)} \frac{Px^3}{2} \quad \text{(b)} \frac{Px^2}{3}$$
- $$\text{(c)} \frac{Px^3}{3} \quad \text{(d)} \frac{Px^2}{2}$$
107. 40% mixture of 0.2 mole of N_2 and 0.6 mole of H_2 react to give NH_3 according to the equation:
- $$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$
- at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases is:
- 4 : 5
 - 5 : 4
 - 7 : 10
 - 8 : 5
108. Two systems,
- $$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$
- and
- $$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$$
- are simultaneously in equilibrium in a vessel at constant volume. If some $\text{CO}(g)$ is introduced in the vessel at constant volume, then at new equilibrium, the concentration of:
- PCl_5 is greater
 - PCl_3 remains unchanged
 - PCl_5 is less
 - Cl_2 is greater
109. For the reaction, $[\text{Ag}(\text{CN})_2]^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$, the equilibrium constant K_c at 25°C is 4×10^{-19} ; then Ag^+ concentration in a solution which has 0.1 M KCN and 0.03 M AgNO_3 is:
- 7.5×10^{18}
 - 7.5×10^{-18}
 - 7.5×10^{19}
 - 7.5×10^{-19}
110. When NaNO_3 is heated in a closed vessel, oxygen is liberated and NaNO_2 is left behind. At equilibrium:
- addition of NaNO_2 favours reverse reaction
 - addition of NaNO_2 favours forward reaction
 - increasing temperature favours forward reaction
 - decreasing pressure favours reverse reaction
111. For the reaction,
- $$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(s) + 2\text{H}_2\text{O}(g)$$
- which one is the correct representation?
- $K_p = [p_{\text{H}_2\text{O}}]^2$
 - $K_c = [\text{H}_2\text{O}]^2$
 - $K_p = K_c(RT)^2$
 - All of these
112. Which one is the correct representation for,
- $$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)?$$

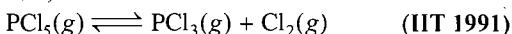
$$(a) K_p = \frac{[p_{SO_3}]^2}{[p_{SO_2}]^2 [p_{O_2}]}$$

$$(b) K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$$

$$(c) K_p = \frac{[n_{SO_3}]^2}{[n_{SO_2}]^2 [n_{O_2}]} \times \left[\frac{P}{\text{Total mole}} \right]^{-1}$$

(d) All of the above

113. For the reaction,



The forward reaction at constant temperature is favoured by:

- (a) introducing inert gas at constant volume
- (b) introducing chlorine gas at constant volume
- (c) introducing an inert gas at constant pressure
- (d) none of the above

114. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2 . At equilibrium, when the flask is heated to $100^\circ C$ the brown colour deepens and on cooling, the brown colour became less coloured. The change in enthalpy ΔH for the system is: (KCET 1993)

- (a) negative
- (b) positive
- (c) zero
- (d) not defined

115. Le Chatelier's principle is not applicable to:

- (a) $Fe(s) + S(s) \rightleftharpoons FeS(s)$
- (b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- (d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

116. Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase in pressure on the equilibrium $C_{\text{diamond}} \rightleftharpoons C_{\text{graphite}}$:

- (a) favours backward reaction
- (b) favours forward reaction
- (c) has no effect
- (d) increases the reaction rate

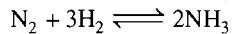
117. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ in a vessel, after the addition of equal number of moles of N_2 and H_2 equilibrium state is achieved. Which of the following is correct?

- (a) $[H_2] = [N_2]$
- (b) $[H_2] < [N_2]$
- (c) $[H_2] > [N_2]$
- (d) $[H_2] > [NH_3]$

118. If pressure is applied to the equilibrium of solid \rightleftharpoons liquid, the melting point of the solid:

- (a) will not change
- (b) may increase or decrease depending upon its nature
- (c) will always increase
- (d) will always decrease

119. If concentrations of N_2 , H_2 and NH_3 are 1, 2 and 3 respectively, their concentration at equilibrium will be:



- | | | | |
|-----|-----------|----------|----------|
| (a) | $(1-x)$ | $(2-3x)$ | $2x$ |
| (b) | $(1-x/3)$ | $(2-x)$ | $2x/3$ |
| (c) | $(1-x)$ | $(2-x)$ | $(3+x)$ |
| (d) | $(1-x)$ | $(2-3x)$ | $(3+2x)$ |

120. A reaction attains equilibrium, when the free energy change is:

- (a) zero
- (b) positive and large
- (c) negative and small
- (d) negative and large

121. If 340 g of a mixture of N_2 and H_2 in the correct ratio gave a 20% yield of NH_3 , the mass produced would be:

- (a) 16 g
- (b) 17 g
- (c) 20 g
- (d) 68 g

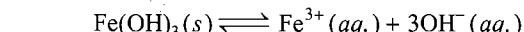
122. If the pressure of N_2 / H_2 mixture in a closed apparatus is 100 atm and 20% of the mixture then reacts, the pressure at the same temperature would be:

- (a) 100
- (b) 90
- (c) 85
- (d) 80

123. The equilibrium constants for the reaction, $Br_2 \rightleftharpoons 2Br$, at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is:

- (a) endothermic
- (b) exothermic
- (c) fast
- (d) slow

124. If the concentration of OH^- ions in the reaction:



is decreased by $\frac{1}{4}$ times, then equilibrium concentration of Fe^{3+} will increase by: [CBSE (PMT) 2008]

- (a) 64 times
- (b) 4 times
- (c) 8 times
- (d) 16 times

125. K_c for $A + B \rightleftharpoons C + D$ is 10 at $25^\circ C$. If a container contains 1, 2, 3 and 4 mol per litre of A, B, C and D respectively at $25^\circ C$, the reaction shall:

- (a) proceed from left to right
- (b) proceed from right to left
- (c) be at equilibrium
- (d) none of these

126. In the preparation of CaO from $CaCO_3$ using the equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

K_p is expressed as:

$$\log K_p = 7.282 - \frac{8500}{T}$$

For complete decomposition of $CaCO_3$ the temperature in celsius to be used is:

- (a) 1167
- (b) 894
- (c) 8500
- (d) 850

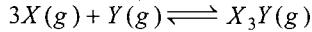
127. To the system,



already at equilibrium, more water vapour is added without altering T or V of the system. When equilibrium is re-established, the pressure of water vapour is doubled. The pressure of HCl present in the system increases by a factor of:

- (a) 2
- (b) $2^{1/2}$
- (c) 3
- (d) 4

128. For the chemical reaction,



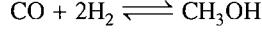
the amount of X_3Y at equilibrium is affected by: (IIT 1999)

- (a) temperature and pressure
- (b) temperature only
- (c) pressure only
- (d) temperature, pressure and catalyst

129. In a 500 mL capacity vessel CO and Cl_2 are mixed to form $COCl_2$. At equilibrium, it contains 0.2 mole of $COCl_2$ and 0.1 mole of each of CO and Cl_2 . The equilibrium constant K_c for reaction, $CO + Cl_2 \rightleftharpoons COCl_2$ is: (CBSE 1998)

- (a) 5
- (b) 10
- (c) 15
- (d) 20

130. The partial pressures of CH_3OH , CO and H_2 in the equilibrium mixture for the reaction,



at $427^\circ C$ are 2.0, 1.0 and 0.1 atm respectively. The value of K_p for the decomposition of CH_3OH into CO and H_2 is:

(IIT 1999)

- (a) 1×10^2 atm (b) 2×10^2 atm $^{-1}$
 (c) 50 atm 2 (d) 5×10^{-3} atm 2
131. 8 mole of a gas AB_3 are introduced into a 1.0 dm 3 vessel. It dissociates as:
- $$2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$$
- At equilibrium, 2 mole of A_2 are found to be present. The equilibrium constant of the reaction is: [IIT 1997]
- (a) $2 \text{ mol}^2 \text{ L}^{-2}$ (b) $3 \text{ mol}^2 \text{ L}^{-2}$
 (c) $27 \text{ mol}^2 \text{ L}^{-2}$ (d) $36 \text{ mol}^2 \text{ L}^{-2}$
132. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction,
- $$N_2O_4 \rightleftharpoons 2NO_2$$

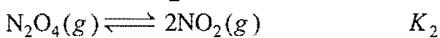
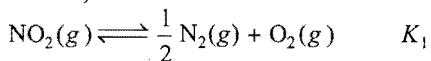
is expressed by:

$$K_p = \frac{4x^2 P}{(1-x^2)}$$

Where, P = pressure, x = extent of decomposition. Which one of the following statements is true? [IIT (Screening) 2000]

- (a) K_p increases with increase of P
 (b) K_p increases with increase of x
 (c) K_p increases with decrease of x
 (d) K_p remains constant with change in P and x

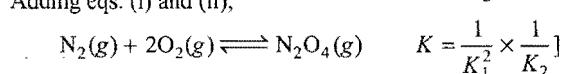
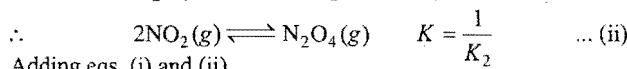
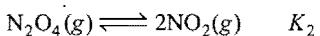
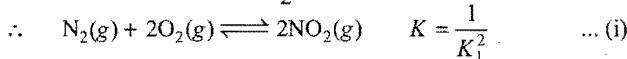
133. Consider the reactions,



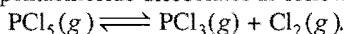
Give the equilibrium constant for the formation of N_2O_4 from N_2 and O_2 : [DCE 2006]

- (a) $\frac{1}{K_1^2} \times \frac{1}{K_2}$ (b) $\frac{1}{2K_1} + \frac{1}{K_2}$ (c) $\sqrt{\frac{1}{K_1 K_2}}$ (d) $\frac{K_2}{K_1}$

[Hint: $NO_2(g) \rightleftharpoons \frac{1}{2} N_2(g) + O_2(g) K_1$



134. Phosphorous pentachloride dissociates as follows:



If total pressure at equilibrium is P and the degree of dissociation of PCl_5 is x , the partial pressure of PCl_3 will be: [AIEEE 2006]

- (a) $\left(\frac{x}{x+1}\right)P$ (b) $\left(\frac{2x}{1-x}\right)P$ (c) $\left(\frac{x}{x-1}\right)P$ (d) $\left(\frac{x}{1-x}\right)P$

135. At $t = 0$ a vessel (volume 1 litre) contains 1 mole N_2 , 3 mole H_2 and 2 mole NH_3 . The value of K_c for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is $17.5 \text{ L}^2 \text{ mol}^{-2}$. Then:

- (a) total gaseous weight at equilibrium is more than 68 g
 (b) total number of moles (gaseous) at equilibrium are more than 6 moles

(c) $\frac{dM}{dt}$ is +ve for $t \in (0, T_{eq.})$ where, M is average molar mass of the reaction mixture

(d) total gaseous weight at equilibrium is less than 68 g

136. A vessel (volume = 2 L) contains 60 g of water gas. When steam is passed through the vessel, the reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$ occurs and equilibrium is attained:

- (a) $\frac{n(H_2)}{n(CO)} < 1$ (at equilibrium)
 (b) $n(H_2) + n(CO) = 4$ (at any instant)
 (c) $\frac{dM}{dt} > 0$ (where, M is average molar mass of gas mixture before the attainment of equilibrium)
 (d) $\frac{dM}{dt} < 0$

137. A vessel contains CO_2 and CO with pressures 2 atm and 3 atm respectively at $27^\circ C$. At a temperature of $2727^\circ C$, the reaction $2CO(g) \rightleftharpoons CO_2(g) + C(s)$ occurs and equilibrium is attained. If the equilibrium pressure is 45 atm, then:

- (a) $K_p = 2/9 \text{ atm}^{-1}$
 (b) $p_{CO} : p_{CO_2} = 4 : 5$ at equilibrium
 (c) $K_p = 16 \text{ atm}^{-1}$
 (d) % dissociation of $CO = 0.333$

138. A vessel (volume 8.2 L) contains $H_2(g)$ at 2 atm pressure. When $H_2S(g)$ at a pressure of 4 atm is introduced into the vessel, the reaction, $8H_2S(g) \rightleftharpoons 8H_2(g) + S_8(s)$ occurs at a temperature of 2000 K. It is found that:

$$\left[\frac{n(H_2)}{n(H_2S)} \right]_{\text{at equilibrium}} = \left[\frac{n(H_2S)}{n(H_2)} \right]_{\text{at } t=0}$$

- (a) maximum weight of solid formed is 32 g
 (b) maximum weight of solid formed is 0.32 g
 (c) $K_p = K_c RT$
 (d) $K_c = 256$

139. $N_2(g)$ and $H_2(g)$ are taken in a vessel in mass ratio of 7 : 1. The only reaction $N_2 + 2H_2 \rightleftharpoons N_2H_4(g)$ occurs. Pressure due to N_2H_4 at equilibrium is 0.2 times of total pressure ' P '. Then at equilibrium:

- (a) partial pressure of $N_2 = 2P/15$
 (b) partial pressure of $H_2 = 8P/25$
 (c) $2p_{N_2} = p_{H_2}$
 (d) $p_{N_2} = 2p_{H_2}$

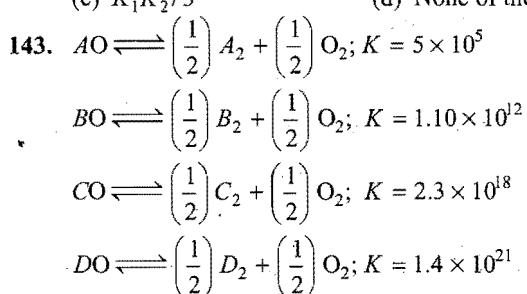
140. In the equilibrium, $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ at 2000 K and 10 atm pressure, % Cl_2 = % $SO_2 = 40$ by volume. Then:

- (a) $K_p = 2 \text{ atm}$
 (b) $\frac{n(SO_2Cl_2)}{n(SO_2)} = \frac{1}{4}$ at equilibrium
 (c) $K_p = 8 \text{ atm}$
 (d) $n(SOCl_2) = n(SO_2) = n(Cl_2)$

141. A 20 litre box contains O_3 and O_2 at equilibrium at 202 K. $K_p = 2 \times 10^{14}$ for $2O_3 \rightleftharpoons 3O_2$. Assume that $p_{O_2} \gg p_{O_3}$ and total pressure is 8 atm; the partial pressure of O_3 is:

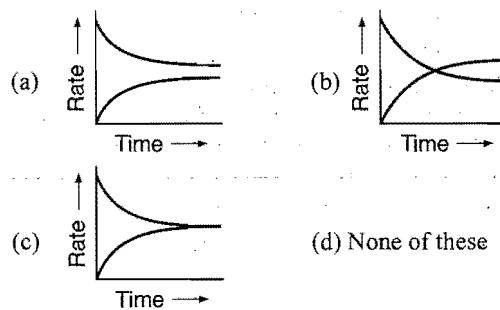
- (a) exactly 1.6×10^{-6} atm
 (b) sufficiently less than 1.6×10^{-6} atm

- (c) slightly more than 1.6×10^{-6} atm
 (d) very slightly less than 1.6×10^{-6} atm
142. For the reactions, $A \rightleftharpoons B, B \rightleftharpoons C$ and $C \rightleftharpoons D$, equilibrium constants are K_1, K_2 and K_3 respectively. What is the value of equilibrium constant for $A \rightleftharpoons D$?
 (a) $K_1 + K_2 + K_3$ (b) $K_1 \times K_2 \times K_3$
 (c) $K_1 K_2 / 3$ (d) None of these



Which oxide is most stable?

- (a) AO (b) BO (c) CO (d) DO
144. Which graph will show equilibrium condition?



145. For the reaction, $N_2 + O_2 \rightleftharpoons 2NO$ equilibrium constant $K_c = 2$. Degrees of dissociation of N_2 and O_2 are:

- (a) $\frac{1}{1+\sqrt{2}}, \frac{1}{1-\sqrt{2}}$ (b) $\frac{1}{1-\sqrt{2}}, \frac{1}{1+\sqrt{2}}$
 (c) both are $\frac{1}{1+\sqrt{2}}$ (d) $\frac{2}{1+\sqrt{2}}, \frac{2}{1-\sqrt{2}}$

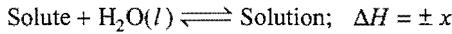
146. $A \rightleftharpoons 2B, K_p$; $C \rightleftharpoons D + E, K_{p'}$. If degrees of dissociation of A and C are same and $K_p = 2K_{p'}$, then the ratio of total pressure $p/p' = ?$
 (a) 1/2 (b) 1/3 (c) 1/4 (d) 2

147. Equilibrium constants for four different reactions are given as: $K_1 = 10^6, K_2 = 10^{-4}, K_3 = 10, K_4 = 1$. Which reaction will take maximum time to attain equilibrium?

- (a) $K_1 = 10^6$ (b) $K_2 = 10^{-4}$
 (c) $K_3 = 10$ (d) $K_4 = 1$

148. Solubility of a solute in water is dependent on temperature as given by,

$$S = Ae^{-\Delta H/RT} \text{ where, } \Delta H = \text{heat of solution}$$



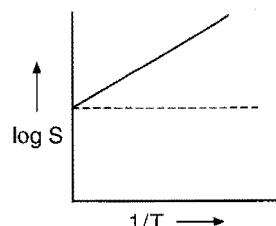
For a given solution, variation of $\log S$ with temperature is shown graphically. Hence, solute is:

- (a) $CuSO_4 \cdot 5H_2O$

- (b) $NaCl$

- (c) sucrose

- (d) CaO



149. $CH_3 - \overset{\overset{O}{||}}{C} - CH_3(g) \rightleftharpoons CH_3 - CH_3(g) + CO(g)$

Initial pressure of CH_3COCH_3 is 100 mm. When equilibrium is achieved, the mole fraction of $CO(g)$ is 1/3 hence, K_p is:

- (a) 100 mm (b) 50 mm (c) 25 mm (d) 150 mm

150. In which of the following equilibrium, change in the volume of the system does not alter the number of moles?

(AIEEE 2002)

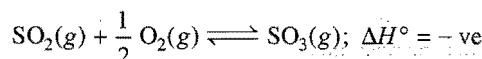
- (a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

- (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

- (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- (d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

151. What are the most favourable conditions for the reaction;

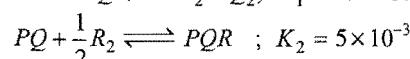
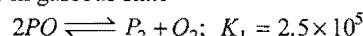


to occur? [DPMT 2002; JEE (Orissa) 2003]

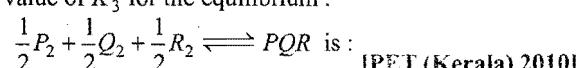
- (a) low temp. and high press. (b) low temp. and low press.

- (c) high temp. and low press. (d) high temp. and high press.

152. Consider the following reactions in which all the reactants and products are in gaseous state



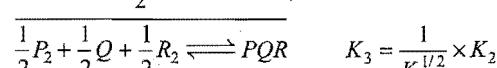
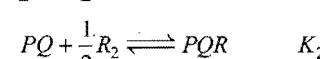
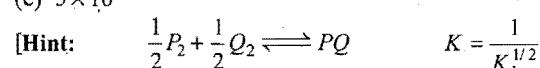
The value of K_3 for the equilibrium :



- (a) 2.5×10^{-3} (b) 2.5×10^3

- (c) 10×10^{-5} (d) 5×10^3

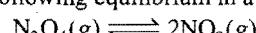
- (e) 5×10^{-3}



$$= \frac{5 \times 10^{-3}}{(2.5 \times 10^5)^{1/2}}$$

$$= 1 \times 10^{-5}$$

153. Consider the following equilibrium in a closed container,



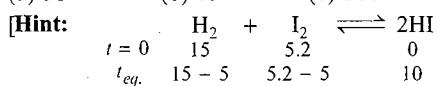
At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
 (HT 2002)

- (a) neither K_p nor ' α ' changes

- (b) both K_p and ' α ' change

167. 15 moles of H_2 and 5.2 moles of I_2 are mixed and allowed to attain equilibrium at $500^\circ C$. At equilibrium, the concentration of HI is found to be 10 moles. The equilibrium constant for the formation of HI is:

(a) 50 (b) 15 (c) 100 (d) 25

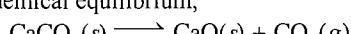


$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{100}{10 \times 0.2} = 50$$

168. For the reaction: $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, K_c at $427^\circ C$ is $3 \times 10^6 \text{ L mol}^{-1}$. The value of K_p is nearly:

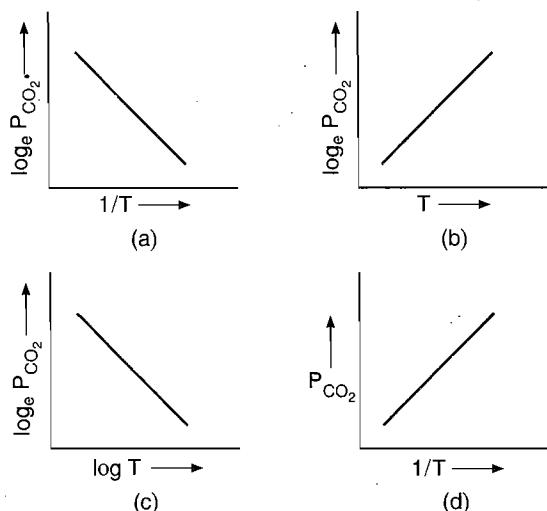
(a) 7.5×10^{-5} (b) 2.5×10^{-5} (c) 2.5×10^{-4} (d) 1.75×10^{-4}

169. For the chemical equilibrium,



ΔH_r° can be determined from which one of the following plots?

(AIIMS 2005)



[Hint: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = P_{CO_2}$$

According to Arrhenius equation:

$$K = Ae^{-\Delta H_r^\circ / RT}$$

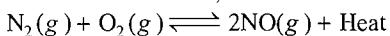
$$\log K_p = \log A - \frac{\Delta H_r^\circ}{2.303RT}$$

$$\log P_{CO_2} = \log A - \frac{\Delta H_r^\circ}{2.303R} \frac{1}{T} \quad \dots (i)$$

$$Y = C + MX$$

Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.]

170. In gaseous reversible reaction,

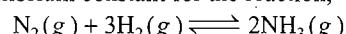


If pressure is increased, then the equilibrium constant would be:

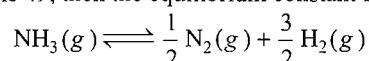
[UGET (Manipal, Medical) 2006]

- (a) unchanged
(b) increased
(c) decreased
(d) sometimes increased, sometimes decreased

171. If the equilibrium constant for the reaction,



at 750 K is 49, then the equilibrium constant for the reaction,

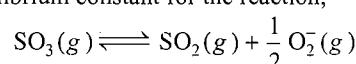


at the same temperature is:

[PMT (Kerala) 2006]

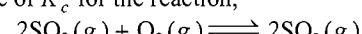
- (a) 1/49 (b) 49 (c) 7 (d) 49^2
(e) 1/7

172. The equilibrium constant for the reaction,



is $K_c = 4.9 \times 10^{-2}$.

The value of K_c for the reaction,



(AIEEE 2006)

will be:

- (a) 416 (b) 2.40×10^{-3}
(c) 9.8×10^{-2} (d) 4.9×10^{-2}

[Hint: $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$; $K_c = 4.9 \times 10^{-2}$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad K_c = \left(\frac{1}{4.9 \times 10^{-2}} \right)^2 = 416.5 \approx 416]$$

173. For a reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 721 K , the value of equilibrium constant is 50. If 0.5 mol each of H_2 and I_2 is added to the system, the value of equilibrium constant will be:

[VMMC (Safdarjung) 2006]

- (a) 40 (b) 60 (c) 50 (d) 30

[Hint: Equilibrium constant does not change on adding the reactant.]

174. In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, in a 2 litre flask 0.4 mole of each H_2 and I_2 are taken. At equilibrium 0.5 mole of HI are formed. What will be the value of equilibrium constant K_c ?

[PMT (Raj.) 2006]

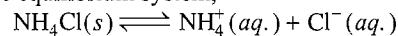
- (a) 20.2 (b) 25.4 (c) 0.284 (d) 11.1

175. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with:

[VITEEE 2007]

- (a) total pressure (b) catalyst
(c) the amount of H_2 and I_2 (d) temperature

176. Given the equilibrium system,



$$(\Delta H^\circ = +3.5 \text{ kcal/mol})$$

what change will shift the equilibrium to the right?

[VITEEE 2007]

- (a) Decreasing the temperature

- (b) Increasing the temperature

- (c) Dissolving NaCl crystals in equilibrium mixture

- (d) Dissolving NH_4NO_3 crystals in the equilibrium mixture

177. The equilibrium constant (K_p) for the decomposition of gaseous H_2O :

$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)$ is related to degree of dissociation (α) at a total pressure P is given by:

[PMT (Kerala) 2007]

- (a) $K_p = \frac{\alpha^3 P^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$ (b) $K_p = \frac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$
 (c) $K_p = \frac{\alpha^{3/2} P^2}{(1-\alpha)(2+\alpha)^{1/2}}$ (d) $K_p = \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$
 (e) $K_p = \frac{\alpha^2 P}{\sqrt{2}}$

[Hint: $\text{H}_2\text{O}(g) \rightleftharpoons \text{H}_2(g) + \frac{1}{2}\text{O}_2(g)$

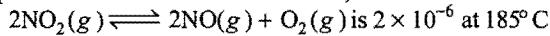
$$\begin{array}{cccc} t=0 & 1 & 0 & 0 \\ t_{eq} & 1-\alpha & \alpha & \alpha/2 \\ \Sigma n = 1-\alpha + \alpha + \frac{\alpha}{2} & = 1 + \frac{\alpha}{2} = \left(\frac{2+\alpha}{2}\right) \end{array}$$

$$K_p = \frac{n_{\text{H}_2} \times n_{\text{O}_2}^{1/2}}{n_{\text{H}_2\text{O}}} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

$$= \frac{\alpha \times \left(\frac{\alpha}{2}\right)^{1/2}}{(1-\alpha)} \times \left[\frac{P}{\left(\frac{2+\alpha}{2}\right)}\right]^{1/2}$$

$$= \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

178. The equilibrium constant for the reaction,



is 2×10^{-6} at 185°C

Then, the equilibrium constant for the reaction,
 $4\text{NO}(g) + 2\text{O}_2(g) \rightleftharpoons 4\text{NO}_2(g)$ at the same temperature
 would be: [PET (Kerala) 2007]

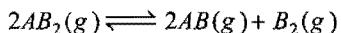
- (a) 2.5×10^{-5} (b) 4×10^{-12} (c) 2.5×10^{11} (d) 2×10^6
 (e) 5×10^5

179. 1 mole of H_2 and 2 mole of I_2 are taken initially in a 2 L vessel.
 The number of moles H_2 at equilibrium is 0.2. Then, the
 number of moles of I_2 and HI at equilibrium are:

[PMT (Raj.) 2007]

- (a) 1.2, 1.6 (b) 1.8, 1.0 (c) 0.4, 2.4 (d) 0.8, 2.0

180. The dissociation equilibrium of a gas AB_2 can be represented
 as,



The degree of dissociation is x and is small as compared to 1.
 The expression relating the degree of dissociation (x) with
 equilibrium constant K_p and total pressure P is:

- (a) $(2K_p/P)^{1/2}$ (b) K_p/P (c) $2K_p/P$ (d) $(2K_p/P)^{1/3}$
 [CBSE (PMT) 2008]

[Hint: $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

$$\begin{array}{cccc} t_0 & 2 & 0 & 0 \\ t_{eq} & 2(1-x) & 2x & x \quad \text{Total moles} = 2+x \\ \text{Partial pressure} & \frac{2(1-x)}{2+x} \times P & \frac{2x}{2+x} \times P & \frac{x}{2+x} \times P \end{array}$$

$$K_p = \frac{p_{AB}^2 \times p_{B_2}}{(p_{AB_2})^2} = \frac{\left[\frac{2}{(2+x)} P\right]^2 \left[\frac{x}{(2+x)} P\right]}{\left[\frac{2(1-x)}{2+x} \times P\right]^2}$$

$$= \frac{4x^3 \times P}{4(2+x)(1-x)^2}$$

$$(2+x) \approx 2, (1-x) \approx 1$$

$$K_p = \frac{Px^3}{2} \quad \therefore x = (2K_p/P)^{1/3}$$

181. In which of the following reactions, the concentration of the product is higher than the concentration of reactant at equilibrium? (K = equilibrium constant) (AIIMS 2008)

- (a) $A \rightleftharpoons B ; K = 0.001$ (b) $M \rightleftharpoons N ; K = 10$
 (c) $X \rightleftharpoons Y ; K = 0.005$ (d) $R \rightleftharpoons P ; K = 0.01$

182. 1.6 mole of $\text{PCl}_5(g)$ is placed in 4 dm³ closed vessel. When the temperature is raised to 500 K, it decomposes and at equilibrium 1.2 mole of $\text{PCl}_5(g)$ remains. What is the K_c value for the decomposition of $\text{PCl}_5(g)$ to $\text{PCl}_3(g)$ and $\text{Cl}_2(g)$ at 500 K? [PET (Kerala) 2008]

- (a) 0.013 (b) 0.050 (c) 0.033 (d) 0.067
 (e) 0.045

183. Consider the following statements regarding chemical equilibrium:

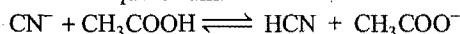
- For the gaseous reaction, the equilibrium can be established in open vessel.
- The state of equilibrium is dynamic in nature.
- If temperature is kept constant, the colour of the reacting system changes with time.

Which of the statements given above is/are correct?

(SCRA 2009)

- (a) 1 (b) 2 only
 (c) 3 only (d) 2 and 3 only

184. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium:



would be: [CBSE (PMT) 2009]

- (a) 3×10^4 (b) 3×10^5
 (c) 3×10^{-5} (d) 3×10^{-4}

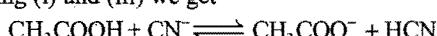
[Hint : Given

$$(i) \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \quad K_1 = 1.5 \times 10^{-5}$$

$$(ii) \text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^- \quad K_2 = 4.5 \times 10^{-10}$$

$$(iii) \text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN} \quad K_3 = \frac{1}{K_2} = \frac{1}{4.5 \times 10^{-10}}$$

Adding (i) and (iii) we get

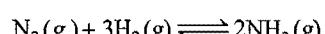


$$K = 1.5 \times 10^{-5} \times \frac{1}{4.5 \times 10^{-10}} = 3 \times 10^4$$

185. One mole of N_2O_4 is heated in a flask with a volume of 0.1 dm³. At equilibrium, 1.708 mole of NO_2 and 0.146 mole of N_2O_4 were found at 134°C . The equilibrium constant will be: (MPPEB 2009)

- (a) 250 mol dm^{-3} (b) 300 mol dm^{-3}
 (c) 200 mol dm^{-3} (d) 230 mol dm^{-3}

186. What is the effect of a tenfold increase in pressure on K_p in the reaction?



At equilibrium :

(EAMCET 2010)

- (a) a tenfold increase (b) a tenfold decrease
 (c) no change (d) equal to K_c

Set-2: The Questions given below may have more than one correct answers

1. Unit of equilibrium constant is:
 (a) $(\text{mol/L})^{1-n}$ (b) $(\text{mol/L})^{\Delta n}$
 (c) $(\text{atm})^{\Delta n}$ (d) all of these

2. Which is/are correct?
 (a) $2.303 \log K = -\Delta H^\circ/RT + \Delta S^\circ/R$
 (b) $\Delta G^\circ = -2.303RT \log K$
 (c) $-2.303 \log K = -\Delta H^\circ/RT^2 + \Delta S^\circ/R$
 (d) $2.303 \log K = (1/RT)(\Delta H^\circ + \Delta S^\circ)$

3. For the reaction, $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$, which is correct representation?
 (a) $K_p = (p_{\text{CO}_2})$ (b) $K_p = K_c(RT)$
 (c) $K_c = (\text{CO}_2)/1$ (d) All of these

4. $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$, $K_1; \left(\frac{1}{2}\right) \text{N}_2 + \left(\frac{1}{2}\right) \text{O}_2 \rightleftharpoons \text{NO}$, K_2 ;
 $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$, K_3 ; $\text{NO} \rightleftharpoons \left(\frac{1}{2}\right) \text{N}_2 + \left(\frac{1}{2}\right) \text{O}_2$, K_4
 Correct relation(s) between K_1, K_2, K_3 and K_4 is/are:
 (a) $K_1 \times K_3 = 1$ (b) $\sqrt{K_1} \times K_4 = 1$
 (c) $\sqrt{K_3} \times K_2 = 1$ (d) none of these

5. For the reaction, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, if degree of dissociation of N_2O_4 are 25%, 50%, 75% and 100%, the gradation of observed vapour densities is:
 (a) $d_1 > d_2 > d_3 > d_4$ (b) $d_4 > d_3 > d_2 > d_1$
 (c) $d_1 = d_2 = d_3 = d_4$ (d) none of these

6. The equation, $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for:
 (a) $A \rightleftharpoons nB / 2 + nC / 3$ (b) $A \rightleftharpoons nB / 3 + (2n/3)C$
 (c) $A \rightarrow (n/2)B + (n/4)C$ (d) $A \rightleftharpoons (n/2)B + C$

7. For a reaction, $nA \rightleftharpoons A_n$, degree of dissociation when A trimerises is:
 (a) $2 \left(\frac{d-D}{d} \right)$ (b) $\frac{3}{2} \left(\frac{d-D}{d} \right)$ (c) $\frac{4}{3} \left(\frac{d-D}{d} \right)$ (d) $2 \left(\frac{D-d}{d} \right)$.

8. For the reaction,

$$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$

 the forward reaction at constant temperature is favoured by:
 (a) introducing an inert gas at constant volume
 (b) introducing chlorine gas at constant volume
 (c) introducing an inert gas at constant pressure
 (d) increasing the volume of the container
 (e) introducing PCl_5 at constant volume

9. Which of the following will favour the formation of NH_3 by Haber's process?
 (a) Increase of temperature (b) Increase of pressure
 (c) Addition of catalyst (d) Addition of promoter

10. Which of the following will not affect the value of equilibrium constant of a reaction?

 - Change in the concentration of the reactants
 - Change in temperature
 - Change in pressure
 - Addition of catalyst

11. Which of the following statements is/are wrong?

 - At equilibrium, concentrations of reactants and products become constant because the reaction stops
 - Addition of catalyst speeds up the forward reaction more than the backward reaction
 - Equilibrium constant of an exothermic reaction decreases with increase of temperature
 - K_p is always greater than K_c

12. For the gas phase reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6; \quad \Delta H^\circ = -136.8 \text{ kJ mol}^{-1}$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by: [BHU (Mains) 2008]

 - increasing the temperature
 - decreasing the pressure
 - removing some H_2
 - adding some C_2H_6

13. When $NaNO_3$ is heated in a closed vessel oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, which are not correct?

 - Addition of $NaNO_2$ favours reverse reaction
 - Addition of $NaNO_3$ favours forward reaction
 - Increasing temperature favours forward reaction
 - Increasing pressure favours reverse reaction

14. An increase in temperature increases which of the following?

 - The rate constant of a reaction
 - The ionic product of water
 - The equilibrium constant of an exothermic reaction

Select the correct answer using the code given below:

(SCRA 2007)

 - 1 and 2 only
 - 1 and 3 only
 - 2 and 3 only
 - 1, 2 and 3 only

15. In the following question, more than one answers are correct. Select the correct answer and mark it according to the codes : Codes : [BHU (Mains) 2010]

 - 1, 2 and 3 are correct
 - 1 and 2 are correct
 - 2 and 4 are correct
 - 1 and 3 are correct

Water gas, an industrial fuel, consisting CO and H_2 in equimolar amounts is obtained by passing steam over red-hot carbon in accordance with the reaction :

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g); \quad \Delta H = +130.5 \text{ kJ}$$

The yield of water gas can be increased by

 - Reducing the total pressure of the system
 - Increasing pressure of steam
 - Raising the temperature
 - Introducing hot carbon

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 - (b) If both (A) and (R) are correct and (R) is not the correct explanation for (A).
 - (c) If (A) is correct but (R) is incorrect.
 - (d) If (A) is incorrect but (R) is correct.
1. (A) K_p can be equal to or less than or even greater than the value of K_c .
(R) $K_p = K_c (RT)^{\Delta n}$
Relation between K_p and K_c depends on the change in the number of moles of gaseous reactants and products.
2. (A) For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the equilibrium constant is 'K' then for $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ the equilibrium constant will be \sqrt{K} .
(R) If concentrations are changed to half the equilibrium constant will be halved.
3. (A) A catalyst does not influence the values of equilibrium constant.
(R) Catalysts influence the rate of both forward and backward reactions equally.
4. (A) The active mass of pure solid and pure liquid is taken unity.
(R) The active mass of pure solids and liquids depends on density and molecular mass. The density and molecular mass of pure liquids and solids are constant.
5. (A) For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If more Cl_2 is added the equilibrium will shift in backward direction hence, equilibrium constant will decrease.

(R) Addition of inert gas to the equilibrium mixture at constant volume, does not alter the equilibrium.

6. (A) At equilibrium $\Delta G = 0$
(R) $\Delta G^\circ = -RT \log_e K_c$ at equilibrium.
7. (A) At equilibrium $\Delta G = 0$
(R) The Gibbs free energy of reactants and products decreases and become equal at equilibrium.
8. (A) Equilibrium constant of a reaction changes on changing the stoichiometric coefficients of the reaction.
(R) The reactions : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ and $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ have same equilibrium constant.
9. (A) The Q_c for the reaction :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
 is $Q_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$
(R) When $Q_c < K_c$, the reaction is not at equilibrium and it will be fast in backward direction.
10. (A) The equilibrium of $[PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)]$ is not affected by changing the volume of container.
(R) $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$
Equilibrium constant K_c does not depend on the volume of vessel.
11. (A) The reaction : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ will shift in forward direction by increase in pressure.
(R) On increasing the pressure, the equilibrium will shift in forward direction.

Answers : OBJECTIVE QUESTIONS

● Set-1

- | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (b) | 2. (d) | 3. (c) | 4. (c) | 5. (a) | 6. (a) | 7. (b) | 8. (d) |
| 9. (d) | 10. (b) | 11. (c) | 12. (a) | 13. (d) | 14. (d) | 15. (b) | 16. (a) |
| 17. (b) | 18. (c) | 19. (c) | 20. (d) | 21. (a) | 22. (b) | 23. (d) | 24. (d) |
| 25. (c) | 26. (c) | 27. (a) | 28. (b) | 29. (d) | 30. (a) | 31. (a) | 32. (c) |
| 33. (d) | 34. (d) | 35. (d) | 36. (b) | 37. (d) | 38. (c) | 39. (d) | 40. (b) |
| 41. (a) | 42. (c) | 43. (b) | 44. (d) | 45. (d) | 46. (c) | 47. (b) | 48. (b) |
| 49. (c) | 50. (a) | 51. (d) | 52. (b) | 53. (b) | 54. (c) | 55. (d) | 56. (a) |
| 57. (d) | 58. (b) | 59. (a) | 60. (c) | 61. (c) | 62. (a) | 63. (b) | 64. (b) |
| 65. (d) | 66. (d) | 67. (a) | 68. (c) | 69. (b) | 70. (d) | 71. (a) | 72. (c) |
| 73. (b) | 74. (a) | 75. (d) | 76. (d) | 77. (a) | 78. (b) | 79. (c) | 80. (c) |
| 81. (d) | 82. (a) | 83. (d) | 84. (c) | 85. (b) | 86. (c) | 87. (a) | 88. (b) |
| 89. (c) | 90. (a) | 91. (d) | 92. (b) | 93. (a) | 94. (b) | 95. (b) | 96. (d) |
| 97. (c) | 98. (b) | 99. (a) | 100. (a) | 101. (a) | 102. (b) | 103. (c) | 104. (a) |
| 105. (a) | 106. (a) | 107. (a) | 108. (c) | 109. (b) | 110. (c) | 111. (d) | 112. (d) |
| 113. (c) | 114. (b) | 115. (a) | 116. (a) | 117. (b) | 118. (b) | 119. (d) | 120. (a) |
| 121. (d) | 122. (b) | 123. (a) | 124. (a) | 125. (a) | 126. (b) | 127. (b) | 128. (a) |
| 129. (b) | 130. (d) | 131. (c) | 132. (d) | 133. (a) | 134. (a) | 135. (c) | 136. (b) |
| 137. (b) | 138. (d) | 139. (c) | 140. (c) | 141. (d) | 142. (b) | 143. (d) | 144. (c) |
| 145. (c) | 146. (a) | 147. (b) | 148. (d) | 149. (b) | 150. (a) | 151. (a) | 152. (c) |
| 153. (d) | 154. (d) | 155. (d) | 156. (a) | 157. (b) | 158. (a) | 159. (b) | 160. (a) |
| 161. (a) | 162. (a) | 163. (b) | 164. (a) | 165. (a) | 166. (d) | 167. (a) | 168. (d) |
| 169. (a) | 170. (a) | 171. (e) | 172. (a) | 173. (c) | 174. (d) | 175. (d) | 176. (b) |
| 177. (d) | 178. (c) | 179. (a) | 180. (d) | 181. (b) | 182. (c) | 183. (d) | 184. (a) |
| 185. (c) | 186. (c) | | | | | | |

● Set-2

- | | | | | | | | |
|--------------|---------------|---------------|------------------|---------------|---------|---------|--------------|
| 1. (b, c) | 2. (a, b) | 3. (d) | 4. (a, b, c) | 5. (a) | 6. (b) | 7. (b) | 8. (c, d, e) |
| 9. (b, c, d) | 10. (a, b, d) | 11. (a, b, d) | 12. (a, b, c, d) | 13. (a, b, d) | 14. (a) | 15. (a) | |

Answers : ASSERTION-REASON TYPE QUESTIONS

- | | | | | | | | |
|--------|---------|---------|--------|--------|--------|--------|--------|
| 1. (a) | 2. (c) | 3. (a) | 4. (a) | 5. (c) | 6. (b) | 7. (a) | 8. (c) |
| 9. (c) | 10. (d) | 11. (a) | | | | | |

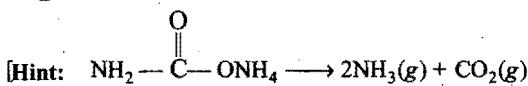
BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. Ammonium carbamate when heated to 200°C gives a mixture of NH₃ and CO₂ vapour with a density of 13. What is the degree of dissociation of ammonium carbamate?

[CEE (Kerala) 2004]

- (a) $\frac{3}{2}$ (b) $\frac{1}{2}$ (c) 2 (d) 1
 (e) $\frac{5}{2}$



Initial vapour density $D = \frac{\text{Molecular mass}}{2}$

$$= \frac{79}{2} \approx 39$$

$$\alpha = \frac{D - d}{(n - 1)d} = \frac{39 - 13}{(3 - 1) \times 13} = \frac{26}{26} = 1$$

here, n = number of moles of product formed by dissociation of 1 mole reactant.]

2. In the heterogeneous equilibrium:



what would be the effect of addition of CaCO₃ on the equilibrium concentration of CO₂?

- (a) Increases (b) Unpredictable
 (c) Decreases (d) Remains unaffected

Hint: Gaseous components are not present on both sides, hence, equilibrium will not be affected on addition of CaCO₃

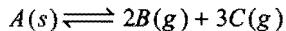
$$K_p = p_{\text{CO}_2} = \text{constant} \quad (\text{at constant temperature})$$

3. For the reaction, N₂O₄(g) \rightleftharpoons 2NO₂(g); if percentage dissociation of N₂O₄ are 25%, 50%, 75% and 100%, then the sequence of observed vapour densities will be:

- (a) $d_1 > d_2 > d_3 > d_4$ (b) $d_4 > d_3 > d_2 > d_1$
 (c) $d_1 = d_2 = d_3 = d_4$ (d) $(d_1 = d_2) > (d_3 = d_4)$

Hint: Lesser is the percentage dissociation; greater is the vapour density.]

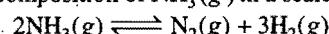
4. In a system:



if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to:

- (a) two times the original value
 (b) one half of its original value
 (c) $2\sqrt{2}$ times the original value
 (d) $\frac{1}{2\sqrt{2}}$ times the original value

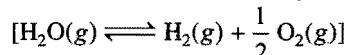
5. For the decomposition of NH₃(g) in a sealed tube:



- (a) K_p does not change with pressure
 (b) concentration of H₂(g) is less than that of nitrogen

- (c) concentration of ammonia does not change with pressure
 (d) K_p changes significantly with pressure

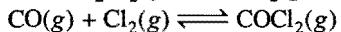
6. The equilibrium constant for the decomposition of water,



is given by:

- (a) $K = \frac{\alpha^3 p^{1/2}}{(1-\alpha)(2-\alpha)^{1/2}}$ (b) $K = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$
 (c) $K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$ (d) $K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

7. On heating a mixture of SO₂Cl₂ and CO, two equilibria are simultaneously established:



On adding more SO₂ at equilibrium what will happen?

- (a) Amount of CO will decrease
 (b) Amount of SO₂Cl₂ and COCl₂ will increase
 (c) Amount of CO will remain unaffected
 (d) Amount of SO₂Cl₂ and CO will increase

8. Consider the reactions,

- (i) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (ii) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

The addition of an inert gas at constant volume:

- (a) will increase the dissociation of PCl₅ as well as N₂O₄
 (b) will reduce the dissociation of PCl₅ as well as N₂O₄
 (c) will increase the dissociation of PCl₅ and step up the formation of NO₂
 (d) will not disturb the equilibrium of the reactions

Hint: At constant volume, inert gas will not affect any of the equilibrium.]

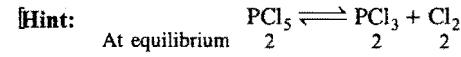
9. Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase of pressure on the equilibrium



- (a) favours backward reaction (b) favours forward reaction
 (c) has no effect (d) increases the reaction rate

10. A reaction at equilibrium involving 2 moles each of PCl₅, PCl₃ and Cl₂ is maintained at 250°C and a total pressure of 3 atm. The value of K_p is:

- (a) 2 (b) 3 (c) 4 (d) 1



$$p_{\text{PCl}_5} = \frac{2}{6} \times 3, p_{\text{PCl}_3} = \frac{2}{6} \times 3, p_{\text{Cl}_2} = \frac{2}{6} \times 3$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{1 \times 1}{1} = 1$$

11. In case of gaseous homogeneous reaction, the active mass of the reactant is given by the expression:

(a) $\frac{RT}{P}$ (b) $\frac{P}{RT}$ (c) $\frac{PV}{RT}$ (d) $\frac{n}{V} RT$

[Hint: $PV = nRT$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\therefore \text{Active mass (mol L}^{-1}\text{)} = \frac{P}{RT}$$

12. In the dissociation of $I_2(g)$ at 1000 K in a container of 1 litre:
 $I_2(g) \rightleftharpoons 2I^-(g); K_c = 10^{-6}$

Select the correct relation:

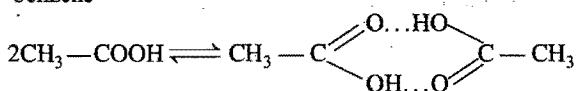
(a) $[I_2] > [I^-]$ (b) $[I_2] < [I^-]$ (c) $[I_2] = [I^-]$ (d) $[I_2] = \frac{1}{2} [I^-]$

[Hint: $K_c = \frac{[I^-]^2}{[I_2]}$

$$10^{-6} = \frac{[I^-]^2}{[I_2]}$$

$$\therefore [I_2] > [I^-]$$

13. Acetic acid undergoes dimerisation, when dissolved in benzene



Molecular mass of acetic acid is found 120. Which among the following relation is correct?

(a) $\alpha = 2\left(\frac{D-d}{d}\right)$ (b) $\alpha = 2\left(\frac{D-d}{D}\right)$
 (c) $\alpha = 2\left(\frac{d-D}{d}\right)$ (d) $\alpha = \frac{2d}{D-d}$

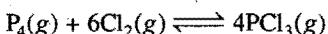
where, d = Observed vapour density

D = Theoretical vapour density

[Hint: For association of molecule

$$\alpha = \frac{d-D}{d(1-1/n)} = \frac{d-D}{d(1-1/2)} = \frac{2(d-D)}{d}$$

14. The equilibrium:



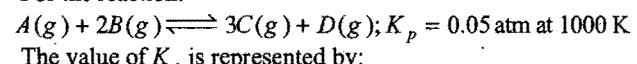
is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium:

(a) $[\text{Cl}_2] > [\text{PCl}_3]$ (b) $[\text{Cl}_2] > [\text{P}_4]$
 (c) $[\text{P}_4] > [\text{Cl}_2]$ (d) $[\text{PCl}_3] > [\text{P}_4]$

15. In the reaction: $A + B \rightleftharpoons 2C + D$. The initial concentration of A and B are 1 M each. The value of K_c is 10^8 . What is the equilibrium concentration of A ?

(a) 2×10^{-4} M (b) 2×10^4 M (c) 0.005 M (d) 0.0025 M

16. For the reaction:



(a) $5 \times 10^{-4} R$ (b) $\frac{5 \times 10^{-4}}{R}$ (c) $5 \times 10^{-5} R$ (d) $\frac{5 \times 10^{-5}}{R}$

[Hint: $K_p = K_c (RT)^{\Delta n}$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.05}{(1000 \times R)^1} = \frac{5 \times 10^{-5}}{R}$$

17. Match the List-I (equilibria) with List-II (conditions) and select the correct answer using the options given below:

List-I	List-II
P. $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$	1. High temperature
Q. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$	2. Low temperature
R. $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$	3. High pressure
	4. Low pressure
	5. Independent of pressure
P	Q
(a) 1, 3	2, 3
(b) 2, 3	1, 4
(c) 1, 5	2, 3
(d) 2, 4	1, 5
R	
	2, 4
	1, 3
	2, 4
	1, 3

18. At constant pressure, the presence of inert gases:

- (a) reduces the dissociation of PCl_5
 (b) increases the dissociation of PCl_5
 (c) does not affect the degree of dissociation of PCl_5
 (d) steps up the formation of PCl_5

[Hint: $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$

On adding inert gas, the equilibrium will shift towards higher volume direction.]

19. Which of the following expressions is correct?

(a) $K_p = K_c \left(\frac{RT}{\Sigma n}\right)^{\Delta n}$	(b) $K_p = K_x \left(\frac{P}{\Sigma n}\right)^{\Delta n}$
(c) $K_p = K_n \left(\frac{P}{\Sigma n}\right)^{\Delta n-1}$	(d) $K_p = K_c \left(\frac{P}{\Sigma n}\right)^{-\Delta n+1}$

20. The most stable oxide of nitrogen will be:

- (a) $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g); K = 2.2 \times 10^{30}$
 (b) $2\text{N}_2\text{O}(g) \rightleftharpoons 2\text{N}_2(g) + \text{O}_2(g); K = 3.5 \times 10^{33}$
 (c) $2\text{N}_2\text{O}_5(g) \rightleftharpoons 2\text{N}_2(g) + 5\text{O}_2(g); K = 1.2 \times 10^{24}$
 (d) $2\text{NO}_2(g) \rightleftharpoons \text{N}_2(g) + 2\text{O}_2(g); K = 6.7 \times 10^{16}$

[Hint: Stability constant = $\frac{1}{K}$

\therefore Smaller is the value of equilibrium constant greater is the stability of oxide.]

21. Equilibrium constant for two complexes are:

A: $\text{K}_4[\text{Fe}(\text{CN})_6] \quad 2.6 \times 10^{37}$ (for dissociation)

B: $\text{K}_3[\text{Fe}(\text{CN})_6] \quad 1.9 \times 10^{17}$ (for dissociation)

- (a) A and B are equally stable (b) A is more stable than B
 (c) B is more stable than A (d) the predictable stability

[Hint: Stability $\propto \frac{1}{\text{Equilibrium constant for dissociation}}$]

22. At the equilibrium of the reaction, $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$, the observed molar mass of N_2O_4 is 77.70 g. The percentage dissociation of N_2O_4 is:

(a) 28.4 (b) 46.7 (c) 22.4 (d) 18.4

[Hint: $\alpha = \frac{M_0 - M}{(n-1)M}$
 $= \frac{92 - 77.7}{(2-1) \times 77.7} = 0.184$

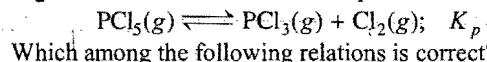
% Dissociation = 18.4]

23. Consider the following statements :

- In the Haber method of synthesis of ammonia
1. Increase of pressure favours the formation of NH_3
 2. Decrease of pressure produces more NH_3
 3. Increase of temperature dissociates NH_3
 4. Addition of inert gas favours the formation of NH_3
- Which of the statements given above are correct?

(SCRA 2009)

- (a) 1 and 3 (b) 2 and 4 (c) 1 and 4 (d) 2 and 3
 24. For the decomposition of $\text{PCl}_5(g)$ in a closed vessel, the degree of dissociation is α at total pressure P .



Which among the following relations is correct?

(a) $\alpha = \sqrt{\frac{K_p}{K_p + P}}$	(b) $\alpha = \sqrt{\frac{K_p + P}{K_p}}$
(c) $\alpha = \sqrt{K_p + P}$	(d) $\alpha = \frac{1}{\sqrt{K_p + P}}$

25. In the decomposition reaction of ammonia:



2 moles of NH_3 are introduced in the vessel of 1 litre. At equilibrium, 1 mole NH_3 was left, the value of K_e will be:

- (a) 0.75 (b) 0.70 (c) 1.75 (d) 1.70

[Hint: $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$

$$\begin{array}{cccc} t=0 & 2 & 0 & 0 \\ t_{eq.} & 1 & 1/2 & 3/2 \end{array}$$

$$K_e = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

$$= \frac{\frac{1}{2} \times \left(\frac{3}{2}\right)^3}{\frac{1}{2}} = 1.685 \approx 1.7$$

26. By which of the following relations, the equilibrium constant varies with temperature?

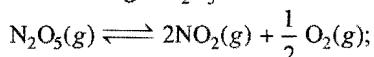
$$(a) \ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$(b) \ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R} \int_{1/T_1}^{1/T_2} d\left(\frac{1}{T^2}\right)$$

$$(c) \ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$(d) \ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R} \int_{1/T_2}^{1/T_1} d\left(\frac{1}{T}\right)$$

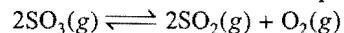
27. For dissociation of a gas N_2O_5 as:



If 'D' is the vapour density of equilibrium mixture and P_0 is the initial pressure of $\text{N}_2\text{O}_5(g)$, then its equilibrium pressure must not be (M is molecular mass of N_2O_5):

(a) $P_0 \frac{(M-2D)}{3D}$	(b) $\frac{P_0 M}{3D-M}$
(c) $\frac{P_0 M}{2D}$	(d) $\frac{2P_0 D}{M}$

28. $\text{SO}_3(g)$ is heated in a closed vessel. An equilibrium:



is established. The vapour density of the mixture, in which SO_3 is 50% dissociated, is:

- (a) 26.5 (b) 35 (c) 42 (d) 55

[Hint: $\alpha = \frac{D-d}{(n-1)d}$

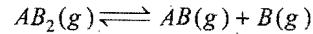
$$0.5 = \frac{40-d}{(2-1)d}$$

$$d = 26.5$$

29. When $\ln K$ is plotted against $\frac{1}{T}$ using the van't Hoff equation, a straight line is expected with a slope equal to:

- (a) $\Delta H^\circ/RT$ (b) $-\Delta H^\circ/R$ (c) $\Delta H^\circ/R$ (d) $R/\Delta H^\circ$

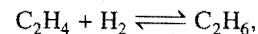
30. $AB_2(g)$ dissociates as,



The initial pressure of AB_2 is 600 mm Hg and total pressure is 800 mm Hg. The equilibrium constant for the reaction will be:

- (a) 500 (b) 100 (c) 200 (d) 400

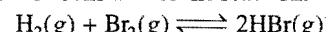
31. For the gaseous reaction,



the equilibrium constant has the units:

- (a) $\text{mol}^2 \text{dm}^{-3}$ (b) $\text{dm}^3 \text{mol}^{-1}$ (c) $\text{dm}^{-3} \text{mol}^{-1}$ (d) mol dm^{-3}

32. The equilibrium constant for the reaction:



is 67.8 at 300 K. The equilibrium constant for the dissociation of HBr is:

- (a) 0.0147 (b) 67.8 (c) 33.90 (d) 8.349

[Hint: $K_{\text{dissociation}} = \frac{1}{K_{\text{formation}}}$]

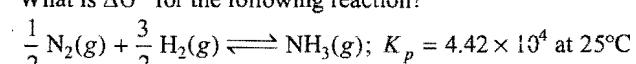
33. A large positive value of ΔG° corresponds to which of these?

- (a) Small positive K (b) Small negative K

- (c) Large positive K (d) Large negative K

[Hint: $\Delta G^\circ = -2.303RT \log K_e$]

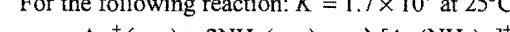
34. What is ΔG° for the following reaction?



- (a) $-26.5 \text{ kJ mol}^{-1}$ (b) $-11.5 \text{ kJ mol}^{-1}$

- (c) -2.2 kJ mol^{-1} (d) $-0.97 \text{ kJ mol}^{-1}$

35. For the following reaction: $K = 1.7 \times 10^7$ at 25°C



what is the value of ΔG° in kJ?

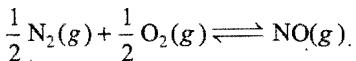
- (a) -41.2 (b) -17.9 (c) $+17.9$ (d) $+41.2$

36. If E_{cell}° for a given reaction is negative, which gives the correct relationships for the values of ΔG° and K_{eq} ?

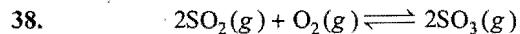
- (a) $\Delta G^\circ > 0, K_{eq} < 1$ (b) $\Delta G^\circ > 0, K_{eq} > 1$

- (c) $\Delta G^\circ < 0, K_{eq} > 1$ (d) $\Delta G^\circ < 0, K_{eq} < 1$

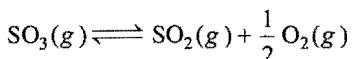
37. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K?



- (a) 8.4×10^{-5} (b) 7.1×10^{-9} (c) 4.2×10^{-10} (d) 1.7×10^{-19}



Given, that the equilibrium constant for the reaction above has a value of 278 at a particular temperature, what is the value of equilibrium constant for the following reaction at same temperature?



- (a) 1.3×10^{-5} (b) 1.8×10^{-3} (c) 3.6×10^{-3} (d) 6×10^{-2}

39. In which of the following reactions, the increase in volume of the container will favour the formation of products?

- (a) $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$
 (b) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
 (c) $4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(l)$
 (d) $3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$

40. Consider the reaction, whose $K_c = 33$,

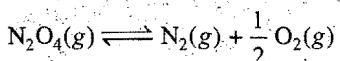


If 0.1 mol each of SO_2 and NO_2 are placed in 1 L container, what is the concentration of SO_2 at equilibrium?

- (a) 0.003 M (b) 0.015 M (c) 0.085 M (d) 0.097 M

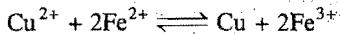
Reaction	K
$\frac{1}{2} \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons \text{NO}_2(g)$	K_1
$2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$	K_2

Using above equations, write down expression for K of the following reaction:



- (a) $K_1 K_2$ (b) $\frac{K_2^2}{K_1}$ (c) $\frac{1}{K_2 K_1^2}$ (d) $\frac{1}{K_1^2 K_2}$

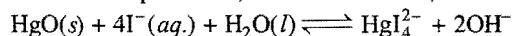
42. Cu^{2+} ions react with Fe^{2+} ions according to the following reaction:



At equilibrium, the concentration of Cu^{2+} ions is not changed by the addition of:

- (a) Cu^{2+} (b) Fe^{2+} (c) Cu (d) Fe^{3+}

43. Consider this equilibrium, for which $\Delta H < 0$,



Which changes will increase the equilibrium concentration of HgI_4^{2-} ?

- I. Increasing the mass of $\text{HgO}(s)$ present.
 II. Increasing $[\text{I}^-]$.
 III. Adding 1 M HCl.
 (a) I only (b) II only
 (c) II and III only (d) I, II and III

44. Which of the following do not change the value of K for a reaction?

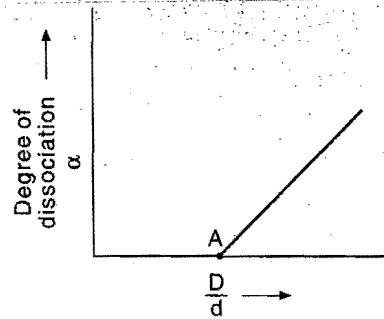
- (a) Addition of catalyst
 (b) Increase in temperature
 (c) Increase in pressure
 (d) Removal of one of the products

45. For which of the following reactions at equilibrium at constant temperature doubling the volume will cause a shift to the right?

- (a) $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 (b) $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$
 (c) $2\text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g)$
 (d) $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$

46. In the reaction,

$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ if D and d are the vapour densities at initial stage and at equilibrium then what will be the value of $\frac{D}{d}$ at point A in the following graph?



- (a) 0 (b) 1.5 (c) 1 (d) 0.5

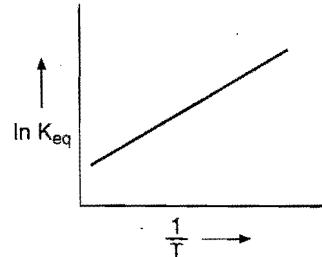
[Hint: $\alpha = \frac{D-d}{(n-1)d}$]

For the given reaction, $n = 2$ and $\alpha = 0$ at A

$$\therefore \frac{D-d}{(2-1)d} = 0$$

$$\frac{D}{d} = 1$$

47. A schematic plot of $\ln K_{\text{eq}}$ versus inverse of temperature for a reaction is shown below:



The reaction must be:

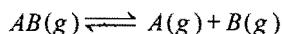
- (a) exothermic
 (b) endothermic
 (c) one with negligible enthalpy change
 (d) highly spontaneous at ordinary temperature

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

X	Y	Z	W
①	●	①	①
①	①	①	①
②	②	②	●
③	③	③	③
④	④	④	④
●	⑤	⑤	⑤
⑥	⑥	⑥	⑥
⑦	⑦	⑦	⑦
⑧	⑧	⑧	⑧
⑨	⑨	●	⑨

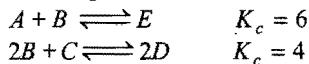
1. For the reaction:



AB is 33% dissociated at a total pressure of p . Then, $\frac{p}{K_p}$ will be equal to :

2. If the reaction $A \rightleftharpoons B$, has $\Delta G^\circ = 0$, then its equilibrium constant will be equal to :

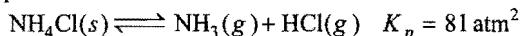
3. Consider the following reaction



What will be the equilibrium constant (K_c) for the following reaction?



4. For the equilibrium of the reaction :



Total pressure at equilibrium will be x times the pressure of NH_3 .

The value of x will be :

5. Mixing 4 moles of A with 4 moles of B forms 2 moles of C at equilibrium, according to the following reaction :



The value of equilibrium constant is :

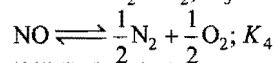
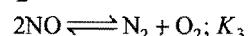
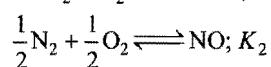
6. A reaction at equilibrium involving 2 mol each of PCl_5 , PCl_3 , Cl_2 is maintained at 250°C and total pressure of 3 atm. The value of K_p is :

7. For the reaction:



The initial concentrations of A and B are equal. The equilibrium concentration of C is two times the equilibrium concentration of A . The value of equilibrium constant is :

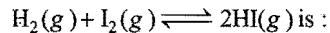
8. $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}; K_1$



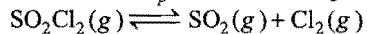
$$K_1 \times K_3 = x; \quad \sqrt{K_1} \times K_4 = y; \quad \sqrt{K_3} \times K_2 = z$$

What will be the value of xyz ?

9. 4.5 moles each of H_2 and I_2 are heated in a sealed 10 L vessel. At equilibrium, 3 mole of HI were found. The equilibrium constant for :



10. SO_2Cl_2 and Cl_2 are introduced into a 3 L vessel. Partial pressure of SO_2Cl_2 and Cl_2 at equilibrium are 1 atm and 2 atm respectively. The value of K_p for the following reaction is 10.



The total pressure in atm at equilibrium would be :

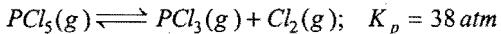
Answers

- | | | | | | | | |
|--------|---------|--------|--------|--------|--------|--------|--------|
| 1. (8) | 2. (1) | 3. (3) | 4. (2) | 5. (1) | 6. (1) | 7. (4) | 8. (1) |
| 9. (1) | 10. (8) | | | | | | |

LINKED COMPREHENSION TYPE QUESTIONS

● Passage 1

Phosphorous pentachloride when heated in a sealed tube at 700 K, it undergoes decomposition as,



vapour density of the mixture is 74.25.

Answer the following questions:

1. The reaction is:
 - (a) endothermic
 - (b) exothermic
 - (c) may be endothermic or exothermic
 - (d) unpredictable
2. Percentage dissociation of PCl_5 may be given as:
 - (a) 4.04
 - (b) 40.4
 - (c) 44.0
 - (d) 0.404
3. Equilibrium constant K_c for the reaction will be:
 - (a) 0.66 M
 - (b) 0.56 M
 - (c) 0.46 M
 - (d) 0.36 M
4. If pressure is increased then the equilibrium will:
 - (a) be unaffected
 - (b) shift in backward direction
 - (c) shift in forward direction
 - (d) cannot be predicted
5. When inert gas is added to the given reversible process then the equilibrium will:
 - (a) be unaffected
 - (b) shift in backward direction
 - (c) shift in forward direction
 - (d) cannot be predicted

● Passage 2

In Haber's process, the ammonia is manufactured according to the following reaction:

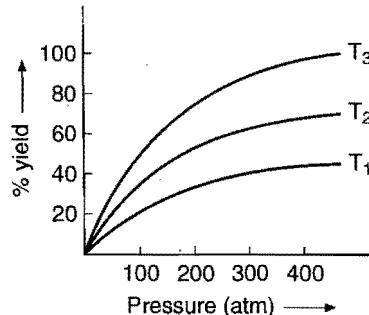


The pressure inside the chamber is maintained at 200 atm and temperature at 500°C. Generally, this reaction is carried out in presence of Fe catalyst.

Answer the following questions:

1. If K_p for the given reaction is 1.44×10^{-5} , then the value of K_c will be:
 - (a) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^2} \text{ mol L}^{-1}$
 - (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^2} \text{ mol L}^{-1}$
 - (c) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2} \text{ mol L}^{-1}$
 - (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}} \text{ mol L}^{-1}$
2. The preparation of ammonia by Haber's process is an exothermic reaction. If the preparation follows the following

temperature pressure relationship for its % yield. Then for temperature T_1 , T_2 and T_3 the correct option is:



- (a) $T_3 > T_2 > T_1$
 - (b) $T_1 > T_2 > T_3$
 - (c) $T_1 = T_2 = T_3$
 - (d) nothing could be predicted
- [Hint: The % yield will decrease with rise in temperature, since it is exothermic.]
3. 500°C is considered optimum temperature for Haber's process because:
 - (a) catalyst has maximum activity at this temperature
 - (b) energy required is easily obtained at this temperature
 - (c) yield is maximum at this temperature
 - (d) rate is fast enough while the yield is also appreciable at this temperature
 4. If K_p for the reaction is 1.44×10^{-5} , then the value of K_p for the decomposition of NH_3 ,



will be:

- (a) $\sqrt{1.44 \times 10^{-5}}$
- (b) $(1.44 \times 10^{-5})^2$
- (c) $\frac{1}{1.44 \times 10^{-5}}$
- (d) 2.88×10^{-5}

5. 30 litre $H_2(g)$ and 30 litre were taken for the reaction in Haber's process which yields only 50% of the expected ammonia due to reversibility of the reaction. What will be the composition of reaction mixture under the given condition?

	NH_3	N_2	H_2
(a)	20 L	20 L	20 L
(b)	10 L	25 L	15 L
(c)	20 L	10 L	30 L
(d)	20 L	25 L	15 L

● Passage 3

When all the coefficients in a balanced chemical equation are multiplied by a constant factor J, the equilibrium constant (originally K) becomes K^J . Similarly, when balanced equations are added together, the equilibrium constant for the combined process is equal to the product of the equilibrium constants for each step.

Equilibrium constant of the reversed reaction is numerically equal to the reciprocal of the equilibrium constant of the original equation.

$$\text{Unit of } K_p = (\text{atm})^{\Delta n}; \text{ Unit of } K_c = [\text{mol L}^{-1}]^{\Delta n}$$

Answer the following questions:

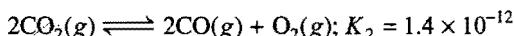
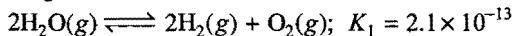
1. Consider the reactions:

- $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g); K_1$
- $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g); K_2$
- $\text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + 4\text{H}_2(g); K_3$

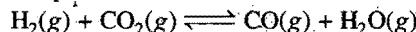
Which of the following is correct?

- $K_3 = K_1 / K_2$
- $K_3 = K_1^2 / K_2^3$
- $K_3 = K_1 K_2$
- $K_3 = K_1 \sqrt{K_2}$

2. The equilibrium constants for the following reactions at 1400 K are given:



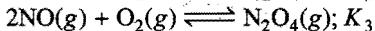
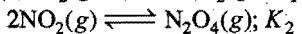
Then, the equilibrium constant K for the reaction,



is:

- 2.04
- 20.5
- 2.6
- 8.4

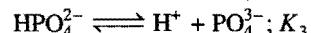
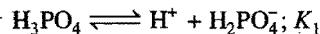
3. Given: $2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g); K_1$



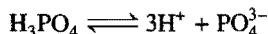
Which of the following relations is correct?

- $K_3 = K_1 / K_2$
- $K_3 = K_1 \times K_2$
- $K_3 = K_1 + K_2$
- $K_3 = \frac{K_1}{\sqrt{K_2}}$

4. H_3PO_4 is a tribasic acid, it undergoes ionization as:

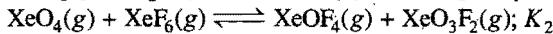
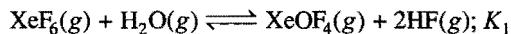


Then, equilibrium constant for the following reaction will be:

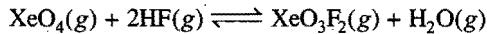


- $K_1 K_2 K_3$
- $\frac{K_1 K_2}{K_3}$
- $\frac{K_1 K_3}{K_2}$
- $\frac{K_1 K_2}{K_3^2}$

5. Consider the two reactions:



Then, the equilibrium constant for the following reaction will be:



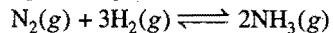
is given by:

- K_1 / K_2^2
- K_1 / K_2
- K_1^2 / K_2
- K_2 / K_1

when $Q > K$, reaction will favour backward direction and when $Q < K$, it will favour forward direction.

Answer the following questions:

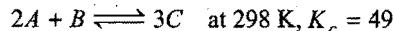
1. The reaction quotient Q for:



is given by $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$. The reaction will proceed in backward direction, when:

- $Q = K_c$
- $Q < K_c$
- $Q > K_c$
- $Q = 0$

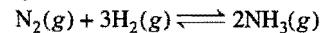
2. For the reaction:



A 3L vessel contains 2, 1 and 3 moles of A , B and C respectively. The reaction at the same temperature:

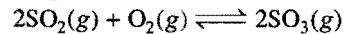
- must proceed in forward direction
- must proceed in backward direction
- must be in equilibrium
- cannot be predicted

3. In a reaction mixture containing H_2 , N_2 and NH_3 at partial pressure of 2 atm, 1 atm and 3 atm respectively, the value of K_p at 725 K is $4.28 \times 10^{-5} \text{ atm}^{-2}$. In which direction the net reaction will go?



- Forward
- Backward
- No net reaction
- Direction cannot be predicted

4. In the following reaction:



the equilibrium is not attained. The rate of forward reaction is greater than that of backward reaction. Thus, which of the following is the correct relation between K_p and Q_p ?

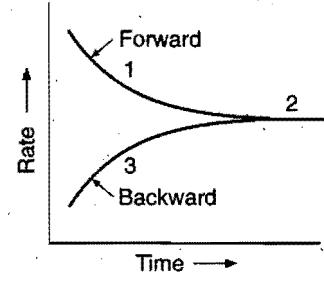
- $K_p = Q_p$
- $Q_p > K_p$
- $Q_p < K_p$
- $K_p = Q_p = 1$

5. In the reaction:



a graph is plotted to show the variation of rate of forward and backward reactions against time:

Which of following is correct?



● Passage 4

Mass action ratio or reaction quotient Q for a reaction can be calculated using the law of mass action,



$$Q = \frac{[C][D]}{[A][B]}$$

The value of Q decides whether the reaction is at equilibrium or not.

At equilibrium,

$$Q = K$$

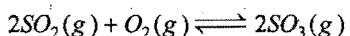
For non-equilibrium process, $Q \neq K$

	$Q > K$	$Q = K$	$Q < K$
(a)	3	2	1
(b)	1	2	3
(c)	2	3	1
(d)	2	1	3

● Passage 5

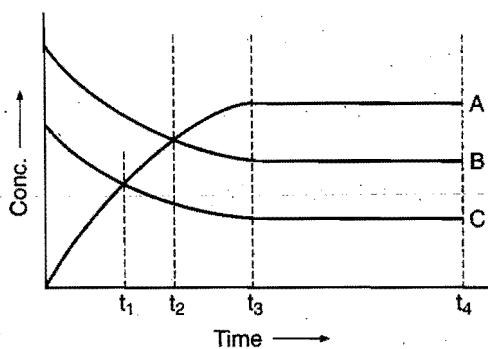
In a reversible chemical reaction, the rate of forward reaction decreases and that of backward reaction increases with the passage of time; at equilibrium the rate of forward and backward reactions become same.

Let us consider the formation of SO_3 in the following reversible reaction:

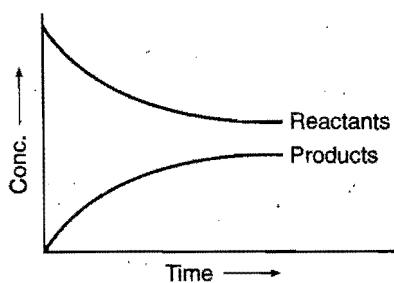


Following graphs are plotted for this reaction:

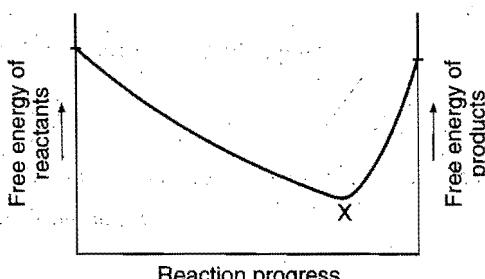
Graph 1



Graph 2



Graph 3



Answer the following questions:

1. In the graph (1), A, B and C respectively are:
 (a) SO_3 , SO_2 and O_2 (b) SO_3 , O_2 and SO_2
 (c) SO_2 , O_2 and SO_3 (d) O_2 , SO_2 and SO_3
2. In the graph (1), the equilibrium state is reached at:
 (a) t_1 (b) t_2 (c) t_3 (d) t_4
3. The graph (2) tells us that:
 (a) the reaction is irreversible
 (b) the reaction is reversible
 (c) the reaction is exothermic
 (d) the reaction is endothermic
4. The graph (2) tells us that:
 (a) equilibrium is never achievable
 (b) equilibrium is achieved after the concentrations of reactants and products become equal
 (c) equilibrium is achieved before the concentrations of reactants and products become equal
 (d) none of the above
5. From the graph (3), it can be interpreted that:
 (a) equilibrium is achieved at X
 (b) reaction is nearer to the completion
 (c) $\Delta G = 0$ at X
 (d) all of the above

Answers

Passage 1.

1. (a) 2. (b)

3. (a) 4. (b)

5. (c)

Passage 2.

1. (d) 2. (b)

3. (d) 4. (c)

5. (b)

Passage 3.

1. (c) 2. (d)

3. (b) 4. (a)

5. (d)

Passage 4.

1. (c) 2. (a)

3. (b) 4. (c)

5. (a)

Passage 5.

1. (a) 2. (c)

3. (b) 4. (c)

5. (d)

SELF ASSESSMENT

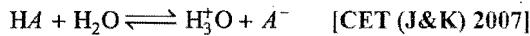
ASSIGNMENT NO. 9

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. By applying the law of mass action, the equilibrium constant K for the reaction:



$$(a) K = \frac{[HA][H_2O]}{[H_3O^+][A^-]} \quad (b) K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$(c) K = \frac{[H_3O^+][H_2O]}{[A^-][HA]} \quad (d) K = \frac{[HA][A^-]}{[H_2O][H_3O^+]}$$

2. For the reaction,



When temperature increases: [PMT (Haryana) 2007]

- (a) formation of NH_3 increases
- (b) formation of NH_3 decreases
- (c) concentration of N_2 decreases
- (d) concentration of H_2 decreases

3. For the reaction 1 g mole of $CaCO_3$ is enclosed in 5 L container

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = 1.16 \text{ atm}$ at 1073 K then percentage dissociation of $CaCO_3$ is:

- (a) 65% (b) 100% (c) 6.5% (d) zero

4. The activation energy for forward and backward reactions are 50 kJ/mol and 40 kJ/mol respectively. If K_1 and K_2 are the equilibrium constants of reaction at temperature T_1 and T_2 respectively and $T_2 > T_1$ then:

- (a) $K_1 < K_2$ (b) $K_1 = K_2$ (c) $K_1 > K_2$ (d) $K_2 = K_1^2$

[Hint: $\Delta H = E_f - E_b = 50 - 40 = 10 \text{ kJ/mol}$. In endothermic reactions, equilibrium constant increases with increase in temperature.]

5. Given, $X(g) \rightleftharpoons nY(g)$.

If degree of dissociation is α , then K_c of the reaction in a vessel of 1 litre is:

$$(a) \frac{n\alpha^n}{1-\alpha} \quad (b) \frac{n\alpha}{1-\alpha} \quad (c) \frac{(n\alpha)^n}{1+\alpha} \quad (d) \frac{(n\alpha)^n}{1-\alpha}$$

6. Consider the following equation in a closed container,



at a fixed temperature, the volume of the reaction container is halved, for this change, which of the following statement holds true regarding the K_p and degree of dissociation ' α '?

- (a) neither K_p nor α changes
- (b) both K_p and α change
- (c) K_p changes but α does not change
- (d) K_p does not change but α changes

7. The reaction, $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ is studied in a vessel of one litre at 250°C. The initial concentration of A was $3x$ and that of B was x . At equilibrium, concentration of C was

found to be equal to the equilibrium concentration of B . What is the concentration of D at equilibrium:

$$(a) \frac{x}{2} \quad (b) 3x - \frac{1}{2} \quad (c) x - \frac{x}{2} \quad (d) x$$

SECTION-II

Multiple Answers Type Objective Questions

8. Equilibrium constant does not depend on:
 - (a) catalyst
 - (b) temperature
 - (c) pressure
 - (d) inert gas
9. Which of the following reactions have $K_p < K_c$?
 - (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 - (b) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
 - (c) $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$
 - (d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
10. Which of the following reactions are not affected by inert gas addition?
 - (a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
 - (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(In a rigid container of constant volume)
 - (c) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
 - (d) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
11. Which of the following are not affected by pressure change?
 - (a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
 - (b) $2NaNO_2(s) + O_2(g) \rightleftharpoons 2NaNO_3(s)$
 - (c) $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
 - (d) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
12. The reaction,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
 (Exothermic)
 will shift in forward direction by:
 - (a) adding SO_3 at constant volume
 - (b) increasing volume of container
 - (c) adding SO_2 at constant volume
 - (d) adding inert gas at constant volume

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
- (b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
- (c) Statement-1 is true; statement-2 is false.
- (d) Statement-1 is false; statement-2 is true.
13. Statement-1: The value of equilibrium constant depends on the stoichiometry of the equation.
Because

Statement-2: The value of equilibrium constant does not change when the equation is multiplied or divided by a number.

14. **Statement-1:** $K_p = K_c$ for all reactions.
Because

Statement-2: K_p and K_c are interrelated by the equation $K_p = K_c (RT)^{\Delta n}$.

15. **Statement-1:** Catalyst does not change the position of equilibrium.
Because

Statement-2: Catalyst only changes the equilibrium time.

16. **Statement-1:** Free energy of both reactants and products are minimum at equilibrium.
Because

Statement-2: The free energy of reactants and products decreases with passage of time and become equal at equilibrium.

17. **Statement-1:** Addition of inert gases at equilibrium will support the dissociation of PCl_5 at constant temperature.
Because

Statement-2: The addition of inert gas at constant volume will not affect the equilibrium.

SECTION-IV

Matrix-Matching Type Questions

This section contains 4 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in List-I have to be matched with statements (p, q, r and s) in List-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
b	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
c	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>

18. Match the List-I with List-II:

List-I	List-II
(a) $A(g) \rightleftharpoons B(g) + C(g)$	(p) $\alpha = \sqrt{\frac{K_p}{K_p + 4P}}$
(b) $A_2(g) \rightleftharpoons 2A(g)$	(q) $\alpha = \sqrt{\frac{K_p}{P + K_p}}$
(c) $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$	(r) $M_{\text{mix}} = \frac{M_{\text{reactant}}}{1 + \alpha}$
(d) $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$	(s) Forward shift on decreasing the pressure

19. Match the List-I with List-II:

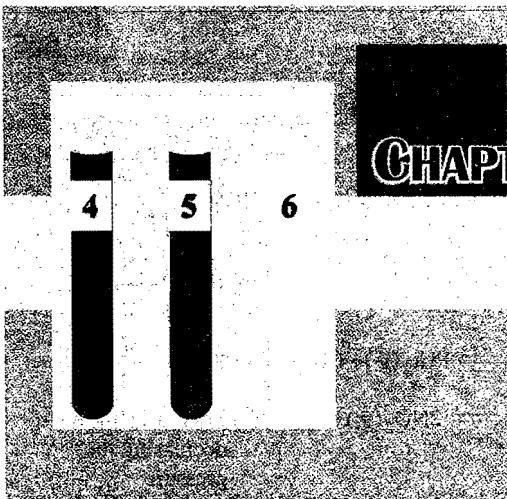
List-I	List-II
(Mathematical process)	(New equilibrium constant)
(a) Divided by n	(p) K^n
(b) Multiplied by n	(q) $\frac{1}{K}$
(c) Reaction is reversed	(r) $K_1 \times K_2 \times K_3 \times \dots \times K_n$
(d) n -equations are added	(s) $(K)^{1/n}$

20. Match the List-I with List-II for the following reaction:
 $\text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)$

List-I	List-II
(a) Partial pressure of $\text{NH}_4\text{HS}(s)$	(p) $p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}$
(b) K_p	(q) $p_{\text{NH}_3} + p_{\text{H}_2\text{S}}$
(c) Total pressure at equilibrium	(r) $(p_{\text{NH}_3} \times p_{\text{H}_2}) (RT)^{-2}$
(d) K_c	(s) Zero

Answers

- | | | | | | | | |
|-----------------------------|--|---------------|------------|-----------------------------|---------|---------|--------------|
| 1. (b) | 2. (b) | 3. (c) | 4. (a) | 5. (d) | 6. (d) | 7. (a) | 8. (a, b, d) |
| 9. (b, d) | 10. (a, b) | 11. (a, b, c) | 12. (a, b) | 13. (c) | 14. (d) | 15. (a) | 16. (a) |
| 17. (b) | 18. (a-q,r,s) (b-p,q,s) (c-q, r,s) (d-p,s) | | | 19. (a-s) (b-p) (c-q) (d-r) | | | |
| 20. (a-s) (b-p) (c-q) (d-r) | | | | | | | |



CHAPTER

10

IONIC EQUILIBRIUM

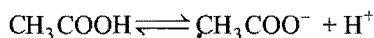
10.1 INTRODUCTION

The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state or in solution.

There are two types of electrolytes:

(1) Strong electrolytes: These electrolytes are almost completely ionised when dissolved in a polar medium like water. In solution they are excellent conductors, e.g., HNO_3 , HCl , KOH , NaOH , etc. Their degree of ionization is high and approaches unity.

(2) Weak electrolytes: These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g., CH_3COOH , H_3PO_4 , H_3BO_3 , NH_4OH , etc. Equilibrium between ions and unionised molecules is established in solution; e.g.,

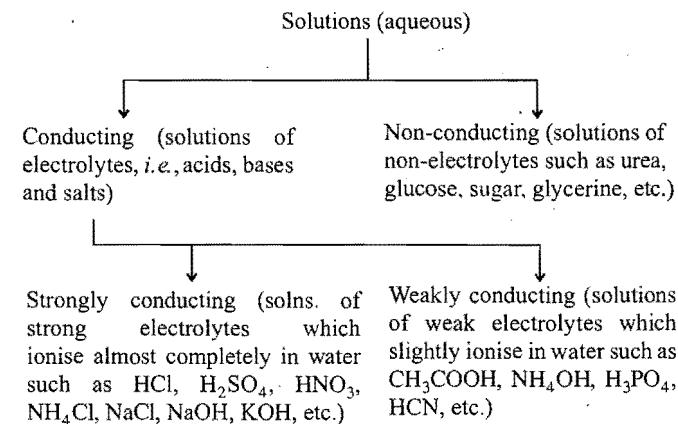


The above equilibrium is termed as ionic equilibrium. Degree of ionization of weak electrolytes is much less than unity.

Degree of ionization ' α ' may be defined as a fraction of total number of molecules of an electrolyte which dissociate into ions.

$$\begin{aligned}\alpha &= \frac{\% \text{ ionization}}{100} \\ &= \frac{\text{Number of molecules dissociated as ions}}{\text{Total number of molecules of electrolyte dissolved}}\end{aligned}$$

The following classification of electrolytes is based on their behaviour in a particular solvent, i.e., water.

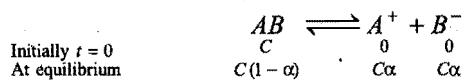


However, an electrolyte may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

10.2 OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolytic dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, **law of mass action** can be applied to such systems also.

Consider a binary electrolyte AB which dissociates into A^+ and B^- ions and the equilibrium state is represented by the equation:



So, dissociation constant may be given as:

$$\begin{aligned} K &= \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} \\ &= \frac{C\alpha^2}{(1-\alpha)} \quad \dots (\text{i}) \end{aligned}$$

For very weak electrolytes,

$$\begin{aligned} \alpha &\ll 1, (1-\alpha) \approx 1 \\ K &= C\alpha^2 \\ \alpha &= \sqrt{K/C} \quad \dots (\text{ii}) \end{aligned}$$

Concentration of any ion = $C\alpha = \sqrt{CK}$.

From equation (ii), it is clear that degree of ionization increases on dilution.

Thus, **degree of dissociation of a weak electrolyte is proportional to the square root of dilution.**

Limitations of Ostwald's dilution law: The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of ' α ' is determined by conductivity measurements by applying the formula Λ / Λ_∞ . The value of ' α ' determined at various dilutions of an electrolyte when substituted in eq. (i) gives a constant value of K only in the case of weak electrolytes like CH_3COOH , NH_4OH , etc. The cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors:

(i) The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionised at all dilutions and Λ / Λ_∞ does not give accurate value of ' α '.

(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, law of mass action in its simple form cannot be strictly applied in the case of strong electrolytes.

SOME SOLVED EXAMPLES

Example 1. A 0.01 M solution of acetic acid is 5% ionised at 25°C . Calculate its dissociation constant.

Solution: According to Ostwald's dilution law,

$$\begin{aligned} K_a &= \frac{\alpha^2}{(1-\alpha)V} \\ \alpha &= 0.05, V = \frac{1}{0.01} = 100 \text{ litre} \end{aligned}$$

$$\text{Hence, } K_a = \frac{0.05 \times 0.05}{(1-0.05)100} = 2.63 \times 10^{-5}$$

Example 2. Calculate the H^+ ion concentration of a 0.01 N weak monobasic acid. The value of dissociation constant is 4.0×10^{-10} .



Applying Ostwald's dilution law for a weak acid,

$$\alpha = \sqrt{K_a V}$$

$$K_a = 4.0 \times 10^{-10}, V = \frac{1}{0.01} = 100 \text{ litre}$$

$$\alpha = \sqrt{4 \times 10^{-10} \times 10^2} = 2 \times 10^{-4}$$

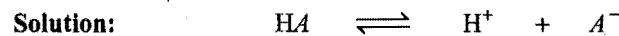
Concentration of hydrogen ions

$$= \frac{\alpha}{V} = \frac{2 \times 10^{-4}}{100} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

or concentration of hydrogen ions

$$= \sqrt{CK} = \sqrt{0.01 \times 4 \times 10^{-10}} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

Example 3. The concentration of H^+ ions in 0.10 M solution of a weak acid is $1.0 \times 10^{-5} \text{ mol L}^{-1}$. Calculate the dissociation constant of the acid.



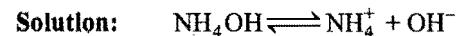
Initial concentration	0.1	0	0
Equilibrium concentration (mol L ⁻¹)	$0.1 - 1.0 \times 10^{-5}$	1.0×10^{-5}	1.0×10^{-5}

[HA] can be taken as 0.1 M as 1.0×10^{-5} is very small.

Applying law of mass action,

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{1.0 \times 10^{-5} \times 1.0 \times 10^{-5}}{0.10} \\ &= 1 \times 10^{-9} \end{aligned}$$

Example 4. What will be the dissociation constant of 0.1 N aqueous ammonia solution in terms of degree of dissociation ' α '? What will be the value if the concentration is 0.01 N ?



$$\text{At equilibrium} \quad (1-\alpha) \quad \alpha \quad \alpha$$

Since, the solution is 0.1 N ,

$$V = \frac{1}{0.1} = 10 \text{ litre}$$

$$[\text{NH}_4\text{OH}] = \frac{(1-\alpha)}{10}, [\text{NH}_4^+] = \frac{\alpha}{10} \text{ and } [\text{OH}^-] = \frac{\alpha}{10}$$

Applying law of mass action,

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{\frac{\alpha}{10} \times \frac{\alpha}{10}}{\frac{1-\alpha}{10}} = \frac{\alpha^2}{10(1-\alpha)}$$

For 0.01 N solution, K_b remains the same at the same temperature but degree of dissociation value becomes different.

Example 5. A 0.0128 N solution of acetic acid has $\Lambda = 14\text{ mho equiv}^{-1}$ and $\Lambda_\infty = 391\text{ mho eq}^{-1}$ at 25°C . Calculate the dissociation constant of the acid.

Solution: Degree of dissociation,

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}} = \frac{14}{391} = 3.58 \times 10^{-2}$$

[$1 - \alpha \rightarrow 1$ as α is very small]

Now applying Ostwald's dilution law,

$$K_a = \frac{\alpha^2}{(1-\alpha)V}$$

$$\alpha = 3.58 \times 10^{-2} \text{ and } V = \frac{1}{0.0128} \text{ litre}$$

$$\text{So, } K_a = 3.58 \times 10^{-2} \times 3.58 \times 10^{-2} \times 0.0128 = 1.64 \times 10^{-5}$$

10.3 COMMON ION EFFECT

Let AB be the weak electrolyte. Considering its dissociation,



and applying law of mass action, we have

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant, K , has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution, it will increase the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increase, i.e., the equilibrium will shift to the left hand side.

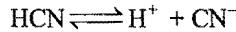
In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionisation is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or $NaOH$ to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH_4^+ or OH^- .

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

SOME SOLVED EXAMPLES

Example 6. The ionisation constant of HCN is 4×10^{-10} . Calculate the concentration of hydrogen ions in 0.2 M solution of HCN containing 1 mol L^{-1} of KCN.

Solution: The dissociation of HCN is represented as



Applying law of mass action,

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \quad \text{or} \quad [H^+] = \frac{K_a [HCN]}{[CN^-]}$$

In presence of strong electrolyte, the total CN^- concentration comes from KCN which undergoes complete dissociation. It is further assumed that dissociation of HCN is very-very small and the concentration of HCN can be taken as the concentration of undissociated HCN.

$$\text{Thus, } [HCN] = 0.2 \text{ M and } [CN^-] = 1 \text{ M}$$

Putting these values in the expression

$$[H^+] = \frac{K_a [HCN]}{[CN^-]} = \frac{4 \times 10^{-10} \times 0.2}{1} = 8 \times 10^{-11} \text{ mol L}^{-1}$$

Note: When KCN is not present, the $[H^+]$ concentration is equal to \sqrt{CK} , i.e., $\sqrt{0.2 \times 4 \times 10^{-10}} = 8.94 \times 10^{-6} \text{ mol L}^{-1}$. This shows that concentration of H^+ ions falls considerably when KCN is added to HCN solution.

Example 7. Determine the concentration of hydroxyl ions in 0.4 M NH_4OH solution having (i) no ammonium chloride and (ii) 5.35 g of NH_4Cl in a litre of the solution. Ionisation constant of NH_4OH is 1.8×10^{-5} .

Solution: (i) Let ' α ' be the degree of dissociation of NH_4OH in absence of NH_4Cl .

$$\alpha = \sqrt{\frac{K_b}{C}}$$

$$\text{So, } [OH^-] = C\alpha = \sqrt{K_b C} = \sqrt{1.8 \times 10^{-5} \times 0.4} = 2.68 \times 10^{-3} \text{ mol L}^{-1}$$

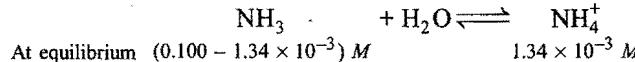
(ii) In presence of NH_4Cl ,

$$[NH_4^+] = \frac{5.35}{53.5} = 0.1 \text{ M and } [NH_4OH] = 0.4 \text{ M}$$

$$\text{So, } [OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]} = \frac{1.8 \times 10^{-5} \times 0.4}{0.1} = 7.2 \times 10^{-5} \text{ mol L}^{-1}$$

Example 8. When 0.100 mole of ammonia, NH_3 , is dissolved in sufficient water to make 1.0 L of solution, the solution is found to have a hydroxide ion concentration of $1.34 \times 10^{-3} \text{ M}$. Calculate K_b for ammonia.

Solution:



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1.34 \times 10^{-3} \times 1.34 \times 10^{-3}}{0.09866} = 1.8199 \times 10^{-5}$$

Example 9. K_a for HA is 4.9×10^{-8} . After making the necessary approximation, calculate for its decimolar solution

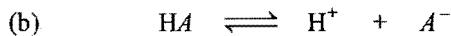
(a) % dissociation

(b) H^+ ion concentration.

Solution: (a) For a weak electrolyte,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9 \times 10^{-8}}{0.1}} = 7 \times 10^{-4}$$

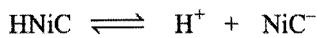
$$\% \text{dissociation} = 100 \times \alpha = 100 \times 7 \times 10^{-4} \\ = 7 \times 10^{-2}$$



$$C(1-\alpha) \quad C\alpha \quad C\alpha \\ [H^+] = C \times \alpha = 0.1 \times 7 \times 10^{-4} = 7 \times 10^{-5} \text{ mol L}^{-1}$$

Example 10. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula $HNiC$. Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2 litre of solution. (IIT 1993)

Solution: Initial concentration of the nicotinic acid $= \frac{0.10}{2} = 0.05 \text{ mol L}^{-1}$



$$\text{Equilibrium conc. } (0.05-x) \quad x \quad x$$

As x is very small, $(0.05-x)$ can be taken as 0.05

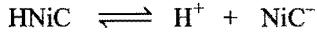
$$K_a = \frac{[H^+][NiC^-]}{[HNiC]} = \frac{x \times x}{0.05}$$

$$\text{or } x^2 = (0.05) \times (1.4 \times 10^{-5})$$

$$\text{or } x = 0.83 \times 10^{-3} \text{ mol L}^{-1}$$

$$\% \text{dissociation} = \frac{0.83 \times 10^{-3}}{0.05} \times 100 = 1.66$$

Alternative method: Let α be the degree of dissociation



$$\text{At equilibrium } 0.05(1-\alpha) \quad 0.05\alpha \quad 0.05\alpha$$

$$K_a = \frac{0.05\alpha \times 0.05\alpha}{0.05(1-\alpha)}$$

As α is very small, $(1-\alpha) \rightarrow 1$.

$$\text{So, } 1.4 \times 10^{-5} = 0.05\alpha^2$$

$$\text{or } \alpha = \sqrt{\frac{1.4 \times 10^{-5}}{0.05}} = 1.67 \times 10^{-2}$$

$$\text{Per cent dissociation} = 100 \times \alpha = 100 \times 1.67 \times 10^{-2}$$

$$= 1.67$$

Example 11. At 30°C , the degree of dissociation of $0.066 \text{ M } HA$ is 0.0145. What would be the degree of dissociation of 0.02 M solution of the acid at the same temperature?

Solution: Let the ionisation constant of the acid be K_a . Degree of dissociation at 0.066 M concentration = 0.0145.

$$\text{Applying } \alpha = \sqrt{\frac{K_a}{C}}$$

$$0.0145 = \sqrt{\frac{K_a}{0.066}} \quad \dots (i)$$

Let the degree of dissociation of the acid at 0.02 M concentration be α_1 .

$$\alpha_1 = \sqrt{\frac{K_a}{0.02}} \quad \dots (ii)$$

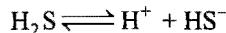
Dividing eq. (ii) by eq. (i),

$$\frac{\alpha_1}{0.0145} = \sqrt{\frac{0.066}{0.02}} = 1.8166$$

$$\text{or } \alpha_1 = 0.0145 \times 1.8166 = 0.0263$$

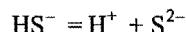
Example 12. A solution contains $0.1 \text{ M } H_2S$ and $0.3 \text{ M } HCl$. Calculate the concentration of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively. (IIT 1992)

Solution:



$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \quad \dots (i)$$

Further



$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \quad \dots (ii)$$

Multiplying both the equations

$$K_{a_1} \times K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Due to common ion, the ionisation of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of $0.3 \text{ M } HCl$.

$$[S^{2-}] = \frac{K_{a_1} \times K_{a_2} [H_2S]}{[H^+]^2} = \frac{1.0 \times 10^{-7} \times 1.3 \times 10^{-13} \times (0.1)}{(0.3)^2} \\ = 1.44 \times 10^{-20} \text{ M}$$

Putting the value of $[S^{2-}]$ in eq. (ii),

$$1.3 \times 10^{-13} = \frac{0.3 \times 1.44 \times 10^{-20}}{[HS^-]}$$

$$\text{or } [HS^-] = \frac{0.3 \times 1.44 \times 10^{-20}}{1.3 \times 10^{-13}} = 3.3 \times 10^{-8} \text{ M}$$

Example 13. What is the H^+ ion concentration of a solution known to contain 0.1g mole of CH_3COONH_4 in one litre of $0.1 \text{ M } CH_3COOH$? Assume effective ionisation of ammonium acetate is 80%. K_a for acetic acid is 1.8×10^{-5} .

Solution: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

The solution also contains CH_3COONH_4 which is 80% dissociated, i.e., $\alpha = 0.8$. Thus, the acetate concentration provided by $0.1 \text{ M } CH_3COONH_4 = 0.1 \times 0.8 = 0.08 \text{ M}$

$$\text{Total } [CH_3COO^-] = (0.08+x) \text{ M}$$

$$\text{So, } K_a = \frac{(0.08+x)x}{(0.1-x)}$$

As x is very small, $(0.1-x) \rightarrow 0.1$ and neglecting x^2 ,

$$K_a = \frac{0.08x}{0.1}$$

or $1.8 \times 10^{-5} \times 0.1 = 0.08x$

$$\text{or } x = [\text{H}^+] = \frac{1.8 \times 10^{-5} \times 0.1}{0.08} = 2.25 \times 10^{-5} \text{ mol L}^{-1}$$

Example 14. Ostwald obtained the following table by determining the equivalent conductivities containing one gram equivalent of acetic acid in V litre. If the equivalent conductivity of acetic acid at infinite dilution be 364, show that the results are in agreement with Ostwald's law.

Volume in litre (V)	Equivalent conductivity
8	4.34
64	12.09
128	16.99

Solution: Degree of dissociation, $\alpha = \frac{\Lambda_V}{\Lambda_\infty}$

$$(i) \quad \alpha_1 = \frac{4.34}{364} = 0.0119$$

$$(ii) \quad \alpha_2 = \frac{12.09}{364} = 0.0332$$

$$(iii) \quad \alpha_3 = \frac{16.99}{364} = 0.0467$$

Now applying Ostwald's dilution law,

$$(i) \quad K_a = \frac{\alpha_1^2}{V_1} = \frac{0.0119 \times 0.0119}{8} = 1.77 \times 10^{-5}$$

$$(ii) \quad K_a = \frac{\alpha_2^2}{V_2} = \frac{0.0332 \times 0.0332}{64} = 1.72 \times 10^{-5}$$

$$(iii) \quad K_a = \frac{\alpha_3^2}{V_3} = \frac{0.0467 \times 0.0467}{128} = 1.70 \times 10^{-5}$$

The values of K_a are nearly the same which show the validity of Ostwald's dilution law.

Example 15. Calculate the dissociation constant of $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) if 0.02 M solution is 2% dissociated.

Solution: $\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$

$$\begin{aligned} K_a &= \frac{[\text{H}^+]^2 [\text{C}_2\text{O}_4^{2-}]}{[\text{H}_2\text{C}_2\text{O}_4]} \\ &= \frac{(2\alpha)^2 \times (\alpha)}{C(1-\alpha)} \\ &= \frac{4C^2\alpha^3}{1-\alpha} \quad [1-\alpha \rightarrow 1 \text{ as } \alpha \text{ is small}] \\ &= 4C^2\alpha^3 \\ &= 4 \times 0.02 \times 0.02 \times (0.02)^3 \\ &= 1.28 \times 10^{-8} \end{aligned}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. A monoprotic acid in 0.1 M solution ionizes to 0.001%. Its ionisation constant is:

(a) 1×10^{-3} (b) 1×10^{-6} (c) 1×10^{-8} (d) 1×10^{-11}

[Ans. (d)]

$$\begin{aligned} \text{Hint: } \alpha &= \sqrt{\frac{K_a}{C}} \quad \text{or} \quad K_a = C\alpha^2 = 0.1 \times \left(\frac{0.001}{100}\right)^2 \\ &= 1 \times 10^{-11} \end{aligned}$$

2. The hydrogen ion concentration in mol/dm³ in 0.2 M solution of weak acid, HA ($K_a = 2 \times 10^{-5}$) is close to:

(a) 2×10^{-5} (b) 2×10^{-4} (c) 2×10^{-3} (d) 2×10^{-2}

[Ans. (c)]

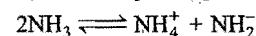
$$\text{Hint: } [\text{H}_3\text{O}^+] = \sqrt{CK_a} = \sqrt{0.2 \times 2 \times 10^{-5}} = 2 \times 10^{-3}$$

3. Autoprotolysis constant of NH_3 is:

$$\begin{array}{ll} (a) [\text{NH}_4^+][\text{NH}_3] & (b) [\text{NH}_2^-][\text{NH}_3] \\ (c) [\text{NH}_4^+][\text{NH}_2^-] & (d) \frac{[\text{NH}_4^+]}{[\text{NH}_2^-]} \end{array}$$

[Ans. (c)]

Hint: Autoprotolysis of NH_3 takes place as:



$$\therefore \text{Autoprotolysis constant} = [\text{NH}_4^+][\text{NH}_2^-]$$

4. The degree of ionization of an acid HA is 0.00001 at 0.1 M concentration. Its dissociation constant will be:

(a) 10^{-9} (b) 10^{-8} (c) 10^{-11} (d) 10^{-7}

[Ans. (c)]

Hint: For monoprotic acid HA:

$$K_a = C\alpha^2 = 0.1 \times (10^{-5})^2 = 10^{-11}$$

5. The first and second dissociation constants of an acid, H_2A , are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be: (AIEEE 2007)

(a) 0.2×10^5 (b) 5.0×10^{-5}
 (c) 5.0×10^{-15} (d) 5.0×10^{15}

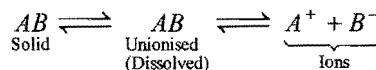
[Ans. (c)]

$$\begin{aligned} \text{Hint: } K_a &= K_{a_1} \times K_{a_2} \\ &= 1 \times 10^{-5} \times 5 \times 10^{-10} \\ &= 5 \times 10^{-15} \end{aligned}$$

104 SOLUBILITY PRODUCT

If to a given amount of solvent at a particular temperature, a solute is added gradually in increasing amounts, a stage is reached when some of the solute remains undissolved, no matter how long we wait or how vigorously we stir. The solution is then said to be saturated. A solution which remains in contact with undissolved solute is said to be saturated. At saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

In case, the solute is an electrolyte, its ionisation occurs in solution and degree of dissociation depends on the concentration of dissolved electrolyte at a particular temperature. Thus, in a saturated solution of an electrolyte two equilibria exist and can be represented as:



Applying the law of mass action to the ionic equilibrium,

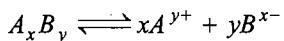
$$\frac{[A^+][B^-]}{[AB]} = K$$

Since, the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, i.e., $[AB] = K' = \text{constant}$.

Hence, $[A^+][B^-] = K[AB] = KK' = K_s$ (constant)

K_s is termed as the solubility product. It is defined as the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.

Consider, in general, the electrolyte of the type A_xB_y , which is dissociated as:



Applying law of mass action,

$$\frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]} = K$$

When the solution is saturated,

$$[A_xB_y] = K' \text{ (constant)}$$

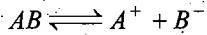
$$\text{or } [A^{y+}]^x[B^{x-}]^y = K[A_xB_y] = KK' = K_s \text{ (constant)}$$

Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

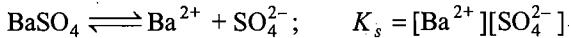
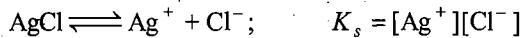
Note: Solubility product is not the ionic product under all conditions but only when the solution is saturated.]

Different Expressions for Solubility Products

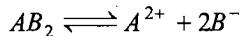
(i) Electrolyte of the type AB : Its ionisation is represented as:



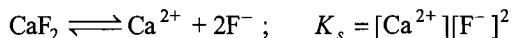
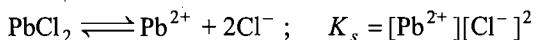
$$\text{Thus, } K_s = [A^+][B^-]$$



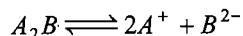
(ii) Electrolyte of the type AB_2 : Its ionisation is represented as:



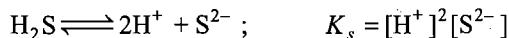
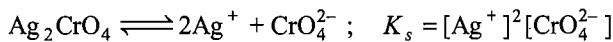
$$\text{Thus, } K_s = [A^{2+}][B^-]^2$$



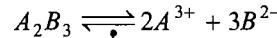
(iii) Electrolyte of the type A_2B : Its ionisation is represented as:



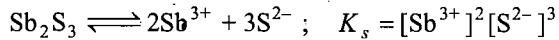
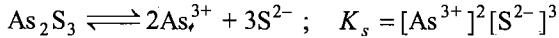
$$\text{Thus, } K_s = [A^+]^2[B^{2-}]$$



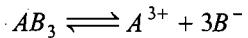
(iv) Electrolyte of the type A_2B_3 : Its ionisation is represented as:



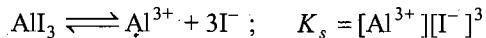
$$\text{Thus, } K_s = [A^{3+}]^2[B^{2-}]^3$$



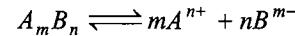
(v) Electrolyte of the type AB_3 : Its ionisation is represented as:



$$\text{Thus, } K_s = [A^{3+}][B^{2-}]^3$$



Solubility product of a weak electrolyte: Let degree of ionisation of weak electrolyte A_mB_n be ' α '.



$$t = 0$$

$$S \quad 0 \quad 0$$

$$t_{\text{eq}} \quad S - S\alpha \quad mS\alpha \quad nS\alpha$$

$$K_{\text{sp}} = [A^{n+}]^m[B^{m-}]^n$$

$$= [mS\alpha]^m[nS\alpha]^n$$

$$K_{\text{sp}} = m^m n^n (\alpha)^{m+n}$$

Criteria of precipitation of an electrolyte: A very useful conclusion is derived from the solubility product concept. No precipitation of the electrolyte occurs if the ionic product is less than the solubility product, i.e., the solution has not reached the saturation stage.

Case I: When $K_{\text{ip}} < K_{\text{sp}}$, then solution is unsaturated in which more solute can be dissolved.

Case II: When $K_{\text{ip}} = K_{\text{sp}}$, then solution is saturated in which no more solute can be dissolved.

Case III: When $K_{\text{ip}} > K_{\text{sp}}$, then solution is supersaturated and precipitation takes place.

When the ionic product exceeds the solubility product, the equilibrium shifts towards left hand side, i.e., increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product. For example, if equal volumes of 0.02 M AgNO_3 solution and 0.02 M K_2CrO_4 solution are mixed, the precipitation of Ag_2CrO_4 occurs as the ionic product exceeds the solubility product of Ag_2CrO_4 which is 2×10^{-12} .

In the resulting solution,

$$[\text{Ag}^+] = \frac{0.02}{2} = 0.01 = 1 \times 10^{-2} \text{ M}$$

$$\text{and } [\text{CrO}_4^{2-}] = \frac{0.02}{2} = 0.01 = 1 \times 10^{-2} \text{ M}$$

$$\text{Ionic product of } \text{Ag}_2\text{CrO}_4 = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

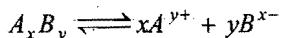
$$= (1 \times 10^{-2})^2 (1 \times 10^{-2}) \\ = 1 \times 10^{-6}$$

1×10^{-6} is higher than 2×10^{-12} and thus precipitation of Ag_2CrO_4 occurs.

Relationship between Solubility and Solubility Product

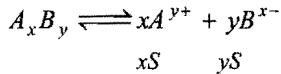
Salts like AgI , BaSO_4 , PbSO_4 , PbI_2 , etc., are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolyte contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, i.e., it is completely dissociated.

The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:



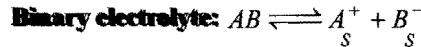
$$\text{Thus, solubility product, } K_s = [\text{A}^{y+}]^x[\text{B}^{x-}]^y$$

Let ' S ' mol litre $^{-1}$ be the solubility of the salt; then



$$\text{So, } K_s = [xS]^x[yS]^y \\ = x^x \cdot y^y (S)^{x+y}$$

(i) 1 : 1 type salts: Examples: AgCl , AgI , BaSO_4 , PbSO_4 , etc.

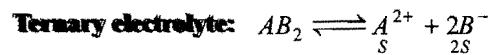


Let solubility of AB be S mol litre $^{-1}$.

$$\text{So, } K_s = [\text{A}^+][\text{B}^-] = S \times S = S^2$$

$$\text{or } S = \sqrt{K_s}$$

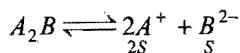
(ii) 1 : 2 or 2 : 1 type salts: Examples: Ag_2CO_3 , Ag_2CrO_4 , PbCl_2 , CaF_2 , etc.



Let solubility of AB_2 be S mol litre $^{-1}$.

$$\text{So, } K_s = [\text{A}^{2+}][\text{B}^-]^2 = S \times (2S)^2 = 4S^3$$

$$\text{or } S = \sqrt[3]{K_s/4}$$



Let S be the solubility of A_2B .

$$K_s = [\text{A}^+]^2[\text{B}^{2-}] \\ = (2S)^2(S) = 4S^3$$

$$\text{or } S = \sqrt[3]{K_s/4}$$

(iii) 1 : 3 type salts: Examples: AlI_3 , Fe(OH)_3 , Cr(OH)_3 , Al(OH)_3 , etc.



Let S mol litre $^{-1}$ be the solubility of AB_3 .

$$K_s = [\text{A}^{3+}][\text{B}^-]^3 = S \times (3S)^3 = 27S^4$$

or

$$S = \sqrt[4]{K_s/27}$$

The presence of common ion affects the solubility of a salt. Let AB be a sparingly soluble salt in solution and $\text{A}'\text{B}$ be added to it. Let S and S' be the solubilities of the salt AB before and after addition of the electrolyte $\text{A}'\text{B}$. Let c be the concentration of $\text{A}'\text{B}$.

$$\text{Before addition of } \text{A}'\text{B}, K_s = S^2 \quad \dots \text{(i)}$$

After addition of $\text{A}'\text{B}$, the concentration of A^+ and B^- ions become S' and $(S' + c)$, respectively.

$$\text{So, } K_s = S'(S' + c) \quad \dots \text{(ii)}$$

Equating eqs. (i) and (ii),

$$S^2 = S'(S' + c)$$

Calculation of remaining concentration after precipitation

sometimes an ion remains after precipitation if it is in excess. Remaining concentration can be determined, e.g.,

$$(i) [\text{A}^+]_{\text{left}} = \frac{K_{\text{sp}}[\text{AB}]}{[\text{B}^-]}$$

$$(ii) [\text{Ca}^{2+}]_{\text{left}} = \frac{K_{\text{sp}}[\text{Ca}(\text{OH})_2]}{[\text{OH}^-]^2}$$

$$(iii) [\text{A}^{n+}]_{\text{left}}^m = \frac{K_{\text{sp}}[\text{A}_m\text{B}_n]}{[\text{B}^{m-}]^n}$$

Percentage precipitation of an ion

$$= \left[\frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}} \right] \times 100$$

Simultaneous Solubility

Solubility of two electrolytes having common ion; when they are dissolved in the same solution, is called simultaneous solubility, e.g.,

(i) Solubility of AgBr and AgSCN , when dissolved together.

(ii) Solubility of CaF_2 and SrF_2 , when dissolved together.

(iii) Solubility of MgF_2 and CaF_2 , when dissolved together.

Calculation of simultaneous solubility is divided into two cases:

Case I: When the two electrolytes are almost equally strong (having close solubility product), e.g.,

$$\text{AgBr} (K_{\text{sp}} = 5 \times 10^{-13}) ; \text{ AgSCN} (K_{\text{sp}} = 10^{-12})$$

(See example 26.)

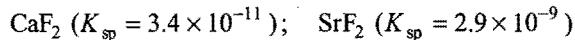
Here, charge balancing concept is applied.

$$\text{Charge of } \text{Ag}^+ = \text{Charge of } \text{Br}^- + \text{Charge of } \text{SCN}^-$$

$$[\text{Ag}^+] = [\text{Br}^-] + [\text{SCN}^-]$$

$$(a + b) = a \quad b$$

Case II: When solubility products of two electrolytes are not close, i.e., they are not equally strong, e.g.,

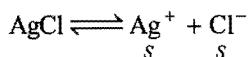


Most of fluoride ions come of stronger electrolyte.

SOME SOLVED EXAMPLES

Example 16. The solubility product of silver chloride is 1.5625×10^{-10} at 25°C . Find its solubility in g L^{-1} .

Solution: Let the solubility of AgCl be $S \text{ mol litre}^{-1}$.



$$\text{Hence, } S^2 = 1.5625 \times 10^{-10}$$

$$\text{or } S = 1.25 \times 10^{-5} \text{ mol L}^{-1}$$

Molecular mass of $\text{AgCl} = (108 + 35.5) = 143.5$

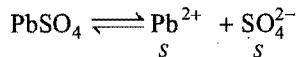
$$\begin{aligned} \text{So, Solubility in g litre}^{-1} &= \text{Mol. mass} \times S \\ &= 143.5 \times 1.25 \times 10^{-5} \\ &= 1.79 \times 10^{-3} \text{ g L}^{-1} \end{aligned}$$

Example 17. The solubility of PbSO_4 in water is 0.038 g L^{-1} at 25°C . Calculate its solubility product at the same temperature.

Solution: Solubility (S) of PbSO_4 in mol L^{-1} ,

$$= \frac{0.038}{\text{Mol. mass of PbSO}_4} = \frac{0.038}{303} = 1.254 \times 10^{-4}$$

The equilibrium is

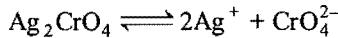


$$\text{So, } K_s = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = S \times S = S^2$$

$$\text{or } K_s = 1.254 \times 10^{-4} \times 1.254 \times 10^{-4} = 1.573 \times 10^{-8}$$

Example 18. The concentration of Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20°C is $1.5 \times 10^{-4} \text{ mol L}^{-1}$. Determine the solubility product of Ag_2CrO_4 at 20°C .

Solution: The equilibrium is:



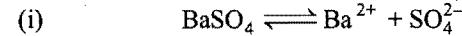
On the basis of this equation, the concentration of CrO_4^{2-} ions will be half of the concentration of Ag^+ ions.

Thus, $[\text{Ag}^+] = 1.5 \times 10^{-4} \text{ M}$ and $[\text{CrO}_4^{2-}] = 0.75 \times 10^{-4} \text{ M}$

$$\begin{aligned} K_s &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (1.5 \times 10^{-4})^2 (0.75 \times 10^{-4}) \\ &= 1.6875 \times 10^{-12} \end{aligned}$$

Example 19. The solubility product of BaSO_4 is 1.5×10^{-9} . Find out the solubility in (i) pure water and (ii) 0.1 M BaCl_2 solution.

Solution: The equilibrium is:



Let S be the solubility in mol litre^{-1} ; then

$$K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = S^2$$

$$\text{or } 1.5 \times 10^{-9} = S^2$$

$$\text{So, } S = 3.87 \times 10^{-5} \text{ mol L}^{-1}$$

(ii) Let S' be the solubility of BaSO_4 in 0.1 M BaCl_2 solution.

Total Ba^{2+} ions concentration = $(S' + c) \text{ mol L}^{-1}$

$$\text{and } \text{SO}_4^{2-} \text{ ions concentration} = S' \text{ mol L}^{-1}$$

$$\text{So, } K_s = (S' + c) S' = (S' + 0.1) S'$$

$$\text{or } 1.5 \times 10^{-9} = (S' + 0.1) S'$$

$$\text{or } (S')^2 + 0.1 S' = 1.5 \times 10^{-9}$$

Neglecting $(S')^2$,

$$0.1 S' = 1.5 \times 10^{-9}$$

$$\text{or } S' = 1.5 \times 10^{-8} \text{ mol L}^{-1}$$

Example 20. The solubility of $\text{Mg}(\text{OH})_2$ in pure water is $9.57 \times 10^{-3} \text{ g L}^{-1}$. Calculate its solubility in g L^{-1} in $0.02 \text{ M Mg}(\text{NO}_3)_2$ solution.

Solution: Solubility of $\text{Mg}(\text{OH})_2$ in pure water

$$= 9.57 \times 10^{-3} \text{ g L}^{-1}$$

$$= \frac{9.57 \times 10^{-3}}{\text{Mol. mass}} \text{ mol L}^{-1}$$

$$= \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mol L}^{-1}$$

Further, $\text{Mg}(\text{OH})_2 \rightleftharpoons \underset{S}{\text{Mg}^{2+}} + \underset{2S}{2\text{OH}^-}$

$$\begin{aligned} K_s &= [\text{Mg}^{2+}][\text{OH}^-]^2 = S \times (2S)^2 = 4S^3 = 4 \times (1.65 \times 10^{-4})^3 \\ &= 17.9685 \times 10^{-12} \end{aligned}$$

Let S' be solubility of $\text{Mg}(\text{OH})_2$ in presence of $\text{Mg}(\text{NO}_3)_2$

$$[\text{Mg}^{2+}] = (S' + c) = (S' + 0.02)$$

$$[\text{OH}^-] = 2S'$$

$$\text{So, } K_s = (S' + 0.02)(2S')^2$$

$$17.9685 \times 10^{-12} = 4(S')^2 (S' + 0.02)$$

$$\frac{17.9685 \times 10^{-12}}{4} = (S')^3 + 0.02(S')^2$$

[neglecting $(S')^3$]

$$4.4921 \times 10^{-12} = 0.02(S')^2$$

$$\text{or } (S')^2 = \frac{4.4921}{0.02} \times 10^{-12}$$

$$\text{or } S' = 14.9868 \times 10^{-6} \text{ mol L}^{-1}$$

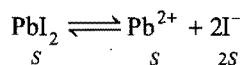
Solubility of $\text{Mg}(\text{OH})_2$ in $\text{g litre}^{-1} = S' \times M$

$$= 14.9868 \times 10^{-6} \times 58$$

$$= 8.69 \times 10^{-4} \text{ g L}^{-1}$$

Example 21. The solubility product of lead iodide is 1.4×10^{-8} . Calculate its molar solubility in 0.1 M KI solution.

Solution: Let the solubility of PbI_2 be S . Then,



Potassium iodide is a strong electrolyte and is completely ionised. It shall provide I^- ion concentration = 0.1 M .

$$[\text{Pb}^{2+}] = S$$

$$[\text{I}^-] = (2S + 0.1) M$$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$$

$$= S \times (2S + 0.1)^2$$

$$= S \times (4S^2 + 0.01 + 0.4S)$$

$$= 4S^3 + 0.01S + 0.4S^2$$

Neglecting S^3 and S^2 ,

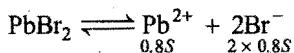
$$1.4 \times 10^{-8} = 0.01S$$

$$\text{or } S = \frac{1.4 \times 10^{-8}}{0.01} = 1.4 \times 10^{-6} \text{ mol L}^{-1}$$

Example 22. The solubility product of lead bromide is 8×10^{-5} . If the salt is 80% dissociated in saturated solution, find the solubility of the salt.

Solution: Let S be the solubility of the salt.

Degree of dissociation of the salt = 0.8.



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

$$= (0.8S) \times (1.6S)^2$$

$$= 2.048S^3$$

$$\text{or } S^3 = \frac{8 \times 10^{-5}}{2.048} = 3.906 \times 10^{-5}$$

$$S = \sqrt[3]{3.906 \times 10^{-5}} = 3.39 \times 10^{-2} \text{ mol L}^{-1}$$

Mol. mass of PbBr_2 = 367

$$\text{Solubility of } \text{PbBr}_2 = 3.39 \times 10^{-2} \times 367 = 12.44 \text{ g L}^{-1}$$

Example 23. A solution has 0.05 M Mg^{2+} and 0.05 M NH_3 . Calculate the concentration of NH_4Cl required to prevent the formation of $\text{Mg}(\text{OH})_2$ in this solution. K_{sp} of $\text{Mg}(\text{OH})_2$ = 9.0×10^{-12} and ionisation constant of NH_3 = 1.8×10^{-5} .

(IIT 1993)

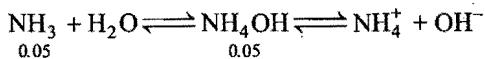
Solution: The maximum concentration of $[\text{OH}^-]$ ions that will precipitate $\text{Mg}(\text{OH})_2$ is calculated by applying the equation

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$[\text{OH}^-]^2 = \frac{K_{\text{sp}}}{[\text{Mg}^{2+}]} = \frac{9.0 \times 10^{-12}}{0.05} = 1.8 \times 10^{-10}$$

$$\text{or } [\text{OH}^-] = 1.34 \times 10^{-5} \text{ M}$$

NH_3 is present in solution in the form of NH_4OH



The ionisation of NH_4OH is suppressed by the addition of NH_4Cl (Strong electrolyte).

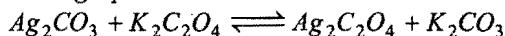
$$K_{\text{NH}_3} = K_{\text{NH}_4\text{OH}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

Whole of the concentration of NH_4^+ ions is provided by NH_4Cl .

$$[\text{NH}_4^+] = \frac{K_{\text{NH}_4\text{OH}} \times [\text{NH}_4\text{OH}]}{[\text{OH}^-]} = \frac{1.8 \times 10^{-5} \times 0.05}{1.34 \times 10^{-5}} = 0.067 \text{ M}$$

$$\text{i.e., } [\text{NH}_4\text{Cl}] = 0.067 \text{ M}$$

Example 24. The solubility product of $\text{Ag}_2\text{C}_2\text{O}_4$ at 25°C is 1.29×10^{-11} $\text{mol}^3 \text{ L}^{-3}$. A solution of $\text{K}_2\text{C}_2\text{O}_4$ containing 0.1520 mole in 500 mL of water is shaken with excess of Ag_2CO_3 till the following equilibrium is reached.



At equilibrium, the solution contains 0.0358 mole of K_2CO_3 . Assuming the degree of dissociation of $\text{K}_2\text{C}_2\text{O}_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3 . (IIT 1991)

Solution:

$\text{Ag}_2\text{CO}_3 + \text{K}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{Ag}_2\text{C}_2\text{O}_4 + \text{K}_2\text{CO}_3$		
Initial	0.1520 mole	0
At equilibrium	$(0.1520 - 0.0358)$	0.0358 mole
Concentration	$= 0.1162 \text{ mole}$	
	2×0.1162	2×0.0358
	= 0.2324 M	= 0.0716 M

$$K_{\text{sp}} \text{ Ag}_2\text{C}_2\text{O}_4 = [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{Ag}^+] = \left[\frac{K_{\text{sp}} \text{ Ag}_2\text{C}_2\text{O}_4}{[\text{C}_2\text{O}_4^{2-}]} \right]^{1/2}$$

$$K_{\text{sp}} \text{ Ag}_2\text{CO}_3 = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$$

$$[\text{Ag}^+] = \left[\frac{K_{\text{sp}} \text{ Ag}_2\text{CO}_3}{[\text{CO}_3^{2-}]} \right]^{1/2}$$

$$\text{So, } \left[\frac{K_{\text{sp}} \text{ Ag}_2\text{C}_2\text{O}_4}{[\text{C}_2\text{O}_4^{2-}]} \right]^{1/2} = \left[\frac{K_{\text{sp}} \text{ Ag}_2\text{CO}_3}{[\text{CO}_3^{2-}]} \right]^{1/2}$$

$$\text{or } K_{\text{sp}} \text{ Ag}_2\text{CO}_3 = \frac{K_{\text{sp}} \text{ Ag}_2\text{C}_2\text{O}_4 \times [\text{CO}_3^{2-}]}{[\text{C}_2\text{O}_4^{2-}]} = K_{\text{sp}} \text{ Ag}_2\text{C}_2\text{O}_4 \frac{[\text{K}_2\text{CO}_3]}{[\text{K}_2\text{C}_2\text{O}_4]}$$

$$= 1.29 \times 10^{-11} \times \frac{0.0716}{0.2324} = 3.97 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

Example 25. 20 mL of 0.001 M AgNO_3 solution is added to 1 litre of 0.002 M K_2CrO_4 solution. Will there be any precipitation? K_{sp} of Ag_2CrO_4 is 2.4×10^{-12} .

Solution: No. of moles of Ag^+ in 20 mL

$$= \frac{20}{1000} \times 0.001 = 2 \times 10^{-5}$$

$$\text{No. of moles CrO}_4^{2-} \text{ in one litre} = 0.002 = 2 \times 10^{-3}$$

After mixing, total volume of the solution

$$= 1000 + 20 = 1020 \text{ mL} = 1.02 \text{ L}$$

$$[\text{Ag}^+] = \frac{2 \times 10^{-5}}{1.02} = 1.96 \times 10^{-5}$$

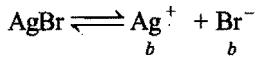
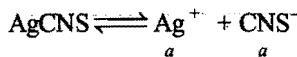
$$[\text{CrO}_4^{2-}] = \frac{2 \times 10^{-3}}{1.02} = 1.96 \times 10^{-3}$$

$$\begin{aligned}\text{Ionic product} &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ &= (1.96 \times 10^{-5})^2 (1.96 \times 10^{-3}) \\ &= 7.53 \times 10^{-13}\end{aligned}$$

There will be no precipitation of Ag_2CrO_4 as ionic product is less than solubility product.

Example 26. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water. K_{sp} of $\text{AgCNS} = 1 \times 10^{-12}$, K_{sp} of $\text{AgBr} = 5 \times 10^{-13}$.

Solution: Let the solubility of AgCNS and AgBr in water be a and b respectively.



$$[\text{Ag}^+] = a + b, [\text{CNS}^-] = a \quad \text{and} \quad [\text{Br}^-] = b$$

$$K_{sp} \text{AgCNS} = [\text{Ag}^+] [\text{CNS}^-] = a(a + b)$$

$$1 \times 10^{-12} = a(a + b) \quad \dots \text{(i)}$$

$$K_{sp} \text{AgBr} = [\text{Ag}^+] [\text{Br}^-] = b(a + b)$$

$$5 \times 10^{-13} = b(a + b) \quad \dots \text{(ii)}$$

Dividing eq. (i) by (ii),

$$\frac{1 \times 10^{-12}}{5 \times 10^{-13}} = \frac{a}{b}$$

$$2 = \frac{a}{b} \quad \text{or} \quad a = 2b$$

Putting the value of a in eq. (i),

$$6b^2 = 1 \times 10^{-12}$$

$$b^2 = \frac{1}{6} \times 10^{-12}$$

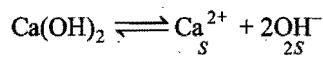
$$b = 4.08 \times 10^{-7} \text{ mol L}^{-1}$$

$$a = 2 \times 4.08 \times 10^{-7}$$

$$= 8.16 \times 10^{-7} \text{ mol L}^{-1}$$

Example 27. The K_{sp} of $\text{Ca}(\text{OH})_2$ is 4.42×10^{-5} at 25°C . 500 mL of saturated solution of $\text{Ca}(\text{OH})_2$ is mixed with equal volume of 0.4 M NaOH . How much $\text{Ca}(\text{OH})_2$ in mg is precipitated? (IIT 1992)

Solution: Let S be the solubility of $\text{Ca}(\text{OH})_2$ in saturated solution.



$$K_{sp} \text{Ca}(\text{OH})_2 = [\text{Ca}^{2+}] [\text{OH}^-]^2$$

$$4.42 \times 10^{-5} = S \times 4S^2 = 4S^3$$

$$S = 0.0223 \text{ mol L}^{-1}$$

After mixing the two solutions, the total volume becomes 1 litre.

$$[\text{Ca}^{2+}] = \frac{0.0223}{1000} \times 500 = 0.01115 \text{ mol L}^{-1}$$

$$[\text{OH}^-] = \frac{0.0223 \times 2 \times 500}{1000} + \frac{0.4 \times 500}{1000} = 0.2223 \text{ mol L}^{-1}$$

[From $\text{Ca}(\text{OH})_2$] [From NaOH]

Under the high concentration of OH^- ions, some $\text{Ca}(\text{OH})_2$ will be precipitated.

$$[\text{Ca}^{2+}]_{\text{left}} [\text{OH}^-]^2 = K_{sp}$$

$$[\text{Ca}^{2+}]_{\text{left}} = \frac{4.42 \times 10^{-5}}{(0.2223)^2} = 8.94 \times 10^{-4} \text{ mol L}^{-1}$$

Moles of $\text{Ca}(\text{OH})_2$ precipitated = Moles of Ca^{2+} precipitated

$$= [\text{Ca}^{2+}]_{\text{initial}} - [\text{Ca}^{2+}]_{\text{left}}$$

$$= 0.01115 - 8.94 \times 10^{-4}$$

$$= 111.5 \times 10^{-4} - 8.94 \times 10^{-4}$$

$$= 102.56 \times 10^{-4} \text{ M} = 102.56 \times 10^{-4} \times 74 \text{ g}$$

$$= 7589.44 \times 10^{-4} \text{ g} = 758.944 \text{ mg}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. The solubility product of sparingly soluble salt Ag_2CrO_4 is 4×10^{-12} . The molar solubility of the salt is:

- (a) $1 \times 10^{-4} \text{ mol L}^{-1}$ (b) $2 \times 10^{-6} \text{ mol L}^{-1}$
 (c) $1 \times 10^{-5} \text{ mol L}^{-1}$ (d) $2 \times 10^{-12} \text{ mol L}^{-1}$

[Ans. (a)]

$$[\text{Hint:}] \quad K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

If solubility of Ag_2CrO_4 is ' S ', then $[\text{Ag}^+] = 2S$ and $[\text{CrO}_4^{2-}] = S$.

$$K_{sp} = 4S^3$$

$$4 \times 10^{-12} = 4S^3$$

$$S = 1 \times 10^{-4} \text{ M}$$

7. The solubility of PbSO_4 at 25°C is $1.1 \times 10^{-4} \text{ mol/L}$. Then its K_{sp} is:

- (a) 1.21×10^{-8} (b) 12.1×10^{-6}
 (c) 121×10^{-11} (d) 1.21×10^{-10}

[Ans. (a)]

[Hint: PbSO_4 is a binary electrolyte, hence its K_{sp} can be calculated as:

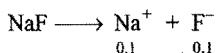
$$K_{sp} = S^2 = [1.1 \times 10^{-4}]^2 = 1.21 \times 10^{-8}$$

8. The solubility of CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$) in 0.1 M solution of NaF would be:

- (a) $3.4 \times 10^{-12} \text{ M}$ (b) $3.4 \times 10^{-10} \text{ M}$
 (c) $3.4 \times 10^{-9} \text{ M}$ (d) $3.4 \times 10^{-13} \text{ M}$

[Ans. (c)]

$$[\text{Hint:}] \quad \text{CaF}_2 \rightleftharpoons \underset{x}{\text{Ca}^{2+}} + \underset{2x}{2\text{F}^-}$$



$$[\text{Ca}^{2+}] = x, \quad [\text{F}^-] = [2x + 0.1] \approx 0.1 M$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$$

$$3.4 \times 10^{-11} = x(0.1)^2$$

$$x = 3.4 \times 10^{-9} M$$

9. The solubility product of AgCl is 1.8×10^{-10} . Precipitation of AgCl will occur only when equal volumes of which of the following solutions are mixed?
- $10^{-4} M \text{ Ag}^+$ and $10^{-4} M \text{ Cl}^-$
 - $10^{-7} M \text{ Ag}^+$ and $10^{-7} M \text{ Cl}^-$
 - $10^{-5} M \text{ Ag}^+$ and $10^{-5} M \text{ Cl}^-$
 - $10^{-10} M \text{ Ag}^+$ and $10^{-10} M \text{ Cl}^-$

[Ans. (a)]

[Hint: After mixing,

$$[\text{Ag}^+] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5} M$$

$$[\text{Cl}^-] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5} M$$

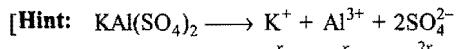
$$K_{\text{ip}} = [\text{Ag}^+][\text{Cl}^-] = (5 \times 10^{-5})^2 = 2.5 \times 10^{-9}$$

Since, ionic product is greater than solubility product, hence precipitation will take place.]

10. If $x \text{ mol L}^{-1}$ is the solubility of $\text{KAl}(\text{SO}_4)_2$, then K_{sp} is equal to:

- x^3
- $4x^4$
- x^4
- $4x^3$

[Ans. (b)]



$$K_{\text{sp}} = [\text{K}^+][\text{Al}^{3+}][\text{SO}_4^{2-}]^2$$

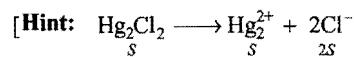
$$= x \times x \times (2x)^2 = 4x^4$$

11. For which of the following sparingly soluble salt, the solubility (S) and solubility product (K_{sp}) are related by the expression:

$$S = \left[\frac{K_{\text{sp}}}{4} \right]^{1/3} \quad \text{[PET (Kerala) 2006]}$$

- BaSO_4
- $\text{Ca}_3(\text{PO}_4)_2$
- Hg_2Cl_2
- Ag_3PO_4

[Ans. (c)]



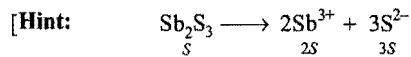
$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = [S][2S]^2 = 4S^3$$

$$S = \left[\frac{K_{\text{sp}}}{4} \right]^{1/3}$$

12. The solubility of Sb_2S_3 in water is $1 \times 10^{-5} \text{ mol/L}$ at 298 K. What will be its solubility product? [PMT (Raj.) 2006]

- 108×10^{-25}
- 1.0×10^{-25}
- 144×10^{-25}
- 126×10^{-24}

[Ans. (a)]



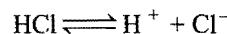
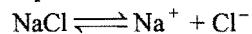
$$K_{\text{sp}} = [\text{Sb}^{3+}]^2[\text{S}^{2-}]^3 = [2S]^2[3S]^3 = 108 S^5$$

$$= 108 \times (10^{-5})^5 = 108 \times 10^{-25}$$

Applications of Solubility Product

(i) Purification of common salt

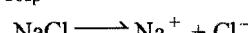
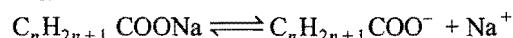
Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:



The concentration of Cl^- ions increases considerably in solution due to ionisation of HCl . Hence, the ionic product $[\text{Na}^+][\text{Cl}^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

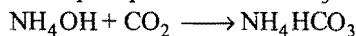
Soap is a sodium salt of higher fatty acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.



Thus, the concentration of Na^+ ions increases considerably on addition of NaCl solution. Hence, the ionic product $[\text{C}_n\text{H}_{2n+1}\text{COO}^-][\text{Na}^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda)

In Solvay's soda process, CO_2 gas is passed through ammonical brine to precipitate out NaHCO_3 .



NaHCO_3 is precipitated first because of its lower solubility product as compared to those of NH_4Cl , NH_4HCO_3 and NaCl .

Thus, baking soda (NaHCO_3) can be quantitatively estimated.

(iv) Application of solubility product in quantitative analysis

- Estimation of barium as barium sulphate:** H_2SO_4 as precipitating agent is added to the aqueous solution of BaCl_2 .



Precipitation of BaSO_4 takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

- Estimation of silver as silver chloride:** NaCl solution is added to the silver nitrate solution; slight excess of NaCl is added to ensure complete precipitation.



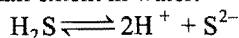
Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

3. In a similar manner, we estimate lead as lead chromate, calcium as calcium oxalate, etc.

(v) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in qualitative analysis.

It ionises to a small extent in water:



Applying law of mass action,

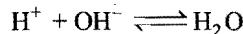
$$K = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

The concentration of S^{2-} ions can be decreased by increasing concentration of H^+ ions and it can be increased by decreasing concentration of H^+ ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products of the sulphides of group IV are high. The values of solubility products of various sulphides are given below:

	Metal sulphide	Solubility product
Group II	Bi_2S_3	1.6×10^{-72}
	HgS	4×10^{-54}
	CuS	1×10^{-44}
	PbS	5×10^{-29}
	CdS	1.4×10^{-28}
Group IV	CoS	3×10^{-26}
	NiS	1.4×10^{-24}
	ZnS	1.0×10^{-22}
	MnS	1.4×10^{-15}

The concentration of S^{2-} ions in group II is lowered by maintaining acidic medium. In the presence of HCl , the ionisation of H_2S is suppressed due to common ion effect. The concentration is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated. However, CdS has somewhat higher value. For its precipitation, dilution of the solution is done which increases ionisation of H_2S and thereby increasing concentration of S^{2-} ions.

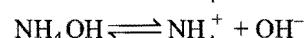
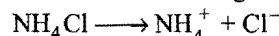
In group IV, higher concentration of S^{2-} ions is needed. This is done by changing the medium from acidic to alkaline. Ammonium hydroxide is added, the OH^- ions furnished by NH_4OH remove H^+ ions from solution in the form of water molecules as,



More of the ionisation of H_2S occurs and, thus, concentration of S^{2-} ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products and they get precipitated.

(vi) Precipitation of III group hydroxides

When NH_4OH is added in presence of NH_4Cl then precipitation of III group hydroxides takes place, i.e., $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ are precipitated. Solubility product of III group hydroxides is less than those of higher group hydroxides.



NH_4^+ ion furnished by NH_4Cl lowers the ionisation of NH_4OH and hence the concentration of hydroxide ion OH^- . At low concentration of hydroxide ion only III group hydroxides precipitate.

Fractional Precipitation

It is a technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion and then the second.

Let us suppose 0.1 M Ba^{2+} and 0.1 M Sr^{2+} in aqueous solution, K_2CrO_4 is added as precipitating agent. K_{sp} of BaCrO_4 is 1.2×10^{-10} and K_{sp} of SrCrO_4 is 3.5×10^{-5} .

$[\text{CrO}_4^{2-}]$ concentration required to precipitate BaCrO_4

$$= \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9}$$

BaCrO_4 will precipitate first because it requires low concentration of CrO_4^{2-} ions. On addition of chromate ions, BaCrO_4 starts precipitating when chromate ion concentration reaches $1.2 \times 10^{-9} \text{ M}$. When CrO_4^{2-} ion concentration reaches up to $3.5 \times 10^{-4} \text{ M}$, then SrCrO_4 also starts precipitating.

Remaining concentration of Ba^{2+} when SrCrO_4 starts precipitation

$$= \frac{K_{sp} \text{ BaCrO}_4}{[\text{CrO}_4^{2-}]} = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}} = 3.4 \times 10^{-7} \text{ M}$$

$$\% \text{ remaining concentration} = \frac{3.4 \times 10^{-7}}{0.1} \times 100 \\ = 0.00034\%$$

Stability Constant

Let us consider dissociation of the ion FeBr^+ .



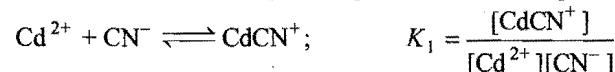
Dissociation constant for above equilibria may be given as:

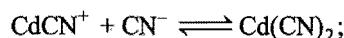
$$K_d = \frac{[\text{Fe}^{2+}][\text{Br}^-]}{[\text{FeBr}^+]}$$

Reciprocal of dissociation constant is called stability constant.

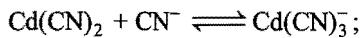
$$K_s = \frac{[\text{FeBr}^+]}{[\text{Fe}^{2+}][\text{Br}^-]}$$

Let us consider the formation of complex $\text{K}_2\text{Cd}(\text{CN})_4$. Complex ion is $\text{Cd}(\text{CN})_4^{2-}$ where oxidation state of central metal Cd^{2+} is (+2). Complexing process proceeds in four steps as:

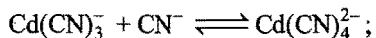




$$K_2 = \frac{[\text{Cd}(\text{CN})_2^-]}{[\text{CdCN}^+][\text{CN}^-]}$$

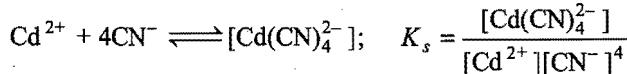


$$K_3 = \frac{[\text{Cd}(\text{CN})_3^-]}{[\text{Cd}(\text{CN})_2^-][\text{CN}^-]}$$



$$K_4 = \frac{[\text{Cd}(\text{CN})_4^{2-}]}{[\text{Cd}(\text{CN})_3^-][\text{CN}^-]}$$

Overall reaction may be given as:



Here,

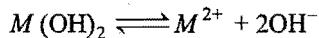
$$K_s = K_1 K_2 K_3 K_4$$

Significance of stability constant: Greater will be the value of stability constant more stable will be the complex.

- Note:** (a) If on addition of a common ion in a salt solution (sparingly soluble), formation of complex ion takes place, then ionisation increases, i.e., equilibrium shifts towards right hand direction to maintain the value of K_{sp} constant. It means, addition of common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the concept of common ion effect.
 (b) When we add an electrolyte to another electrolyte solution having no common ion, then ionisation of the latter increases.
 (c) For a given electrolyte solubility product is always constant at a particular temperature.

Solubility of Metal Hydroxides in Acid Medium

H^+ ion furnished by the medium affects the solubility of metal hydroxide, say $M(\text{OH})_2$, because of neutralization of OH^- ion by H^+ ion.



$$K_{sp} \text{ of } M(\text{OH})_2 = [M^{2+}][\text{OH}^-]^2$$

$$[M^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} \quad \dots (\text{i})$$

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$[\text{OH}^-]^2 = \frac{10^{-28}}{[\text{H}^+]^2} \quad \dots (\text{ii})$$

From eqs. (i) and (ii), we have

$$[M^{2+}] = \frac{K_{sp} [\text{H}^+]^2}{10^{-28}}$$

10.5 ACIDS AND BASES

The earliest criteria for the characterisation of acids and bases were the experimentally observed properties of aqueous solutions. An acid* was defined as a substance whose water solution tastes sour, turns blue litmus red, neutralises bases and so on. A substance was a base if its aqueous solution tasted bitter, turns red litmus blue, neutralises acids and so on. Faraday termed acids, bases and salts as electrolytes and Liebig proposed that acids are compounds containing hydrogen that can be replaced by metals.

Different concepts have been put forth by different investigators to characterise acids and bases but the following are the three important modern concepts of acids and bases:

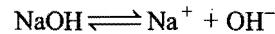
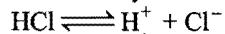
* Acid is a Latin word—*acidus*, meaning sour.

(1) Arrhenius concept

According to Arrhenius concept, all substances which give H^+ ions when dissolved in water are called acids while those which ionise in water to furnish OH^- ions are called bases.

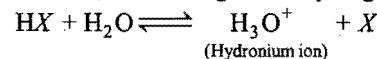


Thus, HCl is an acid because it gives H^+ ions in water. Similarly, NaOH is a base as it yields OH^- ions in water.



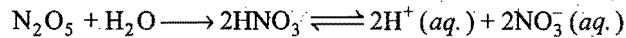
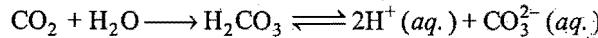
Some acids and bases ionise almost completely in solutions and are called strong acids and bases. Others are dissociated to a limited extent in solutions and are termed weak acids and bases. HCl , HNO_3 , H_2SO_4 , HClO_4 , etc., are examples of strong acids and NaOH , KOH , $(\text{CH}_3)_4\text{NOH}$ are strong bases. Every hydrogen compound cannot be regarded as an acid, e.g., CH_4 is not an acid. Similarly, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, etc., have OH groups but they are not bases.

Actually free H^+ ions do not exist in water. They combine with solvent molecules, i.e., have strong tendency to get hydrated.

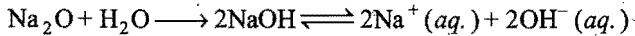


The proton in aqueous solution is generally represented as H^+ (*aq.*). It is now known that almost all the ions are hydrated to more or less extent and it is customary to put (*aq.*) after each ion.

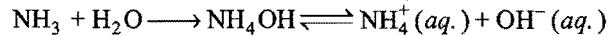
The oxides of many non-metals react with water to form acids and are called acidic oxides or acid anhydrides.



Many oxides of metals dissolve in water to form hydroxides. Such oxides are termed basic oxides.



The substance like NH_3 and N_2H_4 act as bases as they react with water to produce OH^- ions.



The reaction between an acid and a base is termed neutralisation. According to Arrhenius concept, the neutralisation in aqueous solution involves the reaction between H^+ and OH^- ions or hydronium and OH^- ions. This can be represented as



Limitations: (i) For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid. HCl is regarded as an acid only when dissolved in water and not in any other solvent.

(ii) The concept does not explain acidic and basic character of substances in non-aqueous solvents.

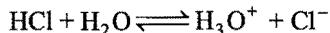
(iii) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in the absence of solvent.

(iv) It cannot explain the acidic character of certain salts such as AlCl_3 in aqueous solution.

(v) An artificial explanation is required to explain the basic nature of NH_3 and metallic oxides and acidic nature of non-metal oxides.

(2) Bronsted-Lowry concept—The proton-donor-acceptor concept

In 1923, Bronsted and Lowry independently proposed a broader concept of acids and bases. According to Bronsted-Lowry concept an acid is a substance (molecule or ion) that can donate proton, i.e., a hydrogen ion, H^+ , to some other substance and a base is a substance that can accept a proton from an acid. More simply, an acid is a proton-donor (protogenic) and a base is a proton acceptor (protophilic). Consider the reaction,



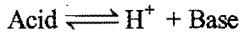
In this reaction, HCl acts as an acid because it donates a proton to the water molecule. Water, on the other hand, behaves as a base by accepting a proton from the acid.

The dissolution of ammonia in water may be represented as

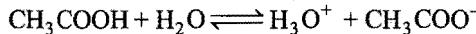


In this reaction, H_2O acts as an acid as it donates a proton to NH_3 molecule and NH_3 molecule behaves as a base as it accepts a proton.

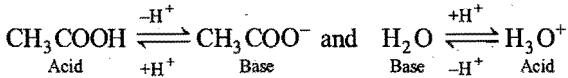
When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a base.



The acid and base which differ by a proton are known to form a **conjugate pair**. Consider the following reaction:

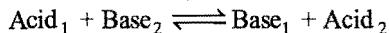


It involves two conjugate pairs. The acid-base pairs are:

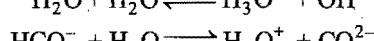
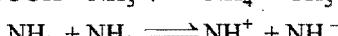
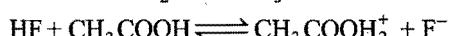
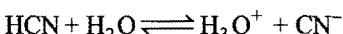


Such pairs of substances which can be formed from one another by loss or gain of a proton are known as **conjugate acid-base pairs**.

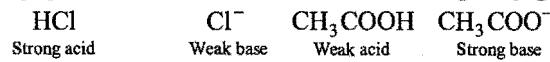
If in the above reaction, the acid CH_3COOH is labelled acid₁ and its conjugate base, CH_3COO^- as base₁. H_2O is labelled as base₂ and its conjugate acid H_3O^+ as acid₂, the reaction can be written as:



Thus, any acid-base reaction involves two conjugate pairs, i.e., when an acid reacts with a base, another acid and base are formed. Some more examples are given below:

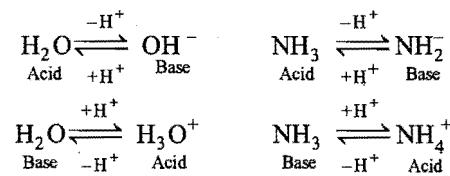


Thus, every acid has its conjugate base and every base has its conjugate acid. It is further observed that strong acids have weak conjugate bases while weak acids have strong conjugate bases.



There are certain molecules which have dual character of an acid and a base. These are called **amphotropic** or **amphoteric**.

Examples are NH_3 , H_2O , CH_3COOH , etc.



The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton.

Acid-base chart containing some common conjugate acid-base pairs

Acid	Conjugate base
HClO_4 (Perchloric acid)	ClO_4^- (Perchlorate ion)
H_2SO_4 (Sulphuric acid)	HSO_4^- (Hydrogen sulphate ion)
HCl (Hydrogen chloride)	Cl^- (Chloride ion)
HNO_3 (Nitric acid)	NO_3^- (Nitrate ion)
H_3O^+ (Hydronium ion)	H_2O (Water)
HSO_4^- (Hydrogen sulphate ion)	SO_4^{2-} (Sulphate ion)
H_3PO_4 (Ortho-phosphoric acid)	H_2PO_4^- (Dihydrogen phosphate ion)
CH_3COOH (Acetic acid)	CH_3COO^- (Acetate ion)
H_2CO_3 (Carbonic acid)	HCO_3^- (Hydrogen carbonate ion)
H_2S (Hydrogen sulphide)	HS^- (Hydrosulphide ion)
NH_4^+ (Ammonium ion)	NH_3 (Ammonia)
HCN (Hydrogen cyanide)	CN^- (Cyanide ion)
$\text{C}_6\text{H}_5\text{OH}$ (Phenol)	$\text{C}_6\text{H}_5\text{O}^-$ (Phenoxyde ion)
H_2O (Water)	OH^- (Hydroxide ion)
$\text{C}_2\text{H}_5\text{OH}$ (Ethyl alcohol)	$\text{C}_2\text{H}_5\text{O}^-$ (Ethoxide ion)
NH_3 (Ammonia)	NH_2^- (Amide ion)
CH_4 (Methane)	CH_3^- (Methide ion)

Increasing order of basic strength

In acid-base strength series, all acids above H_3O^+ in aqueous solution fall to the strength of H_3O^+ . Similarly, the basic strength of bases below OH^- fall to the strength of OH^- in aqueous solution. This is known as **levelling effect**.

The strength of an acid also depends upon the solvent. The acids HClO_4 , H_2SO_4 , HCl and HNO_3 which have nearly the same strength in water will be in the order of $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$ in acetic acid, since, the proton accepting tendency of acetic acid is much weaker than water. So, the real strength of acids can be judged by solvents. On the basis of proton interaction, solvents can be classified into four types:

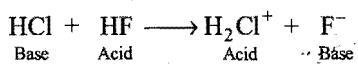
(i) Protophilic solvents: Solvents which have greater tendency to accept protons, *i.e.*, water, alcohol, liquid ammonia, etc.

(ii) Protogenic solvents: Solvents which have the tendency to produce protons, *i.e.*, water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) Amphiprotic solvents: Solvents which act both as protophilic or protogenic, *e.g.*, water, ammonia, ethyl alcohol, etc.

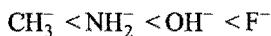
(iv) Aprotic solvents: Solvents which neither donate nor accept protons, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as acid in H_2O , stronger acid in NH_3 , weak acid in CH_3COOH , neutral in C_6H_6 and a weak base in HF .

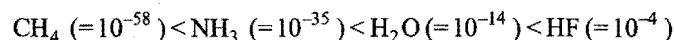


Periodic Variations of Acidic and Basic Properties

(a) Hydracids of the elements of the same period: Consider the hydracids of the elements of II period, *viz.*, CH_4 , NH_3 , H_2O and HF . These hydrides become increasingly acidic as we move from CH_4 to HF . CH_4 has negligible acidic properties while HF is a fairly stronger acid. The increase in acidic nature is due to the fact that the stability of their conjugate bases increases in the order



The increase in acidic properties is supported by the successive increase in the dissociation constant.



(b) Hydracids of the elements of same group: (i) Hydrides of V group elements (NH_3 , PH_3 , AsH_3 , SbH_3 and BiH_3) show basic character which decreases due to increase in size and decrease in electronegativity from N to Bi. There is a decrease in electron density in sp^3 -hybrid orbital and thus electron donor capacity decreases.

(ii) Hydracids of VI group elements (H_2O , H_2S , H_2Se and H_2Te) act as weak acids. The strength increases in the order

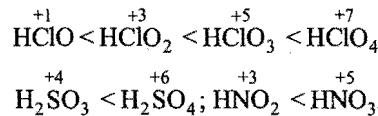


The increasing acidic character reflects decreasing trend in the electron donor capacity of OH^- , HS^- , HSe^- or HTe^- ions.

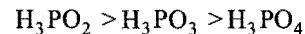
(iii) Hydracids of VII group elements (HF , HCl , HBr and HI) show acidic nature which increases from HF to HI . This is

explained by the fact that bond energies decrease. ($\text{H}-\text{F} = 135$ kcal/mol, $\text{HCl} = 103$, $\text{HBr} = 88$ and $\text{HI} = 71$ kcal/mol)

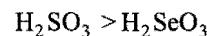
(c) Oxyacids: (i) The acidic character of oxyacids of the same element which is in different oxidation states increases with increase in oxidation number.



But this rule fails in oxyacids of phosphorus.



(ii) The acidic character of the oxyacids of different elements which are in the same oxidation state decreases as the atomic number increases. This is due to increase in size and decrease in electronegativity.



Limitations: There are number of acid-base reactions in which no proton transfer takes place, *e.g.*,

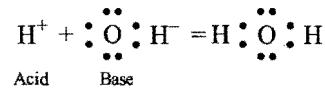


Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as COCl_2 , SO_2 , N_2O_4 , etc.

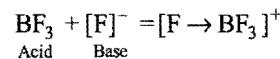
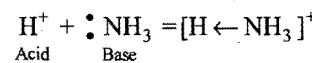
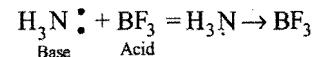
(3) Lewis concept

This concept was proposed by G.N. Lewis, in 1939. According to this concept, a base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons. The acid is also known as electron acceptor or electrophile while the base is electron donor or nucleophile.

A simple example of an acid-base is the reaction of a proton with hydroxyl ion.



Some other examples are:



Lewis concept is more general than the Bronsted Lowry concept.

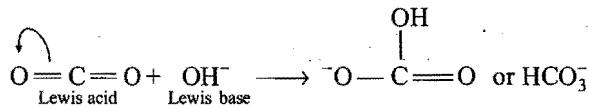
According to Lewis concept, the following species can act as Lewis acids:

(i) Molecules in which the central atom has incomplete octet: All compounds having central atom with less than 8 electrons are Lewis acids, *e.g.*, BF_3 , BCl_3 , AlCl_3 , MgCl_2 , BeCl_2 , etc.

(ii) Simple cations: All cations are expected to act as Lewis acids since they are deficient in electrons. However, cations such as Na^+ , K^+ , Ca^{2+} , etc., have a very little tendency to accept electrons, while the cations like H^+ , Ag^+ , etc., have greater tendency to accept electrons and, therefore, act as Lewis acids.

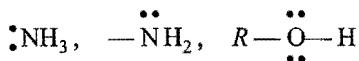
(iii) Molecules in which the central atom has empty d-orbitals: The central atom of the halides such as SiX_4 , GeX_4 , TiCl_4 , SnX_4 , PX_3 , PF_5 , SF_4 , SeF_4 , TeCl_4 , etc., have vacant d-orbitals. These can, therefore, accept an electron pair and act as Lewis acids.

(iv) Molecules having a multiple bond between atoms of dissimilar electronegativity: Typical examples of molecules falling in this class of Lewis acids are CO_2 , SO_2 and SO_3 . Under the influence of attacking Lewis base, one π -electron pair will be shifted towards the more negative atom.

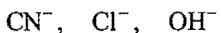


The following species can act as Lewis bases:

(i) Neutral species having at least one lone pair of electrons: For example, ammonia, amines, alcohols, etc., act as Lewis bases because they contain a pair of electrons.



(ii) Negatively charged species or anions: For example, chloride, cyanide, hydroxide ions, etc., act as Lewis bases.



It may be noted that all Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

Limitations: Since, the strength of the Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

The choice of which definition of acids and bases one wishes to use in a particular instance depends largely on the sort of chemistry that is studied. But Arrhenius concept is perfectly satisfactory and simplest for dealing with reactions in aqueous solutions. It explains satisfactorily the strength of acids and bases in aqueous solutions, neutralisation, salt hydrolysis, etc.

10.6 RELATIVE STRENGTH OF ACIDS AND BASES

According to Arrhenius concept, an acid is a substance which furnishes H^+ ions when dissolved in water. All the acid properties on an acid are due to H^+ ions present in the solution.

The extent to which an acid property is given by an acid is a measure of its strength. The strength of the acid solution does not depend on its concentration but on the number of H^+ ions present. The concentration of H^+ ions depends on the ionisation of an acid in solution. On dilution, the ionisation increases and more of H^+ ions come to solution with the result that the strength of the acid increases. Thus, strength of the acid increases on dilution while its concentration decreases. At

infinite dilution the dissociation of an acid is nearly complete and all acids are equally strong at infinite dilution.

The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. Thus, to measure the relative strength of the two acids, the measurements of hydrogen ion concentration, i.e., degree of dissociation is made of equinormal solutions of the two acids. Various methods are used for this purpose. Some are described below.

(i) The conductivity method: The degree of dissociation of a weak acid is equal to conductivity ratio $\frac{\Lambda}{\Lambda_\infty}$. Thus, the

degrees of dissociation α_1 and α_2 for two equinormal acids are given by:

$$\text{For acid I}, \quad \alpha_1 = \frac{\Lambda_1}{\Lambda_{\infty_1}}$$

$$\text{and} \quad \text{For acid II}, \quad \alpha_2 = \frac{\Lambda_2}{\Lambda_{\infty_2}}$$

At infinite dilution, all weak electrolytes have almost the same value of Λ_∞ ; hence,

$$\begin{aligned} \Lambda_{\infty_1} &= \Lambda_{\infty_2} \\ \frac{\text{Strength of acid I}}{\text{Strength of acid II}} &= \frac{\alpha_1}{\alpha_2} = \frac{\Lambda_1}{\Lambda_2} = \frac{\frac{1000 \times \text{sp. cond. acid I}}{C}}{\frac{1000 \times \text{sp. cond. acid II}}{C}} \\ &= \frac{\text{Sp. cond. acid I}}{\text{Sp. cond. acid II}} \end{aligned}$$

The relative strength of two acids is, thus, equal to the ratio of their equivalent conductance or specific conductance of equinormal solutions which can be determined experimentally.

(ii) Comparing dissociation constants: Let K_1 and K_2 be the dissociation constants of two acids and let α_1 and α_2 be their degree of dissociation in equinormal solutions.

Applying Ostwald's dilution law, $\alpha_1 = \sqrt{\frac{K_1}{C}}$ and $\alpha_2 = \sqrt{\frac{K_2}{C}}$

$$\text{Thus, } \frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}$$

Dissociation constants of some weak acids are given in the table:

Acid-ionization constants at 25°C

Substance	Formula	K_a
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.7×10^{-5}
Benzoic acid	$\text{HC}_6\text{H}_5\text{O}_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3 HCO_3^-	4.3×10^{-7} 4.8×10^{-11}
Cyanic acid	HOCl	3.5×10^{-4}

Substance	Formula	K_a
Formic acid	HCHO_2	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulphate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulphide	H_2S HS^-	8.9×10^{-8} 1.2×10^{-13}
Hypochlorous acid	HClO	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$ HC_2O_4^-	5.6×10^{-2} 5.1×10^{-5}
Phosphoric acid	H_3PO_4 H_2PO_4^- HPO_4^{2-}	6.9×10^{-3} 6.2×10^{-8} 4.8×10^{-13}
Phosphorous acid	H_2PHO_3^- $\text{H}_2\text{P}\text{H}_2\text{O}$	1.6×10^{-2} 7.0×10^{-7}
Propionic acid	$\text{HC}_3\text{H}_5\text{O}_2$	1.3×10^{-5}
Pyruvic acid	$\text{HC}_3\text{H}_5\text{O}_3$	1.4×10^{-4}
Sulphurous acid	H_2SO_3 HSO_3^-	1.3×10^{-2} 6.3×10^{-8}

(iii) **Thomson thermal method:** In this method, heat of neutralisation of two acids is first determined separately with NaOH. Let it be 'x' and 'y' calorie. The one gram equivalent of each of the two acids is mixed and one gram equivalent of NaOH is added. Let the heat evolved in this case be 'z' calorie. The two acids will neutralise a fraction of the base proportional to their relative strength. Suppose n gram equivalent of NaOH is neutralised by acid I and the rest $(1-n)$ by acid II.

$$\text{Total heat evolved, } z = nx + (1-n)y \\ = nx + y - ny$$

$$\text{or } z - y = n(x - y)$$

$$\text{or } n = \frac{(z - y)}{(x - y)}$$

$$\frac{(z - y)}{(x - y)}$$

$$\text{So, Strength of acid I} = \frac{n}{(1-n)} = \frac{(x-y)}{1-\frac{(z-y)}{(x-y)}} = \frac{(z-y)}{(x-z)}$$

Relative strength of bases: A base is a substance which gives OH^- ions when dissolved in water. The strength of the base depends on OH^- ion concentration. The above methods can be used for measuring relative strengths of bases also. In the Thomson thermal method, the two bases and their mixtures will be neutralised by strong acid, say HCl.

The relative strengths of some of the acids are as follows:

- (i) $\text{HClO}_4 > \text{HBr} > \text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{H}_3\text{O}^+ > \text{H}_2\text{SO}_3$
 $> \text{H}_2\text{CO}_3 > \text{CH}_3\text{COOH}$
- (ii) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$
- (iii) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

- (iv) $\text{HClO}_3 > \text{HBrO}_3 > \text{HIO}_3$
- (v) $\text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{CH}_2\text{ClCOOH}$
 $> \text{CH}_3\text{COOH}$
- (vi) $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{C}_2\text{H}_5\text{COOH}$

The relative strengths of some of the bases are as follows:

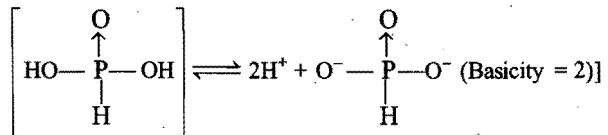
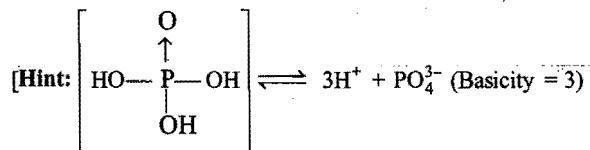
- (i) $\text{KOH} > \text{NaOH} > \text{Ca}(\text{OH})_2 > \text{NH}_4\text{OH}$
- (ii) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
- (iii) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > (\text{C}_2\text{H}_5)_3\text{N}$
- (iv) $\text{NaOH} > \text{NH}_3 > \text{H}_2\text{O}$
- (v) $\text{NH}_3 > \text{NH}_2\text{NH}_2 > \text{NH}_2\text{OH}$
- (vi) $\text{NH}_3 > \text{C}_5\text{H}_5\text{N} > \text{C}_6\text{H}_5\text{NH}_2$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

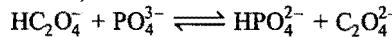
13. Which one is correct statement? (DCE 2007)

- (a) Basicity of H_3PO_4 and H_3PO_3 are 3 and 3 respectively
- (b) Acidity of H_3PO_4 and H_3PO_3 are 3 and 3 respectively
- (c) Acidity of H_3PO_4 and H_3PO_3 are 3 and 2 respectively
- (d) Basicity of H_3PO_4 and H_3PO_3 are 3 and 2 respectively

[Ans. (d)]



14. In the reaction,



the Bronsted base are:

- (a) PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$
- (b) PO_4^{3-} , HPO_4^{2-}
- (c) HC_2O_4^- , HPO_4^{2-}
- (d) HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$

[Ans. (a)]

[Hint: Acid - H^+ = Conjugate base]

15. Conjugate base of HCO_3^- is:

- (a) CO_2
- (b) H_2CO_3
- (c) H_2O
- (d) CO_3^{2-}

[Ans. (d)]

[Hint: Acid - H^+ = Conjugate base, $\text{HCO}_3^- - \text{H}^+ = \text{CO}_3^{2-}$]

16. Four species are listed below :

- (i) HCO_3^-
- (ii) H_3O^+
- (iii) HSO_4^-
- (iv) HSO_3F

Which one of the following is the correct sequence of their acid strength ? (AIEEE 2008)

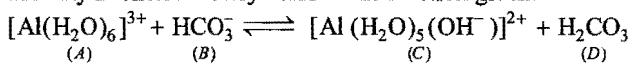
- (a) (iii) < (i) < (iv) < (ii)
- (b) (iv) < (ii) < (iii) < (i)
- (c) (ii) < (iii) < (i) < (iv)
- (d) (i) < (iii) < (ii) < (iv)

[Ans. (d)]

[Hint : $\text{HCO}_3^- < \text{HSO}_4^- < \text{H}_3\text{O}^+ < \text{HSO}_3\text{F}$

HSO_3F is super acid and it is most acidic. H_3O^+ is more acidic than anions (HCO_3^- , HSO_4^-) because anions (HCO_3^- , HSO_4^-) do not release H^+ ion easily. HSO_4^- is more acidic than HCO_3^- because sulphur is more electronegative than carbon.]

17. Identify Bronsted-Lowry acids in the reaction given:



The correct answer is: [EAMCET (Med.) 2008]

- (a) A, C (b) B, D (c) A, D (d) B, C

[Ans. (c)]

[Hint : $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and H_2CO_3 are proton donor or Bronsted acids]

18. Conjugate base of H_2PO_4^- is: [Comed (Karnataka) 2008]

- (a) HPO_4^{2-} (b) PO_4^{3-} (c) H_3PO_4 (d) HPO_4^-

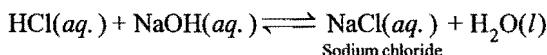
[Ans. (a)]

[Hint : Acid - H^+ = Conjugate base

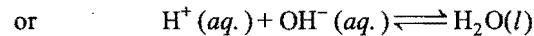
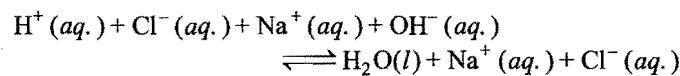
$$\text{H}_2\text{PO}_4^- - \text{H}^+ = \text{HPO}_4^{2-}$$

10.7 ACID-BASE NEUTRALISATION—SALTS

When aqueous solutions of hydrochloric acid and sodium hydroxide are mixed in the proper proportion, a reaction takes place to form sodium chloride and water.



Such a reaction is termed neutralisation because both acidic (H^+) and basic (OH^-) properties are eliminated during the reaction. The hydrogen ion, which is responsible for the acidic properties, has reacted with the hydroxyl ion which is responsible for the basic properties, producing neutral water. The Na^+ and Cl^- ions have undergone no chemical change and appear in the form of crystalline sodium chloride upon evaporation of the solution. Sodium chloride is an example of the class of compounds called salts.



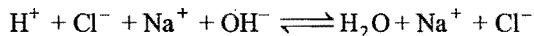
Thus, the neutralisation of a base with an acid involves the interaction between OH^- and H^+ ions.

Or

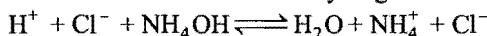
The reaction between an acid and a base to form salt and water is termed neutralisation.

The process of neutralisation does not produce the resulting solution always neutral; no doubt it involves the interaction of H^+ and OH^- ions. The nature of the resulting solution depends on the particular acid and a particular base involved in the reaction. The following examples illustrate this point when equivalent amounts of acids and bases are reacted in aqueous solution.

- (i) A strong acid plus a strong base gives a neutral solution because both are completely ionised and the reaction goes to completion.



- (ii) A strong acid plus a weak base gives an acidic solution as the weak base is not completely ionised. The reaction does not go to completion and there is an excess of hydrogen ions in solution.



- (iii) A weak acid plus a strong base gives a basic solution as the weak acid is not completely ionised. The reaction does not go to completion and there is an excess of hydroxyl ions in solution.



- (iv) A weak acid plus a weak base gives an acidic or a basic or a neutral solution depending on the relative strength of acid and base. In case, both have equal strength, the resulting solution is neutral in nature.



Salts: Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds. Salts may taste salty, sour, bitter, astringent or sweet or tasteless. Solutions of salts may be acidic, basic or neutral. Fused salts and aqueous solutions of salts conduct electricity and undergo electrolysis. The properties of salts in aqueous solutions are the properties of ions. The salts are generally crystalline solids.

The salts are classified into the following classes:

- (i) Simple salts:** The salt formed by the neutralisation process, i.e., interaction between acid and base, is termed as simple salt. These are of three types:

- (a) Normal salts:** The salts formed by the loss of all possible protons (replaceable hydrogen atoms as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen or a hydroxyl group.

Examples are: NaCl , NaNO_3 , K_2SO_4 , $\text{Ca}_3(\text{PO}_4)_2$, Na_3BO_3 , Na_2HPO_3 (one H atom is not replaceable as H_3PO_3 is a dibasic acid), NaH_2PO_2 (both H atoms are not replaceable as H_3PO_2 is a monobasic acid), etc.

- (b) Acid salts:** Salts formed by incomplete neutralisation of poly-basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen atoms. These salts when neutralised by bases form normal salts.

Examples are: NaHCO_3 , NaHSO_4 , NaH_2PO_4 , Na_2HPO_4 , etc.

- (c) Basic salts:** Salts formed by incomplete neutralisation of polyacidic bases are called basic salts. Such salts still contain one or more hydroxyl groups. These salts when neutralised by acids form normal salts.

Examples are: $\text{Zn}(\text{OH})\text{Cl}$, $\text{Mg}(\text{OH})\text{Cl}$, $\text{Fe}(\text{OH})_2\text{Cl}$, $\text{Bi}(\text{OH})_2\text{Cl}$, etc.

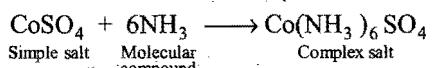
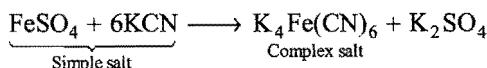
- (ii) Double salts:** The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only.

Examples are: Ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, Potash alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ and other alums.

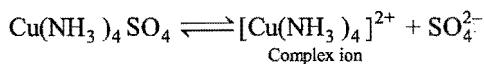
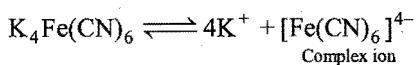
- Properties:** (a) When dissolved in water, it furnishes all the ions present in the simple salts from which it has been constituted.

- (b) The solution of double salt shows the properties of the simple salts from which it has been constituted.

- (iii) Complex salts:** These are formed by combination of simple salts or molecular compounds. These are stable in solid state as well as in solutions.



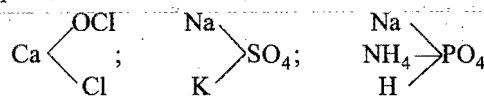
Properties: (a) On dissolving in water, it furnishes a complex ion.



(b) The properties of the solution are different from the properties of the substances from which it has been constituted.

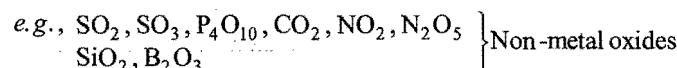
(iv) Mixed salts: The salt which furnishes more than one cation or more than one anion when dissolved in water is called a mixed salt.

Examples are:

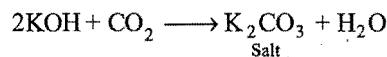
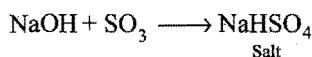
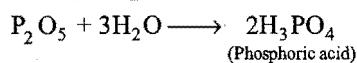
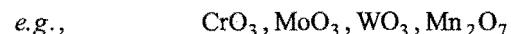


Acidic, Basic and Amphoteric oxides

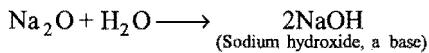
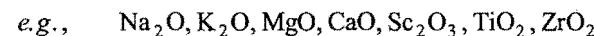
(i) Non-metal oxides are acidic, they dissolve in water to form acid. These oxides form salt with bases.



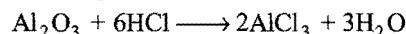
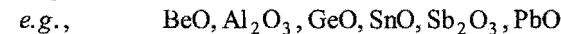
Some Transition metal oxides are also acidic.



(ii) Usually, oxides of highly electropositive metals are basic. These oxides dissolve in water to form base and they form salt with acids.

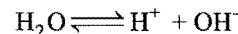


(iii) Oxides of metalloids and less electropositive metals are amphoteric. These oxides form salt with both acids and bases.



10.8 IONIC PRODUCT OF WATER

Pure water is a very weak electrolyte and ionises according to the equation,



Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

or $[\text{H}^+][\text{OH}^-] = K[\text{H}_2\text{O}]$

Since, dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[\text{H}_2\text{O}]$, may be regarded as constant. Thus, the product $K[\text{H}_2\text{O}]$ gives another constant which is designated as K_w . So,

$$[\text{H}^+][\text{OH}^-] = K_w$$

The constant, K_w , is termed as **ionic product of water**.

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as **ionic product of water**. The value of K_w increases with the increase of temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature ($^\circ\text{C}$)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14} . Since, pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

$$[\text{H}^+] = [\text{OH}^-] = x$$

or $[\text{H}^+][\text{OH}^-] = x^2 = 1 \times 10^{-14}$

or $x = 1 \times 10^{-7} \text{ M}$

or $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol litre}^{-1}$

This shows that at 25°C , in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product, $[\text{H}^+][\text{OH}^-]$, remains constant, i.e., equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, i.e.,

$$[\text{H}^+] > [\text{OH}^-]; \quad (\text{Acidic solution})$$

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,

i.e., $[\text{OH}^-] > [\text{H}^+]; \quad (\text{Alkaline or basic solution})$

In neutral solution, $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

In acidic solution, $[\text{H}^+] > [\text{OH}^-]$

or $[H^+] > 1 \times 10^{-7} M$

and $[OH^-] < 1 \times 10^{-7} M$

In alkaline solution, $[OH^-] > [H^+]$

or $[OH^-] > 1 \times 10^{-7} M$

and $[H^+] < 1 \times 10^{-7} M$

Thus, if the hydrogen ion concentration is more than $1 \times 10^{-7} M$, the solution will be acidic in nature and if less than $1 \times 10^{-7} M$, the solution will be alkaline.

$$[H^+] = 10^{-0} \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6} \quad (\text{Acidic})$$

$$[H^+] = \quad \quad \quad 10^{-7} \quad (\text{Neutral})$$

$$[H^+] = 10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8} \quad (\text{Alkaline})$$

We shall have the following table if OH^- ion concentration is taken into account:

$$[OH^-] = 10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8} \quad (\text{Acidic})$$

$$[OH^-] = \quad \quad \quad 10^{-7} \quad (\text{Neutral})$$

$$[OH^-] = 10^{-0} \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6} \quad (\text{Alkaline})$$

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at $25^\circ C$. If one increases, the other decreases accordingly so that the product remains 1×10^{-14} at $25^\circ C$.

If $[H^+] = 10^{-2} M$, then $[OH^-] = 10^{-12} M$; the product, $[H^+][OH^-] = 10^{-2} \times 10^{-12} = 10^{-14}$; the solution is acidic.

If $[H^+] = 10^{-10} M$, then $[OH^-] = 10^{-4} M$; the product, $[H^+][OH^-] = 10^{-10} \times 10^{-4} = 10^{-14}$; the solution is alkaline.

10.9 HYDROGEN ION CONCENTRATION—pH SCALE

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since, H^+ ion concentration can vary within a wide range from 1 mol per litre to about 10×10^{-14} mol per litre, a logarithmic notation has been devised by Sorenson, in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, i.e.,

$$[H^+] = 10^{-\text{pH}}$$

or $\log [H^+] = \log 10^{-\text{pH}} = -\text{pH} \log 10 = -\text{pH}$

or $\text{pH} = -\log [H^+]$

***pK value:** p stands for negative logarithm. Just as H^+ and OH^- ion concentrations range over many negative powers of 10, it is convenient to express them as pH or pOH, the dissociation constant (K) values also range over many negative powers of 10 and it is convenient to write them as pK. Thus, pK is the negative logarithm of dissociation constant.

$$pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b$$

Weak acids have higher pK_a values. Similarly, weak bases have higher pK_b values.

or $\text{pH} = \log \frac{1}{[H^+]}$

pH of a solution is, thus, defined as the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains or pH of the solution is the logarithm of the reciprocal of H^+ ion concentration.

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, i.e.,

$$\text{pOH} = -\log [OH^-]$$

Considering the relationship,

$$[H^+][OH^-] = K_w = 1 \times 10^{-14}$$

Taking log on both sides, we have

$$\log [H^+] + \log [OH^-] = \log K_w = \log (1 \times 10^{-14})$$

$$\text{or } -\log [H^+] - \log [OH^-] = -\log K_w = -\log (1 \times 10^{-14})$$

$$\text{or } \text{pH} + \text{pOH} = \text{p}K_w^* = 14$$

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at $25^\circ C$. The above discussion can be summarised in the following manner:

	$[H^+]$	$[OH^-]$	pH	pOH
Acidic solution	$> 10^{-7}$	$< 10^{-7}$	< 7	> 7
Neutral solution	10^{-7}	10^{-7}	7	7
Basic solution	$< 10^{-7}$	$> 10^{-7}$	> 7	< 7

$[H^+]$	$[OH^-]$	pH	pOH	Nature of solution
10^0	10^{-14}	0	14	Strongly acidic
10^{-2}	10^{-12}	2	12	Acidic
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
10^{-9}	10^{-5}	9	5	Weakly basic
10^{-11}	10^{-3}	11	3	Basic
10^{-14}	10^0	14	0	Strongly basic

The following table shows the pH range for a few common substances:

Substance	pH range	Substance	pH range
Gastric contents	1.0 – 3.0	Milk (cow)	6.3 – 6.6
Soft drinks	2.0 – 4.0	Saliva (human)	6.5 – 7.5
Lemons	2.2 – 2.4	Blood plasma (human)	7.3 – 7.5
Vinegar	2.4 – 3.4	Milk of magnesia	10.5
Apples	2.9 – 3.3	Seawater	8.5
Urine (human)	4.8 – 8.4		

Any method which can measure the concentration of H^+ ions or OH^- ions in a solution can serve for finding pH value.

Limitations of pH Scale: (i) pH values of the solutions do not give us immediate idea of the relative strengths of the solutions. A solution of pH = 1 has a hydrogen ion concentration 100 times that of a solution of pH = 3 (not three times). A $4 \times 10^{-5} N$ HCl is twice concentrated of a $2 \times 10^{-5} N$ HCl solution, but the pH values of these solutions are 4.40 and 4.70 (not double).

(ii) pH value of zero is obtained in 1 N solution of strong acid. In case the concentration is 2 N, 3 N, 10 N, etc. The respective pH values will be negative.

(iii) A solution of an acid having very low concentration, say $10^{-8} N$, cannot have pH 8, as shown by pH formula, but the actual pH value will be less than 7.

[Note: (i) Normality of strong acid = $[H_3O^+]$]

$$\text{Normality of strong base} = [OH^-]$$

$$\therefore pH = -\log[N] \quad \text{for strong acids}$$

$$pOH = -\log[N] \quad \text{for strong bases}$$

(ii) Sometimes, pH of acid comes more than 7 and that of base comes less than 7. It shows that the solution is very dilute; in such cases, H^+ or OH^- contribution from water is also considered, e.g., in $10^{-8} N$ HCl,

$$\begin{aligned}[H^+]_{\text{Total}} &= [10^{-8}]_{\text{Acid}} + [10^{-7}]_{\text{Water}} \\ &= 11 \times 10^{-8} M = 1.1 \times 10^{-7} M\end{aligned}$$

(iii) **pH of mixture:** Let one litre of an acidic solution of pH 2 be mixed with two litre of other acidic solution of pH 3. The resultant pH of the mixture can be evaluated in the following way:

Sample-1

$$pH = 2$$

$$[H^+] = 10^{-2} M$$

$$V = 1 \text{ litre}$$

$$M_1 V_1 + M_2 V_2 = M_R (V_1 + V_2)$$

$$10^{-2} \times 1 + 10^{-3} \times 2 = M_R (1 + 2)$$

$$\frac{12 \times 10^{-3}}{3} = M_R$$

$$4 \times 10^{-3} = M_R \quad (\text{Here, } M_R = \text{Resultant molarity})$$

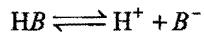
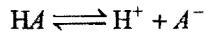
$$pH = -\log(4 \times 10^{-3})$$

(iv) Total concentration of $[H^+]$ or $[H_3O^+]$ in a mixture of weak acid and a strong acid

$$= \frac{C_2 + \sqrt{C_2^2 + 4K_a C_1}}{2}$$

where, C_1 is the concentration of weak acid (in mol litre⁻¹) having dissociation constant K_a and C_2 is the concentration of strong acid.

(v) Let us consider mixture of two weak acids HA and HB.



On applying charge balance

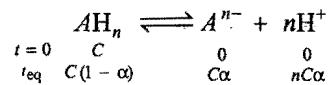
$$\begin{aligned}[H^+] &= [A^-] + [B^-] + [OH^-] \\ &= \frac{K_a [HA]}{[H^+]} + \frac{K_b [HB]}{[H^+]} + \frac{K_w}{[H^+]} \\ [H^+] &= \sqrt{K_a [HA] + K_b [HB] + K_w} \\ &= \sqrt{CK_a + CK_b + K_w}\end{aligned}$$

(vi) Let us consider mixture of two weak bases AOH and BOH with dissociation constant K_1, K_2 and concentration C_1, C_2 respectively

$$[OH^-] = \sqrt{C_1 K_1 + C_2 K_2 + K_w}$$

10.10 pH OF WEAK ACIDS AND BASES

Weak acids and bases are not completely ionised; an equilibrium is found to have been established between ions and unionised molecules. Let us consider a weak acid of basicity 'n'.



$$[H^+] = n\alpha; \quad \therefore pH = -\log_{10} [n\alpha] \quad \dots (i)$$

For monobasic acid, $n = 1$

$$pH = -\log_{10} [\alpha] \quad \dots (ii)$$

Dissociation constant of acid K_a may be calculated as:

$$K_a = \frac{[A^{n-}][H^+]^n}{[AH_n]} = \frac{[\alpha][n\alpha]^n}{C(1 - \alpha)}$$

$$= \frac{\alpha[n\alpha]^n}{(1 - \alpha)} \quad [\text{for weak acids, } \alpha \ll 1]$$

$$\therefore (1 - \alpha) \approx 1$$

$$= \alpha[n\alpha]^n$$

$$nCK_a = n\alpha[n\alpha]^n = [n\alpha]^{(n+1)}$$

$$[n\alpha] = [nCK_a]^{1/(n+1)}$$

$$[H^+] = [nCK_a]^{1/(n+1)}$$

$$\therefore pH = -\frac{1}{(n+1)} \log_{10} (nCK_a) \quad \dots (iii)$$

For monobasic acid, $n = 1$

$$pH = -\log_{10} \sqrt{CK_a} \quad \dots (iv)$$

Since,

$$K_a = \alpha[n\alpha]^n$$

$$\frac{K_a}{\alpha} = (n\alpha)^n$$

$$[n\alpha] = \left[\frac{K_a}{\alpha} \right]^{1/n} = [H^+]$$

$$pH = -\frac{1}{n} \log_{10} \left(\frac{K_a}{\alpha} \right) \quad \dots (v)$$

For $n = 1$,

$$pH = -\log_{10} \left(\frac{K_a}{\alpha} \right) \quad \dots (vi)$$

SOME SOLVED EXAMPLES

Example 28. The hydrogen ion concentration of a solution is 0.001 M. What will be the hydroxyl ion concentration of solution?

Solution: We know that, $[H^+][OH^-] = 1.0 \times 10^{-14}$

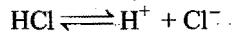
$$\text{Given that, } [H^+] = 0.001 M = 10^{-3} M$$

$$\text{So, } [OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{10^{-3}} = 10^{-11} M$$

Example 29. What is the pH of the following solutions?

- (a) 10^{-3} M HCl (b) 0.0001 M NaOH (c) 0.0001 M H_2SO_4

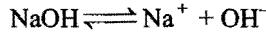
Solution: HCl is a strong electrolyte and is completely ionised.



$$\text{So, } [H^+] = 10^{-3} M$$

$$pH = -\log [H^+] = -\log (10^{-3}) = 3$$

(b) NaOH is a strong electrolyte and is completely ionised.



$$\text{So, } [OH^-] = 0.0001 M = 10^{-4} M$$

$$pOH = -\log (10^{-4}) = 4$$

$$As \quad pH + pOH = 14$$

$$So, \quad pH + 4 = 14 \quad \text{or} \quad pH = 10$$

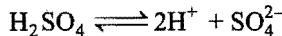
Alternative method: $[OH^-] = 10^{-4} M$

We know that, $[H^+][OH^-] = 1.0 \times 10^{-14}$

$$\text{So, } [H^+] = \frac{1.0 \times 10^{-14}}{10^{-4}} = 10^{-10} M$$

$$pH = -\log [H^+] = -\log (10^{-10}) = 10$$

(c) H_2SO_4 is a strong electrolyte and is ionised completely.



One molecule of H_2SO_4 furnishes $2H^+$ ions.

$$\text{So, } [H^+] = 2 \times 10^{-4} M$$

$$pH = -\log [H^+]$$

$$= -\log (2 \times 10^{-4}) = 3.70$$

Example 30. Calculate the pH of the following solutions assuming complete dissociation:

(a) 0.365 g L^{-1} HCl solution

(b) 0.001 M $Ba(OH)_2$ solution.

Solution: (a) Mole. mass of HCl = 36.5

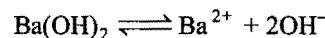
$$\text{Concentration of HCl} = \frac{0.365}{36.5} = 1.0 \times 10^{-2} \text{ mol L}^{-1}$$

HCl is a strong electrolyte and is completely ionised.

$$\text{So, } [H^+] = 1 \times 10^{-2} \text{ mol L}^{-1}$$

$$pH = -\log [H^+] = -\log (1 \times 10^{-2}) = 2$$

(b) $Ba(OH)_2$ is a strong electrolyte and is completely ionised



One molecule on dissociation furnishes $2OH^-$ ions.

So,

$$[OH^-] = 2 \times 10^{-3} M$$

$$pOH = -\log [OH^-]$$

$$= -\log (2 \times 10^{-3}) = 2.7$$

We know that, $pH + pOH = 14$

So,

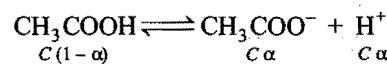
$$pH = (14 - 2.7) = 11.3$$

Example 31. Find the pH of a 0.002 N acetic acid solution, if it is 2.3% ionised at a given dilution.

Solution: Degree of dissociation, $\alpha = \frac{2.3}{100} = 0.023$

Concentration of acetic acid, $C = 0.002 M$

The equilibrium is,



$$\text{So, } [H^+] = C\alpha = 0.002 \times 0.023$$

$$= 4.6 \times 10^{-5} M$$

$$pH = -\log [H^+]$$

$$= -\log (4.6 \times 10^{-5}) = 4.3372$$

Example 32. Calculate the pH value of a solution obtained by mixing 50 mL of 0.2 N HCl with 50 mL of 0.1 N NaOH.

Solution: Number of milli-equivalents of the acid
 $= 50 \times 0.2 = 10$

Number of milli-equivalents of the base
 $= 50 \times 0.1 = 5$

Number of milli-equivalents of the acid left after the addition of base

$$= (10 - 5) = 5$$

Total volume of the solution = $50 + 50 = 100 \text{ mL}$

Thus, 5 milli-equivalents of the acid are present in 100 mL of solution.

or 50 milli-equivalents of the acid are present in one litre of solution.

or 0.05 equivalents of the acid are present in one litre of solution.

The acid is monobasic and completely ionised in solution.

$$0.05 \text{ N HCl} = 0.05 M \text{ HCl}$$

$$\text{So, } [H^+] = 0.05 M$$

$$pH = -\log [H^+] = -\log 5 \times 10^{-2} = -[\log 5.0 + \log 10^{-2}] \\ = -[0.70 - 2] = 1.3$$

Example 33. What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N HCl, assuming the complete ionisation of the acid and the base?

Solution: Number of milli-equivalents of NaOH
 $= 800 \times 0.05 = 40$

Number of milli-equivalents of HCl = $200 \times 0.1 = 20$

Number of milli-equivalents of NaOH left after the addition of HCl

$$= (40 - 20) = 20$$

$$\text{Total volume} = (200 + 800) \text{ mL} = 1000 \text{ mL} = 1 \text{ litre}$$

20 milli-equivalents or 0.02 equivalents of NaOH are present in one litre, i.e.,

0.02 N NaOH = 0.02 M NaOH (Mono-acidic) and the base is completely ionised.

$$\text{So, } [\text{OH}^-] = 0.02 \text{ M}$$

$$\text{or } [\text{OH}^-] = 2 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log(2 \times 10^{-2}) = 1.7$$

$$\text{We know that, pH} + \text{pOH} = 14$$

$$\text{So, } \text{pH} = (14 - 1.7) = 12.3$$

Example 34. What is the hydrogen ion concentration of a solution (i) whose pH is 12, (ii) whose pH is 5.6?

Solution:

$$(i) \text{pH} = -\log[\text{H}^+]$$

$$\text{or } \log[\text{H}^+] = -\text{pH} = -12$$

$$[\text{H}^+] = 10^{-12} \text{ M}$$

$$(ii) \text{pH} = -\log[\text{H}^+]$$

$$\text{or } \log[\text{H}^+] = -5.6$$

$$\text{or } [\text{H}^+] = 10^{-5.6} = 10^{-6} \times 10^{0.4} = 2.5 \times 10^{-6} \text{ M}$$

Example 35. How many moles of calcium hydroxide must be dissolved to produce 250 mL of an aqueous solution of pH 10.65? Assume the complete ionisation.

Solution: We know that,

$$\text{pH} + \text{pOH} = 14$$

$$\text{So, } \text{pOH} = (14 - 10.65) = 3.35$$

$$[\text{OH}^-] = 10^{-3.35} = 10^{-4} \times 10^{0.65}$$

$$= 4.47 \times 10^{-4} \text{ M}$$

One molecule of $\text{Ca}(\text{OH})_2$ furnishes 2 OH^- ions.

Hence, concentration of

$$\text{Ca}(\text{OH})_2 = \frac{4.47 \times 10^{-4}}{2} = 2.235 \times 10^{-4} \text{ M}$$

$$\text{No. of moles in 250 mL} = \frac{2.235 \times 10^{-4}}{4} = 5.58 \times 10^{-5}$$

Example 36. The pH of 0.1 M hydrocyanic acid solution is 5.2. What is the value of K_a for hydrocyanic acid?

$$\text{Solution: } \text{pH} = -\log[\text{H}^+]$$

$$\text{or } \log[\text{H}^+] = -\text{pH} = -5.2$$

$$[\text{H}^+] = 10^{-5.2} = 10^{-6} \times 10^{0.8}$$

$$= 6.3 \times 10^{-6} \text{ M}$$

$$\text{'}\alpha\text{'}, degree of dissociation = \frac{[\text{H}^+]}{C} = \frac{6.3 \times 10^{-6}}{0.1} = 6.3 \times 10^{-5}$$

According to Ostwald's formula for weak electrolyte,

$$K_a = \alpha^2 C = 6.3 \times 10^{-5} \times 6.3 \times 10^{-5} \times 0.1$$

$$= 3.69 \times 10^{-10}$$

Example 37. Calculate the pH of the following solutions:

$$(i) 1.0 \times 10^{-8} \text{ M HCl}, \quad (ii) 1.0 \times 10^{-8} \text{ M NaOH}$$

Solution: (i) The neutral water has $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$

By adding $1.0 \times 10^{-8} \text{ M HCl}$, a concentration of $1.0 \times 10^{-8} \text{ M H}^+$ ions has increased in solution.

$$\text{Thus, total } [\text{H}^+] = (1 \times 10^{-7} + 1 \times 10^{-8}) \text{ M}$$

$$= (1 \times 10^{-7} + 0.1 \times 10^{-7}) \text{ M}$$

$$= 1.1 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(1.1 \times 10^{-7}) = -[\log 1.1 + \log 10^{-7}]$$

$$= -[0.0414 - 7.0] = 6.9586$$

(i) The neutral water has $[\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

By adding $1.0 \times 10^{-8} \text{ M NaOH}$, a concentration of $1.0 \times 10^{-8} \text{ M OH}^-$ ions has increased in solution.

$$\text{Thus, total } [\text{OH}^-] = (1 \times 10^{-7} + 1.0 \times 10^{-8}) \text{ M}$$

$$= 1.1 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log 1.1 \times 10^{-7}$$

$$= 6.9586$$

$$\text{pH} = (14 - \text{pOH}) = (14 - 6.9586) = 7.0414$$

Example 38. Calculate the S^{2-} ion concentration in a saturated solution (0.1 M) of H_2S whose pH was adjusted to 2 by the addition of HCl. ($K_a = 1.1 \times 10^{-21}$)

$$\text{Solution: } \text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$$

$$K_a = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$\text{or } [\text{S}^{2-}] = \frac{K_a [\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

$$\text{pH} = 2; \text{ So, } [\text{H}^+] = 1 \times 10^{-2} \text{ M}$$

H_2S is a weak electrolyte, So, $[\text{H}_2\text{S}] = 0.1 \text{ M}$

$$\text{So, } [\text{S}^{2-}] = \frac{1.1 \times 10^{-21} \times 0.1}{1 \times 10^{-2} \times 1 \times 10^{-2}} = 1.1 \times 10^{-18} \text{ M}$$

Example 39. What is the hydrogen ion concentration of 0.1 N CH_3COOH solution? The ionisation constant of CH_3COOH is 1.8×10^{-5} . What is the pH of the solution?

(IIT 1993)

Solution: Let the degree of dissociation be ' α '.

CH_3COOH is a weak electrolyte; thus,

$$\alpha^2 C = K_a$$

$$\alpha^2 \times 0.1 = 1.8 \times 10^{-5}$$

$$\text{or } \alpha = 1.34 \times 10^{-2}$$

$$[\text{H}^+] = \alpha \cdot C = 1.34 \times 10^{-2} \times 0.1 = 1.34 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 1.34 \times 10^{-3} = 2.8729$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6} \text{ M}$. What is the value of K_w at this temperature? [CBSE (Med.) 2006]
 (a) 10^{-6} (b) 10^{-12} (c) 10^{-13} (d) 10^{-14}

[Ans. (b)]

[Hint: $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-6} \text{ M}$

$$\therefore K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-12}$$

20. The pH of 0.5 M aqueous solution of HF ($K_a = 2 \times 10^{-4}$) is:
 (a) 2 (b) 4 (c) 6 (d) 10

[Ans. (a)]

$$[\text{Hint: } [\text{H}^+] = \sqrt{CK_a} = \sqrt{0.5 \times 2 \times 10^{-4}} = 10^{-2} \text{ M}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log 10^{-2} = 2]$$

21. The hydroxyl ion concentration in a solution having pH value 3 will be:

- (a) 10^{-11} M (b) 10^{-7} M (c) 10^{-3} M (d) 10^{-14} M

[Ans. (a)]

$$[\text{Hint: } \text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH} = 14 - 3 = 11$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11} \text{ M}]$$

22. A 50 mL solution of $\text{pH} = 1$ is mixed with a 50 mL solution of $\text{pH} = 2$. The pH of the mixture will be nearly:

- (a) 0.76 (b) 1.26 (c) 1.76 (d) 2.26

[Ans. (b)]

$$[\text{Hint: } \text{pH} = 1, [\text{H}^+] = 10^{-1} \text{ M}$$

$$\text{pH} = 2, [\text{H}^+] = 10^{-2} \text{ M}$$

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$10^{-1} \times 50 + 10^{-2} \times 50 = M_R \times 100$$

$$M_R = 5.5 \times 10^{-2} \text{ M}$$

(Resultant molarity of H^+ ions)

$$\text{pH} = -\log 5.5 \times 10^{-2} = 1.26]$$

23. The pH of a solution obtained by mixing 50 mL of 0.4 N HCl and 50 mL of 0.2 N NaOH is:

- (a) $-\log 2$ (b) $-\log 0.2$ (c) 1 (d) 2

[Ans. (c)]

$$[\text{Hint: } N_1V_1 \text{ acid} - N_2V_2 \text{ base} = N_R(V_1 + V_2)$$

$$0.4 \times 50 - 0.2 \times 50 = N_R \times 100$$

$$N_R = 0.1$$

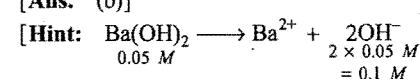
$$\therefore [\text{H}^+] = 0.1 \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 0.1 = 1]$$

24. What will be the pH value of 0.05 M Ba(OH)_2 solution?

- (a) 12 (b) 13 (c) 1 (d) 12.96

[Ans. (b)]



$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.1 = 1$$

$$\text{pH} = 14 - 1 = 13]$$

25. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture? [CBSE (PMT) 2008]

$$(a) 3.7 \times 10^{-3} \text{ M} \qquad (b) 1.11 \times 10^{-3} \text{ M}$$

$$(c) 1.11 \times 10^{-4} \text{ M} \qquad (d) 3.7 \times 10^{-4} \text{ M}$$

[Ans. (d)]

[Hint: $[\text{H}^+] = 10^{-3} \text{ M}$, $[\text{H}^+] = 10^{-4} \text{ M}$, $[\text{H}^+] = 10^{-5} \text{ M}$ for the given acids.

$$M_{\text{mix}} V_{\text{mix}} = M_1 V_1 + M_2 V_2 + M_3 V_3$$

$$M_{\text{mix}} \times 3 = 10^{-3} \times 1 + 10^{-4} \times 1 + 10^{-5} \times 1$$

$$M_{\text{mix}} = \frac{10^{-5} [100 + 10 + 1]}{3} = \frac{111 \times 10^{-5}}{3} = 37 \times 10^{-5} \text{ M} \\ = 3.7 \times 10^{-4} \text{ M}]$$

10.14 BUFFER SOLUTIONS

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is observed that solutions and even pure water ($\text{pH} = 7$) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution**. It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

General Characteristics of a Buffer Solution

- (i) It has a definite pH, i.e., it has reserve acidity or alkalinity.
- (ii) Its pH does not change on standing for long.
- (iii) Its pH does not change on dilution.
- (iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

- (i) by mixing a weak acid with its salt with a strong base, e.g.,
 (a) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 (b) Boric acid + Borax
 (c) Phthalic acid + Potassium acid phthalate
- (ii) by mixing a weak base with its salt with a strong acid, e.g.,
 (a) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
 (b) Glycine + Glycine hydrochloride

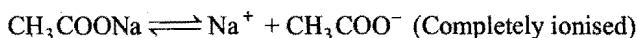
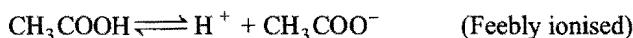
(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, e.g., $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$ or a salt of weak acid and a weak base, such as $\text{CH}_3\text{COONH}_4$.

The first and second type are also called acidic and basic buffers respectively.

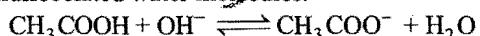
Explanation of Buffer Action

(i) Acidic buffer: Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH_3COOH molecules, CH_3COO^- ions, Na^+ ions, H^+ ions and OH^- ions. Thus, we have the following equilibria in solution:



When a drop of strong acid, say HCl, is added, the H^+ ions furnished by HCl combine with CH_3COO^- ions to form feebly ionised CH_3COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H^+ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.

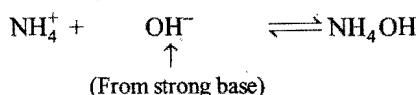


Thus, OH^- ions furnished by a base are removed and pH of the solution is practically unaltered.

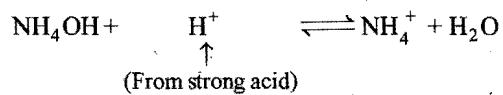
(ii) Basic buffer: Consider the case of the solution containing NH_4OH and its salt NH_4Cl . The solution will have NH_4OH molecule, NH_4^+ ions, Cl^- ions, OH^- ions and H^+ ions.



When a drop of NaOH is added, the added OH^- ions combine with NH_4^+ ions to form feebly ionised NH_4OH whose ionisation is further suppressed due to common ion effect. Thus, pH is not disturbed considerably.



When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.

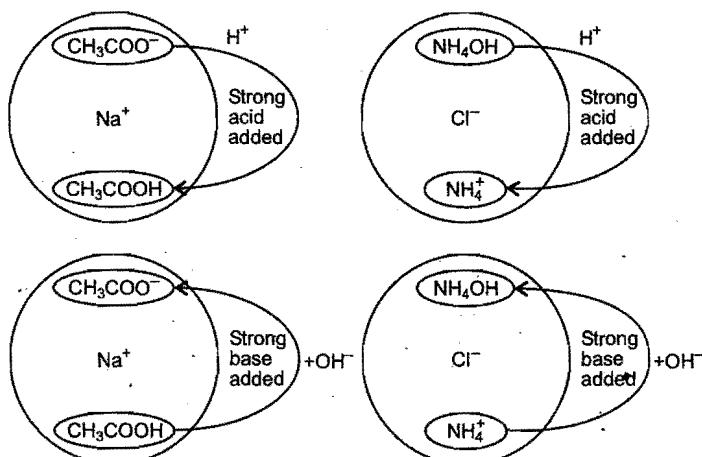


Thus, pH of the buffer is practically unaffected.

Diagrammatic Representation of Buffer Action

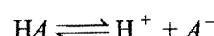
Acid Buffer ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$)

Base Buffer ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$)



Henderson's Equation (pH of a buffer)

(i) Acidic buffer: It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA , can be shown by the equation,

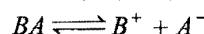


Applying law of mass action,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots (\text{i})$$

$$\text{or} \quad [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad \dots (\text{ii})$$

It can be assumed that concentration of A^- ions from complete ionisation of the salt BA is too large to be compared with concentration of A^- ions from the acid HA .



Thus, $[\text{HA}]$ = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $[\text{A}^-]$ = Initial concentration of the salt as it is completely ionised.

$$\text{So, } [\text{H}^+] = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]} \quad \dots (\text{iii})$$

Taking logarithm and reversing sign,

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{or} \quad \text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$\text{or} \quad \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots (\text{iv})$$

This is known as **Henderson's equation**.

When $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$, then

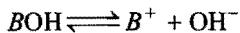
$$\text{pH} = 1 + \text{p}K_a$$

and when $\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{10}$, then

$$\text{pH} = \text{p}K_a - 1$$

So, weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid has a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3.8 to 5.8.

(ii) Basic buffer: It consists of a weak base and its salt with strong acid. Ionisation of a weak base, BOH , can be represented by the equation,



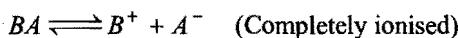
Applying law of mass action,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad \dots (i)$$

or

$$[OH^-] = K_b \frac{[BOH]}{[B^+]} \quad \dots (ii)$$

As the salt is completely ionised, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.



$$\text{So, } [OH^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]} \quad \dots (iii)$$

$$\text{or } pOH = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$\text{or } pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots (iv)$$

Knowing pOH, pH can be calculated by the application of the formula,

$$pH + pOH = 14$$

Buffer capacity: The property of a buffer solution to resist alteration in its pH value is known as **buffer capacity**. It has been found that if the ratio $\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\frac{[\text{Salt}]}{[\text{Base}]}$ is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as **number of moles of acid or base added in one litre of solution as to change the pH by unity, i.e.,**

Buffer capacity

$$\phi = \frac{\text{No. of moles of acid or base added to 1 litre}}{\text{Change in pH}}$$

$$\text{or } \phi = \frac{\partial b}{\partial(pH)}$$

where, ∂b — number of moles of acid or base added to 1 litre solution and $\partial(pH)$ — change in pH.

Buffer capacity is maximum:

- (i) When $[\text{Salt}] = [\text{Acid}]$, i.e., $pH = pK_a$ for acid buffer
- (ii) When $[\text{Salt}] = [\text{Base}]$, i.e., $pOH = pK_b$ for base buffer under above conditions, the buffer is called efficient.

Utility of Buffer Solutions in Analytical Chemistry

Buffers are used:

- (i) To determine the pH with the help of indicators.

- (ii) For the removal of phosphate ion in the qualitative inorganic analysis after second group using $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ buffer.
- (iii) For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$, is used.
- (iv) For precipitation of hydroxides of third group of qualitative analysis, a buffer, $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$, is used.
- (v) A buffer solution of NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ is used for precipitation of carbonates of fifth group in qualitative inorganic analysis.
- (vi) The pH of intracellular fluid, blood is naturally maintained. This maintenance of pH is essential to sustain life because, enzyme catalysis is pH sensitive process. The normal pH of blood plasma is 7.4. Following two buffers in the blood help to maintain pH (7.4):
 - (a) Buffer of carbonic acid (H_2CO_3 and NaHCO_3)
 - (b) Buffer of phosphoric acid (H_2PO_4^- , HPO_4^{2-})

Buffers are used in industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc. Buffers are also employed in agriculture, dairy products and preservation of various types of foods and fruits.

SOME SOLVED EXAMPLES

Example 40. The pH of a buffer is 4.745. When 0.01 mole of NaOH is added to 1 litre of it, the pH changes to 4.832, calculate its buffer capacity.

Solution: From definition,

$$\text{Buffer capacity } (\phi) = \frac{\partial b}{\partial[pH]}$$

$$\partial(pH) = (4.832 - 4.745) = 0.087; \quad \partial b = 0.01$$

Substituting given values,

$$\phi = \frac{0.01}{0.087} = 0.115$$

Example 41. Suppose it is required to make a buffer solution of pH = 4, using acetic acid and sodium acetate. How much of sodium acetate is to be added to 1 litre of N/10 acetic acid?

Dissociation constant of acetic acid = 1.8×10^{-5} .

Solution: Applying Henderson's equation,

$$pH = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$4 = \log [\text{Salt}] - \log (0.1) - \log 1.8 \times 10^{-5}$$

$$\text{So, } \log [\text{Salt}] = (4 - 1 - 5 + 0.2552) = 2.2552$$

$$[\text{Salt}] = 0.018 \text{ g mol L}^{-1}$$

The molecular mass of CH_3COONa = 82

$$\text{Amount of salt} = 0.018 \times 82 = 1.476 \text{ g}$$

Example 42. What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing 1M acetic acid and acetate ion? Assume that the total volume is one litre. (K_a for CH_3COOH = 1.8×10^{-5})

$$8.5 = \log \frac{0.01 - a}{a} - \log 4.1 \times 10^{-10}$$

$$\text{So, } \log \frac{(0.01 - a)}{a} = 8.5 + 0.6127 - 10.0 = 1.1127$$

$$\frac{(0.01 - a)}{a} = 0.1296$$

$$\text{or } a = \frac{0.01}{1.1296} = 0.0089 \text{ mole}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

26. The pH of a solution that is $0.1 M$ NaA and $0.1 M$ HA ($K_a = 1 \times 10^{-6}$) would be:

(a) 5 (b) 6 (c) 3 (d) 7

[Ans. (b)]

$$\text{[Hint: } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ = -\log 10^{-6} + \log \frac{0.1}{0.1} = 6]$$

27. $\text{p}K_a$ for acetic acid is 4.74. What should be the ratio of concentrations of acetic acid and acetate ions to have a solution with pH 5.74?

(a) 1:10 (b) 10:1 (c) 1:1 (d) 2:1

[Ans. (a)]

$$\text{[Hint: } \text{pH} = \text{p}K_a + \log \frac{[\text{Acetate ion}]}{[\text{Acetic acid}]} \\ 5.74 = 4.74 + \log \frac{[\text{Acetate ion}]}{[\text{Acetic acid}]} \\ [\text{Acetic acid}]:[\text{Acetate}] = 1:10]$$

28. What is the pH of the buffer solution containing 0.15 mol of NH_4OH and 0.25 mol of NH_4Cl ? K_b for NH_4OH is 1.98×10^{-5} :

(a) 10 (b) 9 (c) 9.2 (d) 10.2

[Ans. (b)]

$$\text{[Hint: } 14 - \text{pH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ = -\log (1.98 \times 10^{-5}) + \log \left(\frac{0.25}{0.15} \right) \\ \text{pH} = 9]$$

29. The pH of a buffer solution of $0.1 M$ CH_3COOH and $0.1 M$ CH_3COONa is ($\text{p}K_a = 4.745$).

(a) 4.745 (b) 3.745 (c) 5.745 (d) 3.255

[Ans. (a)]

$$\text{[Hint: } \text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ = 4.745 + \log \frac{0.1}{0.1} = 4.745]$$

30. The pH of a buffer solution prepared by adding 10 mL of $0.1 M$ CH_3COOH and 20 mL of $0.1 M$ sodium acetate will be: (Given: $\text{p}K_a$ of $\text{CH}_3\text{COOH} = 4.74$)

(a) 4.05 (b) 3.04 (c) 5.04 (d) 3.05

[Ans. (c)]

[Hint:

$$\text{Number of moles of } \text{CH}_3\text{COOH} = \frac{MV}{1000} = \frac{0.1 \times 10}{1000} = 0.001$$

$$\text{Number of moles of } \text{CH}_3\text{COONa} = \frac{MV}{1000} = \frac{0.1 \times 20}{1000} = 0.002$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ = 4.74 + \log \left[\frac{0.002}{0.001} \right] = 5.04]$$

31. 40 mL of $0.1 M$ ammonium hydroxide is mixed with 20 mL of $0.1 M$ HCl. What is the pH of the mixture? ($\text{p}K_b$ of ammonia solution is 4.74.) (AIIMS 2008)

(a) 4.74 (b) 2.26 (c) 9.26 (d) 5

[Ans. (c)]

[Hint: Since, ammonium hydroxide is 50% neutralised, hence

$$[\text{Salt}] = [\text{Base}]$$

$$\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} = 4.74 + \log_{10} 1 = 4.74$$

$$\text{pH} = 14 - 4.74 = 9.26$$

32. The $\text{p}K_a$ of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA, in which 50% of the acid is ionised, is: (AIIEEE 2007)

(a) 7.0 (b) 4.5 (c) 2.5 (d) 9.5

[Ans. (d)]

$$\text{[Hint: } \text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}]$$

Since, acid is 50% ionised, hence $[\text{A}^-] = [\text{HA}]$

$$\text{or } \text{pH} = \text{p}K_a + \log 1 \\ = 4.5$$

$$\text{pOH} = 14 - 4.5 = 9.5$$

33. $\text{p}K_a$ value of acetic acid is 4.75. If the buffer solution contains $0.125 M$ acetic acid and $0.25 M$ sodium acetate, the pH of buffer solution is : (Camed (Karnataka) 2008)

(a) 5.05 (b) 5.5 (c) 4.9 (d) 5.75

[Ans. (a)]

$$\text{[Hint: } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ = 4.75 + \log \frac{0.25}{0.125} \\ = 5.05]$$

Example 47. The dissociation constants for HCOOH and CH_3COOH are 2.1×10^{-4} and 1.8×10^{-5} respectively. Calculate the relative strengths of the acids.

Solution: The strength of the acid is directly proportional to the square root of the dissociation constant.

$$\text{Strength of the acid} \propto \sqrt{\text{dissociation constant}}$$

$$\text{Hence, } \frac{\text{Strength of HCOOH}}{\text{Strength of CH}_3\text{COOH}} = \sqrt{\frac{K_{\text{HCOOH}}}{K_{\text{CH}_3\text{COOH}}}} \\ = \sqrt{\frac{2.1 \times 10^{-4}}{1.8 \times 10^{-5}}} = 3.415$$

Example 48. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.05 mol L^{-1} of NH_4OH and 0.25 mol L^{-1} of NH_4Cl . Calculate the concentration of aluminium and magnesium ions in solution.

$$K_{sp} \text{ Al(OH)}_3 = 6 \times 10^{-32}; K_b \text{ NH}_4\text{OH} = 1.8 \times 10^{-5}$$

$$K_{sp} \text{ Mg(OH)}_2 = 6 \times 10^{-10}$$

Solution: $\text{pOH} = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$

$$-\log [\text{OH}^-] = \log \frac{0.25}{0.05} - \log 1.8 \times 10^{-5}$$

or $\log [\text{OH}^-] = \log \frac{1.8 \times 10^{-5}}{5}$

$$[\text{OH}^-] = 0.36 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{Al}^{3+}] = \frac{K_{sp} \text{ Al(OH)}_3}{[\text{OH}^-]^3} = \frac{6 \times 10^{-32}}{(0.36 \times 10^{-5})^3} = 1.29 \times 10^{-10} \text{ mol L}^{-1}$$

$$[\text{Mg}^{2+}] = \frac{K_{sp} \text{ Mg(OH)}_2}{[\text{OH}^-]^2} = \frac{6 \times 10^{-10}}{(0.36 \times 10^{-5})^2} = 46.3 \text{ mol L}^{-1}$$

Example 49. Calculate the pH at which Mg(OH)_2 begins to precipitate from a solution containing 0.10 M Mg^{2+} ions.

$$(K_{sp} \text{ Mg(OH)}_2 = 1.0 \times 10^{-11}) \quad (\text{IIT 1992})$$

Solution: $K_{sp} \text{ Mg(OH)}_2 = 1.0 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2$

$$= (0.10)[\text{OH}^-]^2$$

or $[\text{OH}^-]^2 = \frac{1.0 \times 10^{-11}}{0.10} = 1 \times 10^{-10}$

or $[\text{OH}^-] = 1 \times 10^{-5}$

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 1 \times 10^{-9}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1 \times 10^{-9}) = 9.0$$

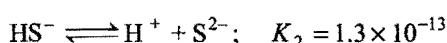
Example 50. An aqueous solution of metal bromide, MBr_2 (0.05 M) is saturated with H_2S . What is the minimum pH at which MS will precipitate? K_{sp} for MS = 6.0×10^{-21} , conc. of saturated H_2S = 0.1 M .

$$K_1 = 10^{-7} \text{ and } K_2 = 1.3 \times 10^{-13} \text{ for } \text{H}_2\text{S} \quad (\text{IIT 1993})$$

Solution: The minimum concentration of S^{2-} ions required to precipitate MS is,

$$[\text{S}^{2-}] = \frac{K_{sp} \text{ MS}}{[\text{M}^{2+}]} = \frac{6.0 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19} \text{ M}$$

H_2S ionises in solution in two steps:



$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = K_1 \quad \text{and} \quad \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = K_2$$

Hence, $K_1 K_2 = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$

or $[\text{H}^+]^2 = \frac{K_1 K_2 [\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{10^{-7} \times 1.3 \times 10^{-13} \times 0.1}{1.2 \times 10^{-19}}$

$$= 1.08 \times 10^{-2}$$

So, $[\text{H}^+] = 1.04 \times 10^{-1}$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.04 \times 10^{-1}) = 0.98$$

Example 51. The pH of blood stream is maintained by a proper balance of H_2CO_3 and NaHCO_3 concentrations. What volume of 5 M NaHCO_3 solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3 , in order to maintain a pH of 7.47? K_a for H_2CO_3 in blood is 7.8×10^{-7} . (IIT 1993)

Solution: Let $V \text{ mL}$ of 5 M NaHCO_3 solution be mixed.

$$\text{Total volume} = (V + 10) \text{ mL}$$

Conc. of H_2CO_3 and NaHCO_3 in the solution becomes

$$[\text{NaHCO}_3] = \frac{5 \times V}{(V + 10)} \text{ M}$$

and $[\text{H}_2\text{CO}_3] = \frac{2 \times 10}{(V + 10)} \text{ M}$

Now applying Henderson's equation,

$$\text{pH} = -\log K_a + \log \frac{[\text{NaHCO}_3]}{[\text{H}_2\text{CO}_3]}$$

$$7.4 = -\log 7.8 \times 10^{-7} + \log \frac{5 \times V}{(V + 10)} \times \frac{(V + 10)}{2 \times 10}$$

$$= -\log 7.8 \times 10^{-7} + \log \frac{V}{4}$$

or $\log \frac{V}{4} = 7.4 + \log 7.8 \times 10^{-7}$

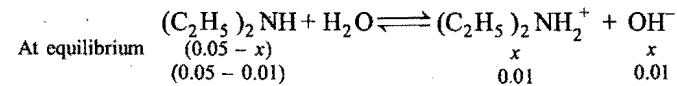
$$V = 78.32 \text{ mL}$$

Example 52. The pH of 0.05 M aqueous solution of diethylamine is 12. Calculate its K_b . (IIT 1993)

Solution: We know that, $\text{pH} + \text{pOH} = 14$

or $\text{pOH} = 14 - \text{pH} = 14 - 12 = 2$

So, $[\text{OH}^-] = 10^{-2}$



$$K_b = \frac{[(\text{C}_2\text{H}_5)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{C}_2\text{H}_5)_2\text{NH}]} = \frac{0.01 \times 0.01}{0.04} = 2.5 \times 10^{-3}$$

Example 53. 100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, vapour pressure of H_2O at 25°C is 23.7 mm .

Solution: Given, $V = 100 \text{ mL} = 0.1 \text{ L}$

$$P = \left(\frac{740 - 23.7}{760} \right) \text{ atm} = 0.9425 \text{ atm}$$

$$R = 0.0821$$

$$T = (25 + 273) \text{ K} = 298 \text{ K}$$

Applying, $PV = nRT$

or $n = \frac{PV}{RT} = \frac{0.9425 \times 0.1}{0.0821 \times 298} = 3.85 \times 10^{-3}$ mol

$$\text{Molarity} = \frac{n}{V} = \frac{3.85 \times 10^{-3}}{1} = 3.85 \times 10^{-3} M$$

HCl is a strong electrolyte. It is completely dissociated.

So, $[\text{H}^+] = 3.85 \times 10^{-3} M$

$$\text{pH} = -\log [\text{H}^+] = -\log 3.85 \times 10^{-3} = 2.4146$$

Example 54. Calculate the $[\text{Cl}^-]$, $[\text{Na}^+]$, $[\text{H}^+]$, $[\text{OH}^-]$ and pH of the resulting solution obtained by mixing 50 mL of 0.6 N HCl and 50 mL of 0.3 N NaOH.

Solution:	HCl	+	NaOH	\longrightarrow	NaCl	+ H ₂ O
Milli-equivalents	50 × 0.6		50 × 0.3		0	0
before reaction	= 30		= 15			
Milli-equivalents after reaction	(30 - 15)		0		15	15

$$\text{Total volume} = 50 + 50 = 100 \text{ mL}$$

$$[\text{Cl}^-] = \frac{15 + 15}{100} = 0.3 M$$

$$[\text{Na}^+] = \frac{15}{100} = 0.15 M$$

$$[\text{H}^+] = \frac{15}{100} = 0.15 M$$

$$[\text{OH}^-] = \frac{10^{-14}}{0.15} = 6.6 \times 10^{-14}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 0.15 = 0.8239$$

Example 55. What is the pH of a 1.0 M solution of acetic acid? To what volume of one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given, $K_a = 1.8 \times 10^{-5}$. (IIT 1990)

Solution: We know that degree of dissociation,

$$\begin{aligned}\alpha &= \sqrt{\frac{K_a}{C}} \\ &= \sqrt{\frac{1.8 \times 10^{-5}}{1}} \\ &= 4.2426 \times 10^{-3}\end{aligned}$$

$$[\text{H}^+] = C \times \alpha = 1 \times 4.2426 \times 10^{-3}$$

$$= 4.2426 \times 10^{-3} \text{ mol L}^{-1}$$

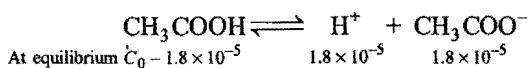
$$\text{pH} = -\log [\text{H}^+] = -\log 4.2426 \times 10^{-3} = 2.3724$$

So, pH of the acetic acid solution after dilution = 2×2.3724

$$= 4.7448$$

$$\text{New } [\text{H}^+] = 10^{-4.7448} = 1.8 \times 10^{-5}$$

Let the new concentration be C_0 .



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{(C_0 - 1.8 \times 10^{-5})} = 1.8 \times 10^{-5}$$

$$\text{So, } C_0 = 3.6 \times 10^{-5}$$

Let the new volume be V litre

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

$$V = \frac{1}{3.6 \times 10^{-5}} = 2.78 \times 10^4 \text{ litre}$$

Example 56. Calculate the change in pH of one litre buffer solution containing 0.10 mole each of NH₃ and NH₄Cl upon addition of (i) 0.02 mole of dissolved gaseous HCl, (ii) 0.02 mole of dissolved NaOH.

Assume no change in volume (K_b for NH₃ = 1.8×10^{-5}).

(IIT 1992)

Solution: pOH of NH₃ and NH₄Cl buffer

$$= -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.75$$

$$\text{pH} = (14 - 4.75) = 9.25$$

First case: NH₃ + HCl \longrightarrow NH₄Cl

$$[\text{Salt}] = (0.1 + 0.02) = 0.12 M$$

$$[\text{Base}] = (0.1 - 0.02) = 0.08 M$$

$$\text{pOH} = -\log K_b + \log \frac{0.12}{0.08}$$

$$= 4.75 + 0.176 = 4.926$$

$$\text{pH} = (14 - 4.926) = 9.074$$

$$\Delta \text{pH} = (9.25 - 9.074) = 0.176 \text{ pH unit}$$

Second case: NH₄Cl + NaOH \longrightarrow NH₃ + NaCl

$$[\text{Salt}] = (0.1 - 0.02) = 0.08 M$$

$$[\text{Base}] = (0.1 + 0.02) = 0.12 M$$

$$\text{pOH} = -\log K_b + \log \frac{0.08}{0.12}$$

$$= (4.75 - 0.176) = 4.576$$

$$\text{pH} = (14 - 4.574) = 9.426$$

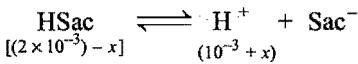
$$\Delta \text{pH} = (9.426 - 9.25) = 0.176 \text{ pH unit}$$

Example 57. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSac. A 4×10^{-4} mole amount of saccharin is dissolved in 200 cm³ water of pH = 3. Assuming no change in volume, calculate the concentration of Sac⁻ ions in the resulting solution at equilibrium. (IIT 1994)

Solution: Concentration of saccharin

$$= \frac{4 \times 10^{-4}}{200} \times 1000 = 2 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3} \text{ mol L}^{-1}$$



$$K_a = \frac{[\text{H}^+][\text{Sac}^-]}{[\text{HSac}]} = \frac{(10^{-3} + x)[\text{Sac}^-]}{[2 \times 10^{-3} - x]}$$

$$[\text{Sac}^-] = \frac{2 \times 10^{-12} \times (2 \times 10^{-3} - x)}{(10^{-3} + x)}$$

Since, x is very small, it can be neglected.

$$[\text{Sac}^-] = \frac{2 \times 10^{-12} \times 2 \times 10^{-3}}{10^{-3}} = 4 \times 10^{-12} \text{ mol L}^{-1}$$

Example 58. An aqueous solution contains 10% ammonia by mass and has a density 0.99 g cm^{-3} . Calculate hydroxyl and hydrogen ion concentration in this solution. (K_a for NH_4^+ $\approx 5.0 \times 10^{-10} \text{ M}$) (IIT 1995)

$$\begin{aligned} \text{Solution: Mass of 1 litre solution} &= 1000 \times 0.99 \text{ g} \\ &= 990 \text{ g} \end{aligned}$$

$$\text{NH}_3 \text{ present in } 990 \text{ g solution} = 99 \text{ g}$$

$$1 \text{ litre solution contains} = \frac{99}{17} = 5.8 \text{ mole}$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x \times x}{(5.8 - x)} \approx \frac{x^2}{5.8}$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5.0 \times 10^{-10}} = 2 \times 10^{-5}$$

$$\text{So, } 2 \times 10^{-5} = \frac{x^2}{5.8}$$

$$x^2 = 2 \times 10^{-5} \times 5.8$$

$$x = 1.078 \times 10^{-2} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = x = 1.078 \times 10^{-2} \text{ M}$$

$$[\text{H}^+] = \frac{10^{-14}}{1.078 \times 10^{-2}} = 9.27 \times 10^{-13} \text{ M}$$

Example 59. 0.15 mole of pyridinium chloride has been added into 500 cm^3 of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume.

$$(K_b \text{ for pyridine} = 1.5 \times 10^{-9} \text{ M})$$

(IIT 1995)

Solution: Concentration of pyridinium chloride

$$= 0.15 \times 2 = 0.3 \text{ M}$$

$$\text{pOH} = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$= \log \frac{0.3}{0.2} - \log 1.5 \times 10^{-9}$$

$$= 9$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9}$$

$$\text{pH} = (14 - \text{pOH}) = (14 - 9) = 5$$

Example 60. How many moles of acetic acid and sodium acetate each should be dissolved to prepare one litre of 0.063 molar buffer solution of pH 4.5?

$$(K_a \text{ for } \text{CH}_3\text{COOH} = 1.8 \times 10^{-5})$$

Solution: Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = 4.5 + \log 1.8 \times 10^{-5} = -0.2447$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \text{antilog} (-0.2447) = 0.5692$$

$$[\text{Salt}] = 0.5692 \times [\text{Acid}]$$

$$\text{Given: } [\text{Acid}] + [\text{Salt}] = 0.063$$

$$[\text{Acid}] = \frac{0.063}{1.5692} = 0.040 \text{ mol L}^{-1}$$

$$[\text{Salt}] = (0.063 - 0.040) = 0.023 \text{ mol L}^{-1}$$

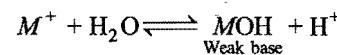
10.12 SALT HYDROLYSIS

Pure water is a weak electrolyte and neutral in nature, i.e., H^+ ion concentration is exactly equal to OH^- ion concentration

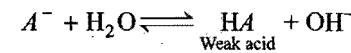
$$[\text{H}^+] = [\text{OH}^-]$$

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[\text{H}^+] > [\text{OH}^-]$, the water becomes acidic and when $[\text{H}^+] < [\text{OH}^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as salt hydrolysis. It is defined as a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.



In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.



The process of hydrolysis is actually the reverse of neutralisation.



If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.

Examples: FeCl_3 , CuCl_2 , AlCl_3 , NH_4Cl , CuSO_4 , etc.

(ii) Salt of a strong base and a weak acid.

Examples: CH_3COONa , NaCN , NaHCO_3 , Na_2CO_3 , etc.

(iii) Salt of a weak acid and a weak base.

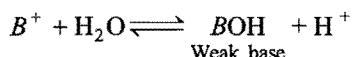
Examples: $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{CO}_3$, NH_4HCO_3 , etc.

(iv) Salt of a strong acid and a strong base.

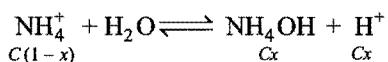
Examples: NaCl , K_2SO_4 , NaNO_3 , NaBr , etc.

1. Salt of a strong acid and a weak base

The solution of such a salt is acidic in nature. The cation of the salt which has come from weak base is reactive. It reacts with water to form a weak base and H^+ ions.



Consider, for example, NH_4Cl . It ionises in water completely into NH_4^+ and Cl^- ions. NH_4^+ ions react with water to form a weak base (NH_4OH) and H^+ ions.



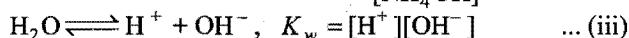
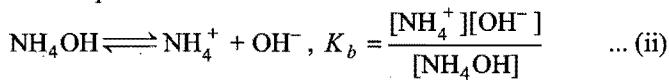
Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$$K_h = \frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{Cx \cdot Cx}{C(1-x)} = \frac{x^2 C}{(1-x)} \quad \dots (\text{i})$$

where, C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are



From eqs. (ii) and (iii),

$$\frac{K_w}{K_b} = \frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = K_h \quad \dots (\text{iv})$$

$$[\text{H}^+] = \frac{K_h[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{K_w}{K_b} \times \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\log [\text{H}^+] = \log K_w - \log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$-\text{pH} = -\text{p}K_w + \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{p}K_w - \text{pH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Relation between Hydrolysis Constant and Degree of Hydrolysis

The extent to which hydrolysis proceeds is expressed as degree of hydrolysis and is defined as the fraction of one mole of

the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as h or x .

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Considering again eq. (i),

$$K_h = \frac{x^2 C}{(1-x)} \quad \text{or} \quad K_h = \frac{h^2 C}{(1-h)}$$

When h is very small ($1-h$) $\rightarrow 1$,

$$h^2 = K_h \times \frac{1}{C}$$

or

$$h = \sqrt{\frac{K_h}{C}}$$

$$= \sqrt{\frac{K_w}{K_b \times C}}$$

$$[\text{H}^+] = h \times C = \sqrt{\frac{C \times K_w}{K_b}}$$

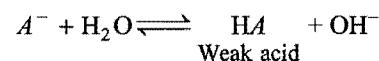
$$\log [\text{H}^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_b$$

$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \log C - \frac{1}{2} \text{p}K_b$$

$$= 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

2. Salt of a weak acid and a strong base

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a weak acid and OH^- ions.



Consider, for example, the salt CH_3COONa . It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a weak acid, CH_3COOH and OH^- ions.

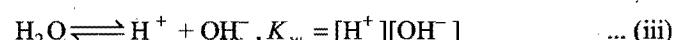
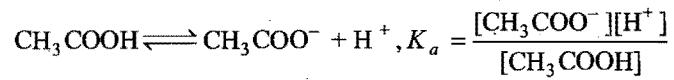


Thus, OH^- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{Cx \times Cx}{C(1-x)} = \frac{Cx^2}{(1-x)} \quad \dots (\text{i})$$

Other equilibria present in the solution are:



From eqs. (ii) and (iii),

$$\frac{K_w}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = K_h \quad \dots (\text{iv})$$

$$[\text{OH}^-] = \frac{K_h[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{K_w}{K_a} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\log [\text{OH}^-] = \log K_w - \log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$-\text{pOH} = -\text{p}K_w + \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{p}K_w - \text{pOH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Considering eq. (i) again,

$$K_h = \frac{Cx^2}{(1-x)} \text{ or } K_h = \frac{Ch^2}{(1-h)}$$

When h is very small, $(1-h) \rightarrow 1$

$$\text{or } h^2 = \frac{K_h}{C}$$

$$\text{or } h = \sqrt{\frac{K_h}{C}}$$

$$[\text{OH}^-] = h \times C = \sqrt{CK_h} = \sqrt{\frac{C \times K_w}{K_a}}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$= \frac{K_w}{\sqrt{\frac{C \times K_w}{K_a}}} = \sqrt{\frac{K_a \times K_w}{C}}$$

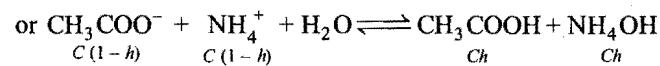
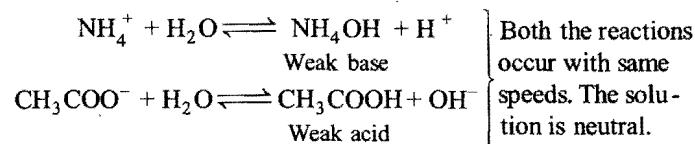
$$-\log [\text{H}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log C$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

$$= 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

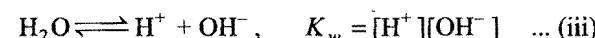
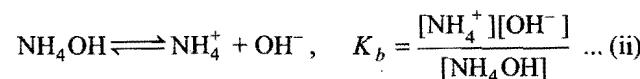
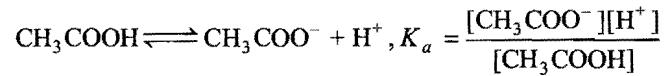
3. Salt of a weak acid and a weak base

Maximum hydrolysis occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H^+ and OH^- ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt $\text{CH}_3\text{COONH}_4$. It gives CH_3COO^- and NH_4^+ ions in solution. Both react with water.



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]}$$

Other equilibria which exist in solution are:



From eqs. (i), (ii) and (iii),

$$K_h = \frac{K_w}{K_a \cdot K_b} = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad \dots (\text{iv})$$

Let C be the concentration and h be the degree of hydrolysis

$$K_h = \frac{h^2}{(1-h)^2}$$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$[\text{H}^+] = K_a \times h$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$= \sqrt{\frac{K_a \times K_w}{K_b}}$$

$$-\log [\text{H}^+] = -\frac{1}{2} \log K_a - \frac{1}{2} \log K_w + \frac{1}{2} \log K_b$$

$$\text{pH} = \frac{1}{2} \text{p}K_a + \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b$$

$$= 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

When $\text{p}K_a = \text{p}K_b$, $\text{pH} = 7$, i.e., solution will be neutral in nature.

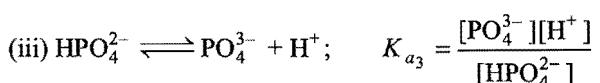
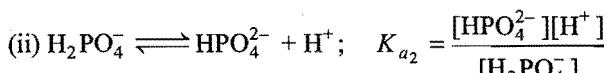
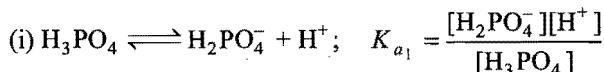
When $\text{p}K_a > \text{p}K_b$, the solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case $\text{p}K_a < \text{p}K_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7.

4. Salt of a strong acid and a strong base

Such a salt, say NaCl, does not undergo hydrolysis as both the ions are not reactive. The solution is thus, neutral in nature.

5. Hydrolysis of amphiprotic anion

Let us consider hydrolysis of amphiprotic anion only, i.e., when counter cation is not hydrolysed example of some salts of this category are NaHCO_3 , NaHS , Na_2HPO_4 , NaH_2PO_4 .



Here, H_2PO_4^- and HPO_4^{2-} are amphiprotic anions, pH after their hydrolysis can be calculated as,

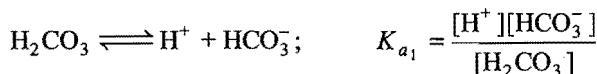
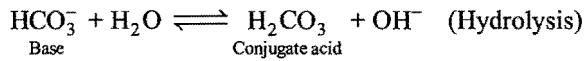
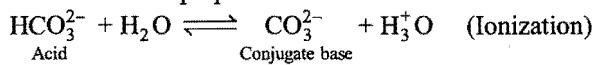
$$\text{pH of H}_2\text{PO}_4^- \text{ in aqueous medium} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$$

$$\text{pH of HPO}_4^{2-} \text{ in aqueous medium} = \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2}$$

Here, HPO_4^{2-} is conjugate base of H_2PO_4^- and H_3PO_4 is conjugate acid of H_2PO_4^- .

Similarly, PO_4^{3-} is conjugate base of HPO_4^{2-} and HPO_4^{2-} is conjugate acid of PO_4^{3-} .

(iv) Let us consider amphiprotic bicarbonate anion.



pH of HCO_3^- ion after hydrolysis in aqueous medium

$$= \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$$

(v) Let us consider the hydrolysis of amphiprotic anion along with cation, e.g., NH_4HCO_3 , NH_4HS .

In above examples both cations and anions are derived from weak base and weak acids respectively, hence both will undergo hydrolysis in aqueous medium.

When these salts are dissolved in water, $[\text{H}_3\text{O}^+]$ concentration can be determined as,

$$[\text{H}_3\text{O}^+] = \sqrt{K_{a_1} \left[\frac{K_w}{K_b} + K_{a_2} \right]}$$

$$\text{pH} = -\log \sqrt{K_{a_1} \left[\frac{K_w}{K_b} + K_{a_2} \right]}$$

Table 10.1 Hydrolysis at a Glance

Salt	Nature	Degree	Hydrolysis Constant	pH
1. NaCl (Strong acid + Strong base)	Neutral	No hydrolysis	—	—
2. CH_3COONa (Weak acid + Strong base)	Basic	$h = \sqrt{\frac{K_w}{CK_a}}$	$K_h = \frac{K_w}{K_a}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$
3. NH_4Cl (Strong acid + Weak base)	Acidic	$h = \sqrt{\frac{K_w}{CK_b}}$	$K_h = \frac{K_w}{K_b}$	$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$
4. $\text{CH}_3\text{COONH}_4$ (Weak acid + Weak base)	*	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$K_h = \frac{K_w}{K_a \times K_b}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$

*In the case of salt of weak acid and weak base, nature of medium after hydrolysis is decided in the following manner:

(i) If $K_a = K_b$, the medium will be neutral.

(ii) If $K_a > K_b$, the medium will be acidic.

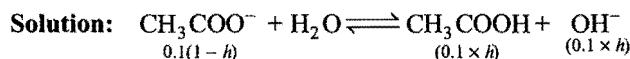
(iii) If $K_a < K_b$, the medium will be basic.

The degree of hydrolysis of salts of weak acids and weak bases is unaffected by dilution because there is no concentration term in the expression of degree of hydrolysis.

[Note: Degree of hydrolysis always increases with increase in temperature because at elevated temperature increase in K_w is greater as compared to K_a and K_b .]

SOME SOLVED EXAMPLES

Example 61. Calculate the degree of hydrolysis and pH of 0.1 M sodium acetate solution. Hydrolysis constant of sodium acetate is 5.6×10^{-10} .



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(0.1 \times h)(0.1 \times h)}{0.1(1-h)}$$

$$h \text{ is small } (1-h) \longrightarrow 1$$

$$5.6 \times 10^{-10} = 0.1 \times h^2$$

$$\text{or } h^2 = \frac{5.6 \times 10^{-10}}{0.1} = 56 \times 10^{-10}$$

$$h = 7.48 \times 10^{-5}$$

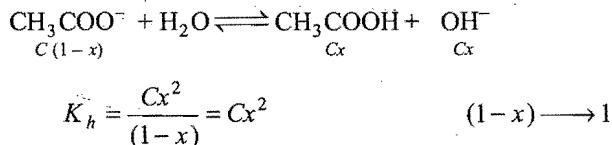
$$[\text{OH}^-] = Ch = 0.1 \times 7.48 \times 10^{-5} = 7.48 \times 10^{-6} \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{7.48 \times 10^{-6}} = 1.33 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.33 \times 10^{-9}) = 8.88$$

Example 62. When 0.2 M acetic acid is neutralised with 0.2 M NaOH in 0.5 litre of water the resulting solution is slightly alkaline. Calculate the pH of the resulting solution. K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$.

Solution: 0.2 M acetic acid will form 0.2 M CH_3COONa in 0.5 litre of water. Hence, concentration of sodium acetate, $[\text{CH}_3\text{COONa}] = 0.1 \text{ mol L}^{-1}$.



$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\text{So, } K_h = Cx^2 = 5.5 \times 10^{-10}$$

$$\text{or } x^2 = \frac{5.5 \times 10^{-10}}{0.1} = 55 \times 10^{-10}$$

$$\text{or } x = 7.42 \times 10^{-5}$$

$$[\text{OH}^-] = Cx = 7.42 \times 10^{-5} \times 0.1 = 7.42 \times 10^{-6} \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{7.42 \times 10^{-6}} = 1.3477 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.3477 \times 10^{-9}) = 8.87$$

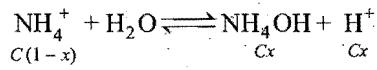
Example 63. Calculate the hydrolysis constant for NH_4Cl , pH value and $[\text{OH}^-]$ in 0.1 M NH_4Cl solution.

$$(K_{\text{NH}_4\text{OH}} = 1.75 \times 10^{-5}, K_w = 1 \times 10^{-14})$$

Solution: We know that, $K_h = \frac{K_w}{K_b}$

$$\text{So, } K_h = \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Hydrolysis of NH_4Cl can be represented as,



$$\text{Thus, } K_h = \frac{Cx^2}{(1-x)}$$

Neglecting 'x' in denominator,

$$x^2 = \frac{K_h}{C} = \frac{5.7 \times 10^{-10}}{0.1} = 57 \times 10^{-10}$$

$$\text{or } x = 7.55 \times 10^{-5}$$

$$[\text{H}^+] = Cx = 0.1 \times 7.55 \times 10^{-5} = 7.55 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (7.55 \times 10^{-6}) = 5.12$$

$$\text{Again, } [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{7.55 \times 10^{-6}} = 1.32 \times 10^{-9} \text{ M}$$

Example 64. Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M sodium hydroxide.

$$K_a \text{ for acetic acid} = 1.9 \times 10^{-5}$$

(IIT 1990)

Solution: Concentration of sodium acetate $= \frac{0.1}{2} = 0.05 \text{ M}$ as equal volumes of the acid and the base will be used.

The equilibrium is,



where, x is the degree of hydrolysis, and

$$K_h = \frac{Cx^2}{(1-x)}$$

We know that,

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$\text{So, } K_h = Cx^2 \text{ as } (1-x) \longrightarrow 1$$

$$5.26 \times 10^{-10} = 0.05 \times x^2$$

$$\text{or } x^2 = \frac{5.26 \times 10^{-10}}{0.05} = 1.05 \times 10^{-8}$$

$$\text{or } x = 1.025 \times 10^{-4}$$

$$[\text{OH}^-] = Cx = 1.025 \times 10^{-4} \times 0.05 = 5.125 \times 10^{-6} \text{ M}$$

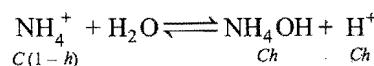
$$[\text{H}^+] = \frac{1 \times 10^{-14}}{5.125 \times 10^{-6}} = 1.95 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.95 \times 10^{-9}) = 8.71$$

Example 65. Calculate the amount of ammonium chloride required to dissolve in 500 mL water to have pH = 4.5. (K_b for NH_4OH is 1.8×10^{-5})

$$\text{Solution: } [\text{H}^+] = 10^{-\text{pH}} = 10^{-4.5} = 10^{-5} \text{ antilog } 0.5 \\ = 3.162 \times 10^{-5} \text{ M}$$

Let C be the concentration of NH_4Cl



If h is small, then

$$K_h = Ch^2 \qquad \left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10} \right]$$

$$h = \frac{K_h}{Ch} = \frac{K_h}{[\text{H}^+]}$$

$$= \frac{5.5 \times 10^{-10}}{3.162 \times 10^{-5}} = 1.739 \times 10^{-5}$$

$$Ch = [\text{H}^+]$$

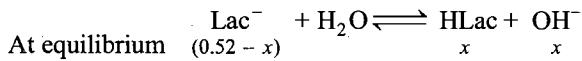
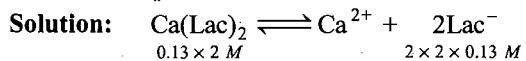
$$C = \frac{[\text{H}^+]}{h} = \frac{3.162 \times 10^{-5}}{1.739 \times 10^{-5}} = 1.8 \text{ mol L}^{-1}$$

$$500 \text{ mL of water contains} = \frac{1.8}{2} = 0.9 \text{ mole}$$

$$\text{Mass in g} = 0.9 \times 53.5 = 48.15 \text{ g}$$

Example 66. Calcium lactate is a salt of a weak organic acid and represented as $\text{Ca}(\text{Lac})_2$. A saturated solution of

$\text{Ca}(\text{Lac})_2$ contains 0.13 mole of this salt in 0.50 litre solution. The $p\text{OH}$ of this solution is 5.60. Assuming a complete dissociation of salt, calculate K_a of the lactic acid. (IIT 1991)



$$K_h = \frac{x^2}{(0.52 - x)} = \frac{x^2}{0.52} \text{ as } x \text{ is small}$$

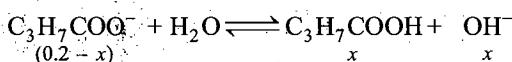
$$[\text{OH}^-] = 10^{-5.6} = 2.51 \times 10^{-6} = x$$

$$K_h = \frac{2.51 \times 10^{-6} \times 2.51 \times 10^{-6}}{0.52} = 12.12 \times 10^{-12}$$

$$K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{12.12 \times 10^{-12}} = 8.26 \times 10^{-4}$$

Example 67. K_a for butyric acid is 2×10^{-5} . Calculate pH and hydroxyl ion concentration of 0.2 M aqueous solution of sodium butyrate. (IIT 1994)

Solution: Butyrate ion hydrolysis in solution into butyric acid and OH^- ions. Let x mole of butyrate ion be hydrolysed.



$$K_h = \frac{x^2}{(0.2 - x)} = \frac{x^2}{0.2} \quad (\text{x being small is neglected as compared to 0.2})$$

So,

$$K_h = \frac{K_w}{K_a}$$

$$\frac{K_w}{K_a} = \frac{x^2}{0.2}$$

$$\frac{10^{-14}}{2 \times 10^{-5}} = \frac{x^2}{0.2}$$

or

$$x^2 = 10^{-10} \text{ or } x = 10^{-5} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 10^{-5} M$$

$$[\text{H}^+] = \frac{10^{-14}}{10^{-5}} = 10^{-9} M$$

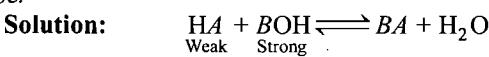
$$\text{pH} = -\log [10^{-9}] = 9$$

Example 68. Calculate the pH of an aqueous solution of 1.0M ammonium formate assuming complete dissociation. pK_a for formic acid = 3.8 and pK_b of ammonia = 4.8. (IIT 1995)

Solution: Ammonium formate is a salt of weak acid and weak base. Hence,

$$\begin{aligned} \text{pH} &= 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b \\ &= 7 + (1/2) \times 3.8 - (1/2) \times 4.8 \\ &= 7 + 1.9 - 2.4 \\ &= 6.5 \end{aligned}$$

Example 69. A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base. (IIT 1991)



$$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]}$$

In the above reaction,

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

So, $K = \frac{1}{K_h}$

We know that, $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0 \times 10^{-4}} = 10^{-10}$

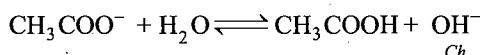
$$K = \frac{1}{10^{-10}} = 10^{10}$$

Example 70. Calculate for 0.01 N solution of sodium acetate:

(a) Hydrolysis constant, (b) degree of hydrolysis, (c) pH. (Given, $K_a = 1.9 \times 10^{-5}$) (MLNR 1991)

Solution: $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-4}$$

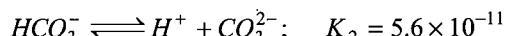


$$\begin{aligned} [\text{OH}^-] &= C \times h = 0.01 \times 2.29 \times 10^{-4} \\ &= 2.29 \times 10^{-6} M \end{aligned}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{2.29 \times 10^{-6}} = 4.37 \times 10^{-9} M$$

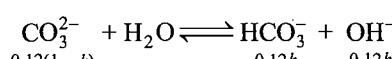
$$\text{pH} = -\log [\text{H}^+] = -\log (4.37 \times 10^{-9}) = 8.36$$

Example 71. H_2CO_3 ionises as,



Calculate the degree of hydrolysis and pH value of 0.12 M Na_2CO_3 solution.

Solution: Na_2CO_3 is a salt of strong base and weak acid. Thus, CO_3^{2-} ion is hydrolysed.



$$K_h = h^2 C$$

or

$$h^2 = \frac{K_h}{C} = \frac{K_h}{0.12}$$

We know that, $K_h = \frac{K_w}{K_a} = \frac{K_w}{K_2} = \frac{10^{-14}}{5.6 \times 10^{-11}} = 1.7857 \times 10^{-4}$

So, $h^2 = \frac{1.7857 \times 10^{-4}}{0.12} = 14.88 \times 10^{-4}$
 $h = 3.85 \times 10^{-2}$

$$[\text{OH}^-] = C \times h = 0.12 \times 3.85 \times 10^{-2} = 0.462 \times 10^{-2} = 4.62 \times 10^{-3}$$

$$[\text{H}^+] = \frac{10^{-14}}{4.62 \times 10^{-3}} = 2.164 \times 10^{-12} M$$

$$\text{pH} = -\log [\text{H}^+] = -\log (2.164 \times 10^{-12}) = 11.665$$

Example 72. How much must a 0.2 M solution of sodium acetate be diluted at 25°C in order to double the degree of hydrolysis?

Solution: Let h be the initial degree of hydrolysis

$$K_h = Ch^2 = 0.2 \times h^2 \quad \dots (\text{i})$$

Let the concentration be C_1 when degree of hydrolysis is $2h$.

$$K_h = C_1(2h)^2 \quad \dots (\text{ii})$$

Dividing both the equations,

$$1 = \frac{0.2 \times (h^2)}{4C_1 \times (h)^2}$$

$$C_1 = \frac{0.2}{4} = 0.05 M$$

Applying,

$$M_1V_1 = M_2V_2$$

$$0.2V_1 = 0.05 \times V_2$$

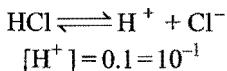
$$V_2 = \frac{0.2}{0.05} V_1 = 4V_1$$

The solution be diluted four times.

Example 73. Calculate change in pH upon ten-fold dilution of the following solutions:

- (a) 0.1 HCl (b) 0.1 M acetic acid (c) 0.1 M NH_4Cl
 $K_a \text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$, $K_b \text{NH}_3 = 1.8 \times 10^{-5}$

Solution: (a) HCl is a strong acid. It is completely ionised in solution.



$$\text{pH} = -\log [\text{H}^+] = -\log (10^{-1}) = 1$$

After dilution, $[\text{H}^+] = 0.01 = 10^{-2} M$

$$\text{pH} = -\log [\text{H}^+] = -\log 10^{-2} = 2$$

pH change from 1 to 2.

- (b) $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
 $(0.1-x) \qquad \qquad \qquad x \qquad \qquad \qquad x$
 $(\text{CH}_3\text{COOH} \text{ is a weak acid})$

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5} \text{ or } x^2 = 1.8 \times 10^{-6} \text{ or } x = 1.34 \times 10^{-3}$$

$$\text{pH} = -\log x = -\log (1.34 \times 10^{-3}) = 2.87$$

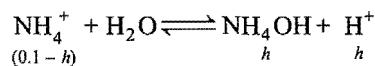
After dilution,

$$\frac{x_1^2}{0.01} = 1.8 \times 10^{-5} \text{ or } x_1^2 = 18 \times 10^{-8} \text{ or } x_1 = 4.24 \times 10^{-4} M$$

$$\text{pH} = -\log x = -\log 4.24 \times 10^{-4} = 3.37$$

pH change from 2.87 to 3.37.

(c) NH_4Cl is a salt of weak base and strong acid.



$$\frac{h^2}{0.1} = K_h \quad \text{or} \quad h^2 = 0.1 \times K_h$$

$$\left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10} \right]$$

$$= 0.1 \times 5.55 \times 10^{-10}$$

$$h = 7.45 \times 10^{-6} = [\text{H}^+]$$

$$\text{pH} = -\log (7.45 \times 10^{-6}) = 5.128$$

After dilution, $h^2 = 0.01 \times K_h = 0.01 \times 5.55 \times 10^{-10}$

$$h = 2.35 \times 10^{-6}$$

$$\text{pH} = -\log 2.35 \times 10^{-6} = 5.627$$

pH change from 5.128 to 5.627.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. The pH of a solution obtained by mixing 100 mL of 0.2 M CH_3COOH with 100 mL of 0.2 M NaOH would be:

(Given: $\text{p}K_a$ for $\text{CH}_3\text{COOH} = 4.74$)

- (a) 4.74 (b) 8.87 (c) 9.10 (d) 8.57

[Ans. (b)]

Hint: Concentration of salt formed will be 0.1 M.



$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

$$= \frac{1}{2} [14 + 4.74 - 1] = 8.87$$

35. The pH of 0.02 M NH_4Cl (aq.) ($\text{p}K_b = 4.73$) is equal to:

- (a) 3.78 (b) 4.73 (c) 5.48 (d) 7.00

[Ans. (c)]

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$$

$$= \frac{1}{2} [14 - 4.73 - \log 0.02]$$

$$= \frac{1}{2} [14 - 4.73 + 1.698] = 5.48$$

36. pH of 0.05 M $(\text{CH}_3\text{COO})_2\text{Ca}$ ($\text{p}K_a = 4.74$) is:

- (a) 8.72 (b) 8.87 (c) 7 (d) 1.30

[Ans. (b)]

Hint: $[\text{CH}_3\text{COO}^-] = 2 \times 0.05 = 0.1$

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

$$= \frac{1}{2} [14 + 4.74 + \log 0.1]$$

$$[\text{H}_3\text{O}^+] = K_{\text{In}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

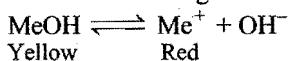
$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} [K_{\text{In}}] - \log_{10} \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]} \quad (\text{Henderson's equation for indicator})$$

At equivalence point:

$$[\text{In}^-] = [\text{HIn}] \quad \text{and} \quad \text{pH} = \text{p}K_{\text{In}}$$

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionised in solution to give Me^+ and OH^- ions.



Applying law of mass action,

$$K = \frac{[\text{Me}^+][\text{OH}^-]}{[\text{MeOH}]}$$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, i.e., yellow.

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

2. Quinonoid theory: According to this theory:

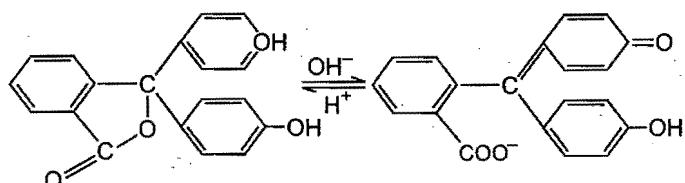
(a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed **benzenoid form** and the other **quinonoid form**.



(b) The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other.

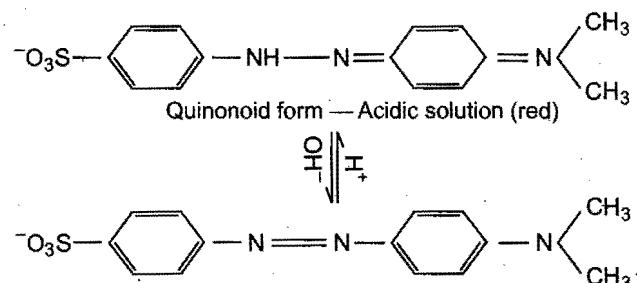
(c) One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The colour of benzenoid form is yellow while that of quinonoid form is red.



Selection of suitable indicator or choice of indicator

The neutralisation reactions are of the following four types:

- A strong acid versus a strong base. [Fig. 10.1 (a)]
- A weak acid versus a strong base. [Fig. 10.1 (b)]
- A strong acid versus a weak base. [Fig. 10.1 (c)]
- A weak acid versus a weak base. [Fig. 10.1 (d)]

In order to choose a suitable indicator, it is necessary to understand the pH changes in the above four types of titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or titration curve. The titration curves of the above four types of neutralisation reactions are shown in Fig. 10.1 (a), 10.1 (b), 10.1 (c) and 10.1 (d).

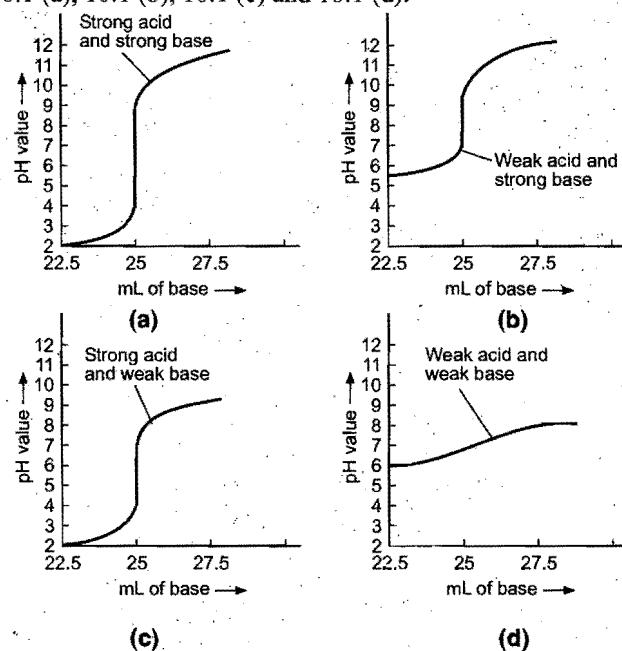


Fig. 10.1

In each case 25 mL of the acid ($N/10$) has been titrated against a standard solution of a base ($N/10$). Each curve becomes almost vertical for some distance [except curve Fig. 10.1 (d)] and then bends away again. This region of abrupt change in pH indicates

the equivalence point. For a particular titration, the indicator should be so selected that it changes its colour within vertical distance of the curve.

(i) Strong acid vs. strong base: pH curve of strong acid (say HCl) and strong base (say NaOH) is vertical over almost the pH range 4–10. So, the indicators phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4–6.5) and methyl orange (pH range 3.2–4.5) are suitable for such a titration.

(ii) Weak acid vs. strong base: pH curve of weak acid (say CH₃COOH or oxalic acid) and strong base (say NaOH) is

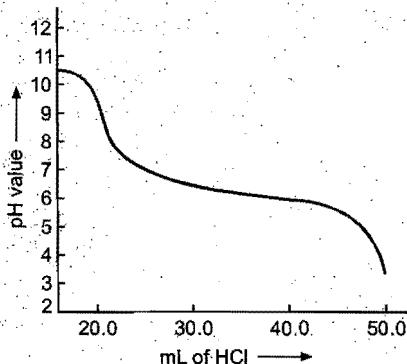


Fig. 10.2

vertical over the approximate pH range 7 to 11. So, phenolphthalein is the suitable indicator for such a titration.

(iii) Strong acid vs. weak base: pH curve of strong acid (say HCl or H₂SO₄ or HNO₃) with a weak base (say NH₄OH) is vertical over the pH range of 4 to 7. So, the indicators methyl red and methyl orange are suitable for such a titration.

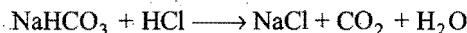
(iv) Weak acid vs. weak base: pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable indicator can be used for such a titration.

Titration of soluble carbonate with strong acid.

pH curve of sodium carbonate with HCl shows two inflection points (Fig. 10.2). First inflection point (pH = 8.5) indicates conversion of carbonate into bicarbonate.



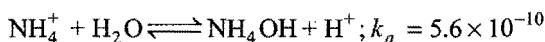
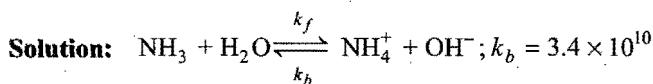
As the inflection point lies in the pH range 8 to 10, phenolphthalein can be used to indicate the above conversion. The second inflection point (pH = 4.3) indicates the following reaction:



As the point lies between 3 to 5, methyl orange can be used.

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. Ionisation constant of NH₄⁺ in water is 5.6 × 10⁻¹⁰ at 25°C. The rate constant for reaction of NH₄⁺ and OH⁻ to form NH₃ and H₂O at 25°C is 3.4 × 10¹⁰ litre mol⁻¹ sec⁻¹. Calculate rate constant for proton transfer from water to NH₃. (IIT 1996)



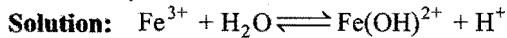
$$K_{\text{Base}} = \frac{k_f}{k_b} = \frac{K_w}{K_{\text{Acid}}} \quad \dots (\text{i})$$

$$K_{\text{Acid}} \times K_{\text{Base}} = K_w \quad \dots (\text{ii})$$

$$\frac{k_f}{3.4 \times 10^{10}} = \frac{10^{-14}}{5.6 \times 10^{-10}}$$

$$k_f = 6.07 \times 10^5$$

Example 2. K_a for the acid ionisation constant of Fe³⁺ to Fe(OH)₂²⁺ and H⁺ is 6.5 × 10⁻³. What is the maximum pH value which could be used so that at least 95% of total Fe³⁺ ion in solution exists free?



$$K = \frac{[\text{Fe(OH)}_2^{2+}][\text{H}^+]}{[\text{Fe}^{3+}]} = \frac{\frac{5}{100} \times [\text{H}^+]}{\frac{95}{100}} = 6.5 \times 10^{-3}$$

$$[\text{H}^+] = 0.12 \text{ M}$$

$$\text{pH} = -\log 0.12 = 0.91$$

Example 3. K_a for ascorbic acid (HAsc) is 5 × 10⁻⁵. Calculate the hydrogen ion concentration and percentage hydrolysis in an aqueous solution in which the concentration of Asc⁻ ions is 0.02 M. (IIT 1997)

Solution:

$$\begin{aligned} \text{Degree of hydrolysis } 'h' &= \sqrt{\frac{K_w}{CK_a}} \\ &= \sqrt{\frac{10^{-14}}{0.02 \times 5 \times 10^{-5}}} = 10^{-4} \end{aligned}$$

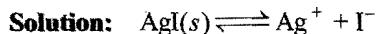
$$\% \text{ hydrolysis} = 0.01$$

$$\begin{aligned} \text{pH} &= \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C] \\ &= \frac{1}{2} [14 + (-\log 5 \times 10^{-5}) + \log 0.02] \end{aligned}$$

$$\text{pH} = 8.3$$

$$[\text{H}^+] = 5 \times 10^{-9} \text{ M}$$

Example 4. Determine the number of moles of AgI which may be dissolved in 1 litre of 1M CN⁻ solution K_{sp} for AgI and K_c for Ag₂(CN)₂⁻ are 1.2 × 10⁻¹⁷ M² and 7.1 × 10¹⁹ M⁻² respectively. (IIT 1998)



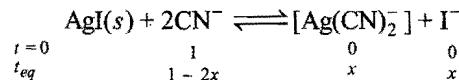
$$K_{sp} = [\text{Ag}^+][\text{I}^-] = 1.2 \times 10^{-17}$$



$$K_f = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 7.1 \times 10^{19}$$

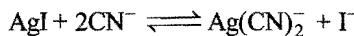
$$K_{eq} = K_{sp} \times K_f \\ = \frac{[\text{Ag}(\text{CN})_2^-][\text{I}^-]}{[\text{CN}^-]^2} = 1.2 \times 10^{-7} \times 7.1 \times 10^{19} \\ = 8.52 \times 10^2$$

Let us consider the following equilibrium:



Let 'x' moles of AgI be dissolved in CN^- solution.

Then,



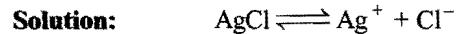
$$K_{eq} = 8.5 \times 10^2 = \frac{x \times x}{(1-2x)^2}$$

$$\frac{x}{1-2x} = 29.2$$

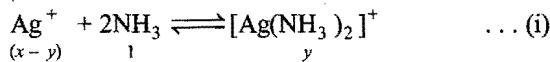
$$x = 0.49 \text{ mole}$$

Example 5. Given $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$, $K_c = 6.2 \times 10^{-8}$ and K_{sp} of AgCl is 1.8×10^{-10} at 298 K.

Calculate concentration of the complex in 1M aqueous ammonia. (IIT 1998)



On adding ammonia solution, complex formation takes place.



where,

x = solubility of AgCl in NH_3

y = amount of complex formed

$$K_{sp} \text{ of } \text{AgCl} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.8 \times 10^{-10} = (x - y) \times x \quad \dots (ii)$$

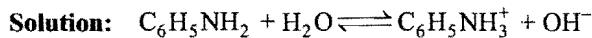
$$K_c \text{ for equation (i)} = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$\frac{1}{6.2 \times 10^{-8}} = \frac{y}{(x-y)^2} \quad \dots (iii)$$

On solving equations (ii) and (iii), we get

$$y = 0.0539 \text{ M}$$

Example 6. An aqueous solution of aniline of concentration 0.24 is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at $1 \times 10^{-8} \text{ M}$? K_a for $\text{C}_6\text{H}_5\text{NH}_3^+$ is $2.4 \times 10^{-5} \text{ M}$. (IIT 1996)



$$\text{Thus, } K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} \quad \dots (i)$$

Also K_b for

$$\text{C}_6\text{H}_5\text{NH}_2 = \frac{K_w}{K_a \text{ for } \text{C}_6\text{H}_5\text{NH}_3^+} = \frac{10^{-14}}{2.4 \times 10^{-5}} \quad \dots (ii)$$

Since, dissociation of $\text{C}_6\text{H}_5\text{NH}_2$ occurs in presence of NaOH and thus dissociation of $\text{C}_6\text{H}_5\text{NH}_2$ will be suppressed.

$$\text{Thus, } [\text{OH}^-] = ? ; [\text{C}_6\text{H}_5\text{NH}_2] = 0.24 ; [\text{C}_6\text{H}_5\text{NH}_3^+] = 10^{-8}$$

$$\text{Therefore, } \frac{10^{-14}}{2.4 \times 10^{-5}} = \frac{10^{-8} \times [\text{OH}^-]}{0.24}$$

$$\therefore [\text{OH}^-] = \frac{0.24 \times 10^{-14}}{2.4 \times 10^{-5} \times 10^{-8}} = 0.01$$

$$[\text{NaOH}] = 0.01 \text{ M}$$

Example 7. A solution contains $0.05 \text{ mol litre}^{-1}$ of Ba^{2+} ions and $0.002 \text{ mol litre}^{-1}$ of Ag^+ ions. The metals are to be precipitated by addition of chromate ions, CrO_4^{2-} . Which ion precipitates first? What percentage of this ion remain in the solution when the second ion begins to precipitate?

$$K_{sp} \text{ Ag}_2\text{CrO}_4 = 3 \times 10^{-12}, \quad K_{sp} \text{ BaCrO}_4 = 1 \times 10^{-10}$$

Solution: CrO_4^{2-} ion concentration required for precipitation:

For BaCrO_4 :

$$[\text{CrO}_4^{2-}] = \frac{K_{sp} \text{ BaCrO}_4}{[\text{Ba}^{2+}]} = \frac{10^{-10}}{0.05} = 20 \times 10^{-10} \text{ M}$$

For Ag_2CrO_4 :

$$[\text{CrO}_4^{2-}] = \frac{K_{sp} \text{ Ag}_2\text{CrO}_4}{[\text{Ag}^+]^2} = \frac{3 \times 10^{-12}}{[0.002]^2} = 0.75 \times 10^{-6} \text{ M}$$

Ba^{2+} will be precipitated first because it requires low concentration of CrO_4^{2-} . Remaining conc. of Ba^{2+} when Ag^+ will start precipitation.

$$[\text{Ba}^{2+}]_{\text{Remaining}} = \frac{K_{sp} \text{ BaCrO}_4}{[\text{CrO}_4^{2-}]} = \frac{10^{-10}}{0.75 \times 10^{-6}} = 1.33 \times 10^{-4} \text{ M}$$

$$\% \text{ of remaining } \text{Ba}^{2+} = \frac{1.33 \times 10^{-4}}{0.05} \times 100 = 0.26\%$$

Example 8. Calculate pH change which results when 50 mL of 0.1 M HNO_3 is added to each of the following at 25°C :

(a) 1.00 litre of pure water.

(b) 1.00 litre of a solution containing acetic acid and sodium acetate each of 0.1 M concentration.

Solution:

(a) Molarity after dilution = M_2

$$M_1 V_1 = M_2 V_2$$

$$0.1 \times 50 = M_2 \times 1050$$

$$M_2 = 0.00476$$

$$\text{pH} = -\log(0.00476) = 2.322$$

Change in pH of water = $7 - 2.322 = 4.68$

$$(b) \quad \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ = 4.7447 + \log \frac{0.1}{0.1} = 4.7447$$

Moles of HNO_3 added = $\frac{0.1}{1000} \times 50 = 5 \times 10^{-3}$; it will convert sodium acetate to acetic acid.

$$\text{pH} = 4.7447 + \log \left[\frac{0.1 - 5 \times 10^{-3}}{0.1 + 5 \times 10^{-3}} \right] = 4.70123$$

Change in pH = $4.7447 - 4.70123 = 0.043$

Example 9. A certain monoprotic acid (weak) serves as indicator. Assuming that colour change is seen when 1/3rd of the indicator has been converted to ions and that at end point the pH of solution is 6, what is the value of $\text{p}K_{\text{In}}$?

Solution: $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$ (Ionization equilibrium of indicator)

$$\begin{aligned} \text{pH} &= \text{p}K_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]} \\ 6 &= \text{p}K_{\text{In}} + \log_{10} \left[\frac{0.33}{0.67} \right] \text{ (1/3rd conversion)} \end{aligned}$$

$$\text{p}K_{\text{In}} = 6.307$$

Example 10. What is the minimum pH of a solution 0.10 M in Mg^{2+} from which $\text{Mg}(\text{OH})_2$ will not precipitate? $K_{\text{sp}} \text{ Mg}(\text{OH})_2 = 1.2 \times 10^{-11} \text{ M}^3$.

Solution: Given that,

$$K_{\text{sp}} \text{ Mg}(\text{OH})_2 = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.2 \times 10^{-11} = [0.1][\text{OH}^-]^2$$

$$[\text{OH}^-]^2 = 1.2 \times 10^{-10}$$

$$[\text{OH}^-] = 1.0954 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log_{10} (1.0954 \times 10^{-5}) = 4.96$$

$$\text{pH} = 14 - 4.96 = 9.04$$

Thus, at 9.04 pH, precipitation will not take place.

Example 11. What is the pH of $10^{-7} \text{ mol litre}^{-1}$ HCl at 25°C ?

$$\begin{aligned} \text{Solution: } [\text{H}^+] &= [\text{H}^+]_{\text{Acid}} + [\text{H}^+]_{\text{Water}} \\ &= 10^{-7} + 10^{-7} = 2 \times 10^{-7} \text{ M} \\ \text{pH} &= -\log (2 \times 10^{-7}) = 6.70 \end{aligned}$$

Example 12. A solution contains 0.1 M Cl^- and $0.001 \text{ M CrO}_4^{2-}$. If solid AgNO_3 is gradually added to this solution, which will precipitate first, AgCl or Ag_2CrO_4 ? Assume that

the addition causes no change in volume. Given $K_{\text{sp}} \text{ AgCl} = 1.7 \times 10^{-10} \text{ M}^2$ and $K_{\text{sp}} \text{ Ag}_2\text{CrO}_4 = 1.79 \times 10^{-12} \text{ M}^3$.

What per cent of Cl^- remains in the solution when CrO_4^{2-} starts precipitating?

Solution: Ag^+ ion concentration required for precipitation:

For AgCl :

$$[\text{Ag}^+] = \frac{K_{\text{sp}} \text{ AgCl}}{[\text{Cl}^-]} = \frac{1.7 \times 10^{-10}}{0.1} = 1.7 \times 10^{-9} \text{ M}$$

For Ag_2CrO_4 :

$$[\text{Ag}^+]^2 = \frac{K_{\text{sp}} \text{ Ag}_2\text{CrO}_4}{[\text{CrO}_4^{2-}]} = \frac{1.79 \times 10^{-12}}{[0.001]}$$

$$\begin{aligned} [\text{Ag}^+] &= [1.79 \times 10^{-9} \text{ M}^2]^{1/2} \\ &= 4.23 \times 10^{-5} \text{ M} \end{aligned}$$

AgCl will precipitate first because it requires low conc. of Ag^+ .

$$\text{Remaining conc. of } [\text{Cl}^-] = \frac{K_{\text{sp}} \text{ of AgCl}}{[\text{Ag}^+]} = \frac{1.7 \times 10^{-10}}{4.23 \times 10^{-5}} = 4.01 \times 10^{-6} \text{ M}$$

$$\% \text{ Remaining conc. of } [\text{Cl}^-] = \frac{4.01 \times 10^{-6}}{0.1} \times 100 = 4 \times 10^{-3} \%$$

Example 13. 25 mL of 0.1 mol dm^{-3} aqueous pyridine ($K_b = 1.7 \times 10^{-9} \text{ mol dm}^{-3}$) is titrated with 0.1 mol dm^{-3} hydrochloric acid. Calculate the pH initially, at equivalence and after 30 cm^3 hydrochloric acid have been added.

Solution: For salt of weak base and strong acid:

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$$

$$\text{p}K_w = 14; \quad \text{p}K_b = -\log_{10} 1.7 \times 10^{-9} = 8.769; \quad C = 0.05$$

$$\text{pH} = \frac{1}{2} [14 - 8.769 + 1.30102] = 3.27 \quad (\text{pH at equivalence})$$

5 cc 0.1 M HCl will be considered for pH.

$$\text{Mole of HCl remaining} = \frac{0.1}{1000} \times 5 = 5 \times 10^{-4}$$

$$\text{New molarity} = \frac{5 \times 10^{-4}}{55} \times 1000 = 0.00909 \text{ M}$$

$$\text{pH} = -\log [0.00909] = 2.04$$

Example 14. If very small amount of phenolphthalein is added to $0.15 \text{ mol litre}^{-1}$ solution of sodium benzoate, what fraction of the indicator will exist in the coloured form? State any assumption that you make.

$$K_a \text{ (Benzoic acid)} = 6.2 \times 10^{-5}, K_w \text{ (H}_2\text{O)} = 1 \times 10^{-14},$$

$$\text{pH} \text{ (Phenolphthalein)} = 3.16 \times 10^{-10}$$

Solution: Formula for pH of salt hydrolysis:

$$\begin{aligned} \text{pH} &= \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C] \\ &= \frac{1}{2} [14 - \log_{10} 6.2 \times 10^{-5} + \log 0.15] \\ &= 8.6918 \end{aligned}$$

Formula for pH of indicator:

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$8.6918 = -\log_{10} (3.16 \times 10^{-10}) + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$0.16 = [\text{In}^-]/[\text{HIn}] = \text{Fraction of indicator in coloured form.}$$

Example 15. How much NH_3 must be added to 0.004 M Ag^+ solution to prevent the precipitation of AgCl when (Cl^-) reaches 0.001 M? K_{sp} for AgCl is 1.8×10^{-10} , and K for $\text{Ag}(\text{NH}_3)_2^+$ is 5.9×10^{-8} .

Solution:

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} \text{ M}$$

NH_3 is added to keep the conc. of Ag^+ below $1.8 \times 10^{-7} \text{ M}$ to prevent precipitation.

$[\text{Ag}(\text{NH}_3)_2]^+$ at above limiting condition

$$= 0.004 - 1.8 \times 10^{-7} \approx 0.004 \text{ M}$$



$$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+}$$

$$5.9 \times 10^{-8} = \frac{[1.8 \times 10^{-7}][\text{NH}_3]^2}{[0.004]}$$

$$[\text{NH}_3] = 0.036 \text{ M}$$

$$\begin{aligned} [\text{NH}_3]_{\text{Total}} &= [\text{NH}_3]_{\text{Free}} + [\text{NH}_3]_{\text{Complexed}} \\ &= 0.036 + 2 \times 0.004 = 0.044 \text{ mol/litre} \end{aligned}$$

Example 16. Calculate the percentage error in hydronium ion concentration made by neglecting ionization of water in 10^{-6} M NaOH .

$$\text{Solution: } [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-6}} = 10^{-8} \text{ M}$$

[Neglecting ionization of water]

Consider ionization of water.

$$[\text{H}_3\text{O}^+] = y [\text{OH}^-] = (y + 10^{-6})$$

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = K_w = 10^{-14}$$

$$y[y + 10^{-6}] = 10^{-14}$$

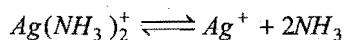
$$y^2 + 10^{-6}y - 10^{-14} = 0$$

On solving for y ,

$$y = 9.9 \times 10^{-9}$$

$$\% \text{ error} = \frac{10^{-8} - 9.9 \times 10^{-9}}{9.9 \times 10^{-9}} \times 100 = 1\%$$

Example 17. Determine the silver ion concentration in a 0.2 M solution of $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$.



$$K_{diss.} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 6.8 \times 10^{-8}$$

Solution: Let concentration of Ag^+ at equilibrium be ' $C \text{ M}$ '.

$$[\text{NH}_3] = 2C \text{ M}$$

$$K = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{C \times 4C^2}{0.2}$$

$$C = 0.0015 \text{ M}$$

Example 18. The solubility of silver acetate in pure water at 25°C is $8.35 \text{ g litre}^{-1}$ and $61.8 \text{ g litre}^{-1}$ in an acid solution of $\text{pH} = 3$. Calculate:

- (i) K_{sp} of silver acetate and
- (ii) dissociation constant of acetic acid.

Solution: (i) CH_3COOAg (mw) = 167

$$S = \frac{8.35}{167} \text{ mol/litre} = 0.05 \text{ M}$$

$$K_{sp} = S^2 = (0.05)^2 = 2.5 \times 10^{-4} \text{ M}$$

(ii) Use expression of salt hydrolysis to calculate K_a .

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

$$K_a = 1.8 \times 10^{-5}$$

Example 19. How many moles of NH_3 must be added to 1 litre of a 0.1 M AgNO_3 to reduce Ag^+ concentration to $2 \times 10^{-7} \text{ M}$?



$$K_{diss.} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 6.8 \times 10^{-8}$$

Solution: $[\text{Ag}(\text{NH}_3)_2]^+ \approx 0.1 \text{ M}$

$$[\text{Ag}^+] = 2 \times 10^{-7}$$

$$K = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+}$$

$$6.8 \times 10^{-8} = \frac{2 \times 10^{-7} [\text{NH}_3]^2}{0.1}$$

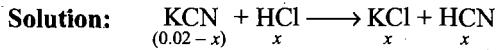
$$[\text{NH}_3] = 0.184 \text{ M}$$

It is the concentration of free NH_3 .

$$\begin{aligned} [\text{NH}_3]_{\text{Total}} &= [\text{NH}_3]_{\text{Free}} + [\text{NH}_3]_{\text{Complexed}} \\ &= 0.184 + 2 \times 0.1 = 0.384 \text{ M} \end{aligned}$$

Example 20. A buffer of $\text{pH} 8.50$ is prepared from 0.02 mole of KCN . The desired volume of buffer solution is to be 1

litre. How will you make this buffer by using HCl? What is the change after addition of 0.5×10^{-4} mole HCl to 100 cm³ and same amount of NaOH in 100 cm³ of buffer? (K_a HCN = 6.2×10^{-10})



$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$8.50 = -\log (6.2 \times 10^{-10}) + \log_{10} \left[\frac{0.02-x}{x} \right]$$

$$8.50 = 9.2076 + \log_{10} \left[\frac{0.02-x}{x} \right]$$

$$x = 0.01672$$

(Buffer is prepared by adding 0.01672 mole of HCl in salt KCN.)

Calculation of pH change when HCl is added:

$$\text{Moles of HCl added in 1 litre buffer} = 0.5 \times 10^{-3}$$

HCl will convert more salt into acid.

$$\text{pH} = 9.2076 + \log_{10} \frac{0.00382 - 0.5 \times 10^{-3}}{0.01672 + 0.5 \times 10^{-3}} = 9.4156$$

$$\text{pH change} = 9.4156 - 8.50 = 0.9156$$

Example 21. What (H_3O^+) must be maintained in a saturated H_2S solution to precipitate Pb^{2+} , but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01 M? (K_{sp} $\text{H}_2\text{S} = 1.1 \times 10^{-22}$ and K_{sp} $\text{ZnS} = 1.0 \times 10^{-21}$) (IIT 2000)

Solution:

$$K_{sp} \text{ ZnS} = [\text{Zn}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-21}$$

$$\text{or } 0.01 \times [\text{S}^{2-}] = 1.0 \times 10^{-21}$$

$$\text{or } [\text{S}^{2-}] = 1.0 \times 10^{-19}$$

To start precipitation of ZnS, the required concentration of sulphide ions is 1.0×10^{-19} .

$$K_{sp} \text{ H}_2\text{S} = [\text{H}^+]^2[\text{S}^{2-}] = 1.1 \times 10^{-22}$$

$$\text{or } [\text{H}^+]^2 = \frac{1.1 \times 10^{-22}}{1.0 \times 10^{-19}} = 1.1 \times 10^{-3}$$

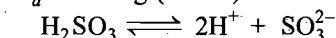
$$\text{or } [\text{H}^+] = 0.0331 \text{ M}$$

Thus, the hydrogen ion concentration higher than 0.0331 M will reduce the concentration of sulphide ions which will not allow the precipitation of Zn^{2+} ions as ZnS and under this condition only PbS precipitation occurs.

Example 22. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is $1.3653 \text{ mol litre}^{-1}$ and the $\text{p}K_a$ of H_2SO_3 is 1.92, estimate the pH of rain on that day. (IIT 2000)

Solution: $\text{p}K_a = 1.92$

$$K_a = \text{antilog} (-1.92) = 0.012$$



$$\begin{array}{ccccc} t=0 & C & 0 & 0 & \\ t_{eq} & C - \alpha & 2\alpha & \alpha & \end{array}$$

$$K_a = \frac{[\text{H}^+]^2[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3]}$$

$$0.012 = \frac{(2\alpha)^2 \times \alpha}{C(1-\alpha)} = \frac{4C^2\alpha^3}{(1-\alpha)} \approx 4C^2\alpha^3$$

$$0.012 = 4 \times (1.3653)^2 \times \alpha^3$$

or

$$\alpha = 0.117$$

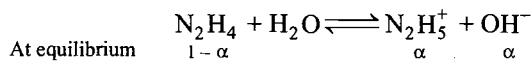
$$[\text{H}^+] = 2C\alpha = 2 \times 1.3653 \times 0.117 = 0.3194$$

$$\text{pH} = -\log_{10} (0.3194) = 0.495$$

Example 23. 0.16 g of N_2H_4 are dissolved in water and the total volume made up to 500 mL. Calculate the percentage of N_2H_4 that has reacted with water at this dilution. The K_b for N_2H_4 is $4.0 \times 10^{-6} \text{ M}$. (IIT 1998)

Solution: Concentration of N_2H_4 ,

$$[\text{N}_2\text{H}_4] = \frac{0.16}{32} \times \frac{1000}{500} = 0.01 \text{ M}$$



$$K_b = C\alpha^2 \text{ or } \alpha^2 = \frac{K_b}{C} = \frac{4.0 \times 10^{-6}}{0.01} = 4 \times 10^{-4}$$

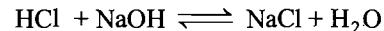
$$\text{or } \alpha = 2 \times 10^{-2}$$

i.e., 2%

Example 24. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12)? (IIT 1998)

Solution: pH of HCl = 2 $\therefore [\text{HCl}] = 10^{-2} \text{ M}$

pH of NaOH = 12 $\therefore [\text{NaOH}] = 10^{-2} \text{ M}$



$$\text{meq after reaction} \quad 0 \quad 100 \times 10^{-2} \\ = 1$$

$$[\text{OH}^-] \text{ after reaction} = \frac{1}{500} = 2 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 2 \times 10^{-3} = 2.7$$

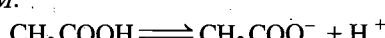
$$\therefore \text{pH} = 14 - 2.7 = 11.3$$

Example 25. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a for acetic acid is $1.75 \times 10^{-5} \text{ M}$. (IIT 2002)

Solution: (a) Conc. of HCl and CH_3COOH after mixing will be 0.1 M.



$t=0$	0.1	0	0.1	(from HCl)
t_{eq}	$0.1 - x$	x	$(0.1 + x)$	

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.75 \times 10^{-5} = \frac{x \times (0.1+x)}{(0.1-x)}$$

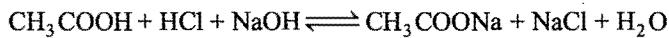
On approximation, $x \approx 1.75 \times 10^{-5}$

$$[\text{H}^+] = 0.1 + x \approx 0.1 \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = 1$$

$$\text{Degree of dissociation of acetic acid} = \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

$$(b) \text{ Number of moles of NaOH added} = \frac{6}{40} = 0.15$$



$t=0$	0.1	0.1	0.15	0	0	0
t_{eq}	0.05	0	0	0.05	0	0

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log 1.75 \times 10^{-5} + \log \frac{0.05}{0.05} = 4.757$$

Example 26. Will the pH of water be same at 4°C and 25°C ? Explain. (IIT 2003)

Solution: We know that,

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$\text{At } 25^\circ\text{C}, [\text{H}^+] = [\text{OH}^-] = 1.01 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} [10^{-7}] = 7$$

At 4°C , ionization of water will be less than that at 25°C .

\therefore at 25°C $K_w = [\text{H}^+][\text{OH}^-]$ will be less than 10^{-14} . Thus, pH of water will be more than 7 at 4°C .

Example 27. 0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point. (IIT 2004)

Solution: Neutralization of HA with NaOH may be given as,



Concentration of salt will be $\frac{0.1}{2} \text{ M}$, i.e., 0.05 M , since volume will be double. pH of the salt after hydrolysis may be calculated as,

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C] \quad \dots (\text{i})$$

$$\text{p}K_w = 14$$

$$\text{p}K_a = -\log K_a = -\log (5.6 \times 10^{-6}) = 5.2518$$

$$\log C = \log 0.05 = -1.3010$$

Substituting the values of $\text{p}K_w$, $\text{p}K_a$ and $\log C$ in eq. (i) we get,

$$\text{pH} = \frac{1}{2} [14 + 5.2518 - 1.3010] = 8.9754$$

Example 28. A solution of acetic acid is 1% ionised. Determine the molar concentration of acetic acid. (ionization constant for acetic acid = 1.8×10^{-5}) [BCECE (Mains) 2006]

Solution: $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\begin{array}{ccccccc} t_0 & C & & 0 & & 0 \\ t_{\text{eq}} & C - C\alpha & & C\alpha & & C\alpha \\ \hline & & & & & & \end{array}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

$$= \frac{C\alpha^2}{1 - \alpha} \quad (\alpha = \frac{1}{100} = 0.01)$$

$$1.8 \times 10^{-5} = \frac{C \times (0.01)^2}{1 - 0.01}$$

$$1.8 \times 10^{-5} \approx C \times 10^{-4}$$

$$C = 0.18 \text{ M}$$

Example 29. A mixture of H_2O and solid AgCl shaken to obtain saturated solution. The solid is filtered and to 100 mL of filtrate, 100 mL of 0.03 M NaBr is added, will a precipitate be formed? [BCECE (Mains) 2006]

$$K_{sp} \text{ AgCl} = 10^{-10}, K_{sp} \text{ AgBr} = 5 \times 10^{-13}$$

Solution: Let solubility of AgCl is 'S'

$$K_{sp} \text{ AgCl} = S^2$$

$$S = \sqrt{K_{sp}} \\ = \sqrt{10^{-10}} = 10^{-5}$$

When, 100 mL of both AgCl and NaBr are mixed then, concentration of Ag^+ and Br^- will be:

$$[\text{Ag}^+] = \frac{100 \times 10^{-5}}{200} = 0.5 \times 10^{-5} \text{ M}$$

$$[\text{Br}^-] = \frac{100 \times 0.03}{200} = 0.015 \text{ M}$$

$$\text{Ionic product of AgBr} = 0.5 \times 10^{-5} \times 0.015$$

$$= 7.5 \times 10^{-8}$$

Since, ionic product of AgBr is greater than its solubility product, hence AgBr will be precipitated.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Strong and weak electrolytes: Electrolytes which ionise almost completely when dissolved in water are termed strong electrolytes while those electrolytes which ionise to small extent are termed as weak electrolytes. The degree of ionisation and electrical conductivity of strong electrolytes have high values

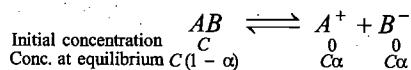
while weak electrolytes possess small values. NaOH , HCl , H_2SO_4 , BaCl_2 , KCl , etc., are strong electrolytes while NH_4OH , CH_3COOH , $(\text{NH}_4)_2\text{CO}_3$, HCN , etc., are weak electrolytes.

Degree of ionisation

Number of molecules of the electrolyte dissociated into ions

Total number of molecules of the electrolyte dissolved

2. Ostwald's dilution law: A dynamic equilibrium exists between ions and unionised molecules of the electrolyte in solution and law of mass action can be applied to this equilibrium also. Consider a binary electrolyte AB .



where, α is the degree of dissociation

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C \times \alpha^2}{(1-\alpha)}$$

K is termed ionisation constant. For a weak electrolyte, the value of α is very small in comparison to 1. Thus, $1-\alpha \rightarrow 1$.

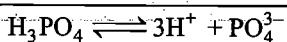
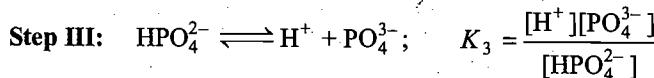
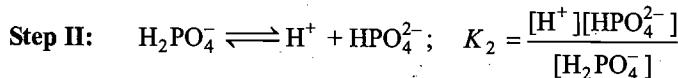
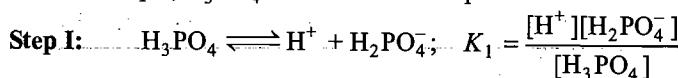
$$K = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad \text{or} \quad \alpha = \sqrt{KV}$$

Where, V is the volume containing one mole of electrolyte.

The degree of dissociation of a weak electrolyte is proportional to the square root of dilution. It increases as V increases and approaches to one at high dilution.

This law holds good for weak electrolytes. In the case of acids, ionisation constant is represented as K_a and in case of bases K_b . Polybasic acids ionise stepwise and each step has its own ionisation constant.

For example, H_3PO_4 ionises in three steps:

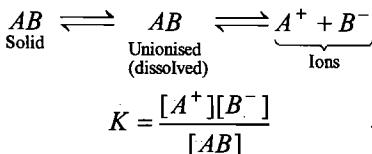


$$K = K_1 \times K_2 \times K_3$$

Generally, $K_1 > K_2 > K_3$

3. Common ion effect: The degree of dissociation of a weak electrolyte is suppressed by the presence of another electrolyte (strong) containing a common ion. As a result of common ion effect, the concentration of the ion not in common in two electrolytes decreases.

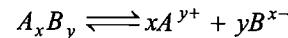
4. Solubility product: In a saturated solution of an electrolyte, two equilibria exist in solution. It can be represented as:



In saturated solution, the value of $[AB]$ is fixed at a definite temperature.

Thus, $K[AB] = [A^+][B^-] = K_s$ (constant)

K_s is termed solubility product. For a general equation,



$$K_s = [A^{y+}]^x [B^{x-}]^y$$

Thus, solubility product is defined as the product of concentrations of ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

For the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

Relationship between solubility and solubility product: Salts like AgI , $PbSO_4$, $BaSO_4$, PbI_2 , etc., which are considered to be insoluble do possess solubility. It is assumed that whole of the dissolved electrolyte is present in the form of ions.

$$A_x \times B_y = xA^{y+} + yB^{x-}$$

Let ' S ' mol per litre be solubility of the salt; then

$$\begin{aligned} K_s &= [A^{y+}]^x [B^{x-}]^y \\ &= (xS)^x (yS)^y \\ &= x^x y^y (S)^{x+y} \end{aligned}$$

(a) 1 : 1 type salts such as $AgCl$, AgI , $BaSO_4$, $PbSO_4$, etc.

$$K_s = S^2 \quad \text{or} \quad S = \sqrt{K_s}$$

(b) 1 : 2 or 2 : 1 type salts such as Ag_2CO_3 , Ag_2CrO_4 , PbI_2 , CaF_2 , etc.

$$K_s = S \times (2S)^2 = 4S^3$$

$$S = \sqrt[3]{\frac{K_s}{4}}$$

(c) 1 : 3 type salts such as AlI_3 , $Fe(OH)_3$, etc.

$$K_s = S \times (3S)^3 = 27S^4$$

$$S = \sqrt[4]{\frac{K_s}{27}}$$

The presence of common ion affects the solubility of salt. Let C be the concentration of strong electrolyte containing common ion and new solubility of salt be S' . For an electrolyte, AB ,

$$S^2 = K_s = S'(S' + C)$$

Applications of Solubility Product and Common ion Effect

- (i) Purification of common salt.
- (ii) Salting out of soap.
- (iii) Precipitation of the sulphides of group (II) and (IV).
- (iv) Precipitation of the hydroxides of group (III).
- (v) Using excess of precipitating agent in gravimetric estimations.
- (vi) Predicting precipitation in ionic reactions.

5. Acids and Bases: Three important concepts are:

(i) Arrhenius concept: All substances which furnish H^+ ions when dissolved in water are called acids while those which

ionise in water to furnish OH^- ions are called bases. Actually free H^+ ions do not exist in water. They combine with water to form hydronium ions (H_3O^+). The reaction between an acid and a base is termed as neutralisation.

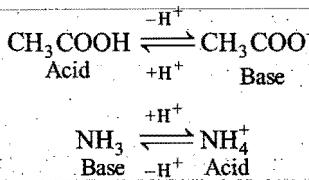
All aqueous solutions contain both H^+ and OH^- ions. However, their relative amounts are different in different solutions.

$\text{H}^+ > \text{OH}^-$ — solution will be acidic

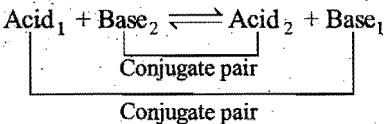
$\text{H}^+ < \text{OH}^-$ — solution will be basic

$\text{H}^+ = \text{OH}^-$ — solution will be neutral

(ii) **Bronsted-Lowry concept:** Any molecule, cation or anion, which provides proton to any other substance is known as an acid and any molecule, cation or anion, which can accept proton from any other substance is known as base. Conjugate acid-base pairs are formed by the loss or gain of a proton.



In a conjugate pair, if acid is strong, the base will be weak and vice-versa. The substances which possess dual nature are termed amphiprotic such as H_2O and NH_3 . The acid-base reaction involves two conjugate pairs.



This concept fails to explain reactions between non-protic acids and bases.

(iii) **Lewis concept:** A base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons, i.e., base is a **nucleophile** and acid is an **electrophile**. All Lewis bases are Bronsted bases but all Lewis acids are not Bronsted acids. All simple cations, molecules whose central atom has incomplete octet, the molecules in which central atom can expand its valence cell and molecules having multiple bonds between atoms of different electronegativities can act as Lewis acids. All simple anions and molecules having one or more lone pairs of electrons can act as Lewis bases.

Arrhenius concept is most simple and explains satisfactorily reactions in aqueous solutions.

6. **Relative strength of acids and bases:** The extent to which an acid property is given by an acid is a measure of its strength. The strength of the acid solution does not depend on its concentration but on the number of H^+ ions present. On dilution, as the number of H^+ ions increases, the strength of an acid also increases. At infinite dilution, all acids are almost completely ionised and, therefore, tend to be equally strong. The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their

degree of dissociation. The relative strength is generally compared in terms of degree of dissociation of equimolar solutions.

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

The strength of the base depends upon OH^- ion concentration.

$$\frac{\text{Strength of base I}}{\text{Strength of base II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

7. **Neutralisation:** The neutralisation is the interaction of H^+ ions furnished by an acid and OH^- ions furnished by a base or a reaction between acid and base to form salt and water is termed neutralisation.

Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base and negative part comes from an acid. The salts are generally crystalline solids. These are classified into the following classes:

(i) **Simple salts:** The salts formed by neutralisation process are of three types:

(a) **Normal salts** are salts formed by the replacement of all replaceable hydrogen atoms at H^+ ions. Examples are NaCl , KNO_3 , CuSO_4 , FeSO_4 , etc.

(b) **Acid salts** are formed by incomplete neutralisation of polybasic acids. Examples are NaHCO_3 , NaHSO_4 , Na_2HPO_4 , etc.

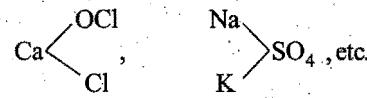
(c) **Basic salts** are salts formed by incomplete neutralisation of polyacidic bases. Examples are: $\text{Zn}(\text{OH})\text{Cl}$, $\text{Mg}(\text{OH})\text{Cl}$, $\text{Fe}(\text{OH})_2\text{Cl}$, etc.

(ii) **Double salts** are the addition compounds formed by combination of two or more simple salts. Such salts are stable in solid state only. Examples are $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, etc. These salts when dissolved in water furnish all the ions present in simple salts.

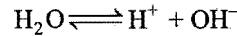
(iii) **Complex salts** are the salts formed by combination of simple salts or molecular compounds. These are stable in solid state. On dissolving in water, they furnish at least one complex ion.

Examples are $\text{K}_4\text{Fe}(\text{CN})_6$, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, etc.

(iv) **Mixed salts** furnish more than one cation or more than one anion when dissolved in water. Examples are:



8. **Ionic product of water:** Pure water is a weak electrolyte and is very slightly dissociated into hydrogen and hydroxyl ions.



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$[\text{H}_2\text{O}]$ can be taken as constant.

$$K[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] = K_w$$

K_w is constant and known as ionic product of water. Its value is 1×10^{-14} at 25°C . The value increases with increase of temperature. Since, water is neutral, $[\text{H}^+] = [\text{OH}^-]$

$$\text{or } [\text{H}^+] = [\text{OH}^-] = 10^{-7}$$

When $[\text{H}^+] > [\text{OH}^-]$, the solution is acidic.

Similarly, when $[\text{H}^+] < [\text{OH}^-]$, the solution is basic in nature. Every aqueous solution, whether acidic, neutral or basic, contains both H^+ and OH^- ions. The product of their concentrations is always 1×10^{-14} at 25°C . If one increases, the other decreases.

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} \quad \text{and} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

9. pH scale: This has been devised by Sorenson in 1909. The negative logarithm of the concentration of hydrogen ions is termed the pH of the solution.

$$\text{pH} = -\log [\text{H}^+] = \log \frac{1}{[\text{H}^+]}$$

pH is thus logarithm of the reciprocal of hydrogen ion concentration.

$$\text{Similarly, } \text{pOH} = -\log [\text{OH}^-] = \log \frac{1}{[\text{OH}^-]}$$

$$\text{pH} + \text{pOH} = 14$$

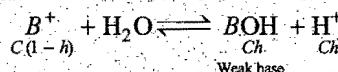
Limitations of pH scale: pH values do not give any immediate idea about the relative strengths of the solution. pH value is zero for $1N$ solution of strong acid. In case of $2N$, $3N$, $4N$, etc., solutions, pH values are negative. A solution of an acid having very low concentration, say $10^{-8} N$, cannot have pH 8 as shown by pH formula but the actual pH value will be less than 7.

10. Hydrolysis: It is the interaction of ions of a salt with water to give acidic, basic or neutral solution. It is found in the salts of weak acids and strong bases, in salts of strong acids and weak bases and in salts of weak acids and weak bases. The process of hydrolysis is actually the reverse of neutralisation.



If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both acid and base are either strong or weak, the solution is generally neutral in nature.

Salt of a strong acid and a weak base: The solution of such a salt is acidic in nature. The cation of the salt is reactive and reacts with water.



The extent to which hydrolysis proceeds is expressed as degree of hydrolysis. It is denoted as h or α .

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Let C be the concentration of salt and h be the degree of hydrolysis.

$$K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{(1-h)} \approx Ch^2 \quad (\text{if } h \text{ is small})$$

$$K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{C \times K_b}}$$

$$= hC = [\text{H}^+] = \frac{\sqrt{C \times K_w}}{K_b}$$

$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

11. Summary pH of mixtures of acids and bases:

Let ' x ' meq of acid (HA) and ' y ' meq of base (BOH) be mixed.

$$\text{meq} = NV \text{ mL}; N = M \times \text{acidity or basicity}$$

Case I. Strong acid and strong base

(a) When $x = y$, then there will be complete neutralisation; the solution will then be neutral with pH = 7.

(b) When $x > y$, then acid will remain after neutralisation.

$$\text{meq of remaining acid} = (x - y)$$

$$N_a = \frac{(x - y)}{V \text{ mL}}$$

$$[\text{H}^+]_{\text{Strong acid}} = N_a = \frac{(x - y)}{V \text{ mL}}$$

$$\text{pH} = -\log_{10} \left[\frac{x - y}{V \text{ mL}} \right]$$

(c) When $y > x$, then base will remain after neutralization.

$$\text{meq of remaining base} = (y - x)$$

$$N_b = \frac{(y - x)}{V \text{ mL}}$$

$$[\text{OH}^-]_{\text{Strong base}} = N_b = \frac{(y - x)}{V \text{ mL}}$$

$$\text{pOH} = -\log_{10} \left[\frac{(y - x)}{V \text{ mL}} \right]; \quad \text{pH} = 14 - \text{pOH}$$

Case II. Strong base and weak acid

(a) If $x = y$, then after complete neutralisation there will be salt of weak acid and strong base. There will be hydrolysis; pH after hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log_{10} C]$$

$$C = \text{Conc. of salt in mol litre}^{-1}$$

(b) If $x > y$, then weak acid will be in excess.

$$\text{Weak acid} = (x - y) \text{ meq}$$

$$\text{Salt} = y \text{ meq}$$

The resultant solution will be acid buffer; its pH may be calculated as:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{Conc. should be taken in mol litre}^{-1}$$

(c) When $y > x$, then excess of strong base will remain after neutralisation. Remaining base = $(y - x)$ meq

$$N_b = \frac{(y-x)}{V \text{ mL}} = [\text{OH}^-]$$

$$\text{pOH} = -\log_{10} \left[\frac{y-x}{V \text{ mL}} \right]$$

Case III. Strong acid and weak base

(a) When $x = y$, there will be salt formation after complete neutralisation. Salt of weak base and strong base will undergo hydrolysis. pH after hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \log_{10} C]$$

C = Conc. of salt in mol litre⁻¹.

(b) When $x > y$, then strong acid will remain after neutralisation.

Remaining acid = $(x - y)$ meq

$$N_a = \frac{(x-y)}{V \text{ mL}} = [\text{H}^+]$$

$$\text{pH} = -\log_{10} \left[\frac{x-y}{V \text{ mL}} \right]$$

(c) When $y > x$, then weak base will remain after salt formation; the resultant mixture will be, therefore, base buffer.

$$14 - \text{pH} = \text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

Remaining base = $(y - x)$ meq

Salt = x meq

Salt and base conc. should be taken in mol litre⁻¹.

Case IV. Weak acid and weak base

(a) When $x = y$, there will be complete neutralisation forming salt of weak acid and weak base. pH after salt hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$$

(b) When $x > y$, weak acid will remain after neutralisation; the mixture of weak acid and salt behaves as acid buffer.

(c) When $y > x$, then weak base will remain after salt formation; the mixture thus behaves as base buffer.

12. Acid-base indicators: In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colours within a certain pH range.

Methyl orange pH range 3.2–4.5 Pink to yellow

Methyl red pH range 4.4–6.5 Red to yellow

Phenolphthalein pH range 8.3–10.5 Colourless to pink

Two theories have been proposed to explain the change of colour of these acid-base indicators. These theories are:

(a) Ostwald's theory (b) Quinonoid theory

The suitable indicators for the following titrations are:

(i) Strong acid *versus* strong base—Phenolphthalein, methyl red and methyl orange.

(ii) Weak acid *versus* strong base—Phenolphthalein.

(iii) Strong acid *versus* weak base—Methyl red and methyl orange.

Questions

1. (a) Mention conjugate base of each of the following:
 HS^- , H_3O^+ , H_2PO_4^- , HSO_4^- , HF , CH_3COOH , $\text{C}_6\text{H}_5\text{OH}$, HClO_4 , NH_4^+
- (b) Mention the conjugate acid of each of the following:
 OH^- , CH_3COO^- , Cl^- , CO_3^{2-} , H_2PO_4^- , CH_3NH_2 , CH_3COOH , NH_3^-
- (c) Which of the following behave both as Bronsted acids as well as Bronsted bases?
 H_2O , HCO_3^- , H_2SO_4 , H_3PO_4 , HS^- , NH_3
- (d) Which is stronger acid in each of the following pairs?
 HCl , HI ; H_2CO_3 , H_2SO_4 ; H_2O , H_2S ; $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{OH}$; Na^+ , K^+
- (e) Which is stronger base in each of the following pairs?
 OH^- , Cl^- ; OH^- , NH_3^- ; OH^- , CH_3COO^- ; CH_3COO^- , Cl^- ; NH_3 , CH_3NH_2
- (f) Classify the following into acids and bases according to Lewis concept:
 S^{2-} , H^+ , OH^- , BF_3 , Ni^{2+} , NF_3 , AlCl_3 , SnCl_4 , NH_3 , $(\text{CH}_3)_2\text{O}$

2. Predict whether the following substances will give acidic, basic or neutral solution?

- (i) K_2CO_3 (ii) NaCl (iii) FeCl_3
- (iv) CuSO_4 (v) AlCl_3 (vi) NH_4Cl
- (vii) $\text{CH}_3\text{COONH}_4$ (viii) NaCN (ix) Na_2S
- (x) $\text{Na}_2\text{B}_4\text{O}_7$

3. [A] Match the List-I with List-II:

**List-I
(Salt)**
**List-II
(pH)**

- | | |
|---|---|
| (a) Salt of strong acid and strong base | (p) $\frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$ |
| (b) Salt of weak acid and strong base | (q) $\frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$ |
| (c) Salt of weak base and strong acid | (r) $\frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$ |
| (d) Salt of weak acid and weak base | (s) $\frac{1}{2} \text{p}K_w$ |

[B] Match the List-I with List-II:

**List-I
(Indicator)**
**List-II
(pH range)**

- | | |
|---------------------|----------------|
| (a) Phenolphthalein | (p) 4.2 – 6.3 |
| (b) Litmus | (q) 3.1 – 4.4 |
| (c) Methyl red | (r) 8.3 – 10.0 |
| (d) Methyl orange | (s) 5.0 – 8.0 |

[C] Match the List-I with List-II:

List-I
List-II

- | | |
|--------------------|---|
| (a) Lewis acid | (p) PH_3 |
| (b) Lewis base | (q) $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ |
| (c) Conjugate acid | (r) $(\text{CH}_3)_3\text{B}$ |
| (d) Conjugate base | (s) H_3O^+ |

4. **Matrix-Matching Problems (For IIT Aspirants):**

[A] Match the List-I with List-II:

List-I
List-II

- | | |
|-----------------------------|--------------------------|
| (a) H_3PO_4 | (p) Monobasic |
| (b) H_3PO_3 | (q) Dibasic |
| (c) H_3PO_2 | (r) Tribasic |
| (d) H_3BO_3 | (s) sp^3 -hybrid state |

[B] Match the List-I with List-II:

**List-I
(Indicator)**
**List-II
(Type of titration)**

- | | |
|------------------------|---|
| (a) Phenolphthalein | (p) $\text{NaOH} + \text{HCl}$ |
| (b) Phenol red | (q) $\text{H}_2\text{SO}_4 + \text{NH}_4\text{OH}$ |
| (c) Bromo cresol green | (r) $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$ |
| (d) Methyl orange | (s) $\text{KOH} + \text{H}_2\text{SO}_4$ |

[C] Match the acid/base in List-I with their nature in List-II:

List-I
List-II

- | | |
|----------------------|-------------------|
| (a) HSO_4^- | (p) Lewis acid |
| (b) BF_3 | (q) Lewis base |
| (c) NH_3 | (r) Bronsted acid |
| (d) OH^- | (s) Bronsted base |

[Note: Consider the normal behaviour of species.]

[D] Match the Column-I with Column-II:

**Column -I
(Salt)**
**Column -II
(Solubility product)**

- | | |
|-------------------------|----------------|
| (a) Zirconium phosphate | (p) $27 S^4$ |
| (b) Aluminium phosphate | (q) $108 S^5$ |
| (c) Calcium phosphate | (r) $6912 S^7$ |
| (d) Sodium phosphate | (s) S^2 |

[E] Match the Column-I with Column-II:

**Column-I
(Salt)**

- (a) NH_4CN
- (b) CH_3COONa
- (c) NaClO_4
- (d) $\text{Fe}(\text{NO}_3)_2$

**Column-II
(Nature of hydrolysis)**

- (p) Only cation hydrolysis
- (q) Only anion hydrolysis
- (r) Both cation and anion hydrolysis
- (s) No hydrolysis

[F] Match the Column-I with Column-II:

**Column-I
(Titration)**

- (a) Strong acid versus strong base
- (b) Weak acid versus strong base
- (c) Strong acid versus weak base
- (d) Weak acid versus weak base

**Column-II
(Indicator used)**

- (p) Methyl orange (3 – 4.4)
- (q) Methyl red (4.3 – 6.3)
- (r) Phenolphthalein (8–10)
- (s) No suitable indicator

Answers

1. (a) $\text{S}^{2-}, \text{H}_2\text{O}, \text{HPO}_4^{2-}, \text{SO}_4^{2-}, \text{F}^-, \text{CH}_3\text{COO}^-, \text{C}_6\text{H}_5\text{O}^-, \text{ClO}_4^-, \text{NH}_3$
 (b) $\text{H}_2\text{O}, \text{CH}_3\text{COOH}, \text{HCl}, \text{HCO}_3^-, \text{H}_3\text{PO}_4, \text{CH}_3\text{NH}_3^+, \text{CH}_3\text{COOH}_2^+, \text{NH}_3$
 (c) $\text{H}_2\text{O}, \text{HCO}_3^-, \text{HS}^-$ and NH_3 behave both as acids and bases.
 (d) $\text{HI} > \text{HCl}; \text{H}_2\text{SO}_4 > \text{H}_2\text{CO}_3; \text{H}_2\text{S} > \text{H}_2\text{O}; \text{C}_6\text{H}_5\text{OH} > \text{C}_2\text{H}_5\text{OH}; \text{Na}^+ > \text{K}^+$
 (e) $\text{OH}^- > \text{Cl}^-; \text{NH}_2^- > \text{OH}^-; \text{OH}^- > \text{CH}_3\text{COO}^-; \text{CH}_3\text{COO}^- > \text{Cl}^-; \text{CH}_3\text{NH}_2 > \text{NH}_3$
 (f) Lewis acids: $\text{H}^+, \text{BF}_3, \text{Ni}^{2+}, \text{AlCl}_3, \text{SnCl}_4$
 Lewis bases: $\text{S}^{2-}, \text{OH}^-, \text{NF}_3, \text{NH}_3, (\text{CH}_3)_2\text{O}$

2. Acidic: $\text{FeCl}_3, \text{CuSO}_4, \text{AlCl}_3, \text{NH}_4\text{Cl}$
 Basic: $\text{K}_2\text{CO}_3, \text{NaCN}, \text{Na}_2\text{S}, \text{Na}_2\text{B}_4\text{O}_7$
 Neutral: $\text{NaCl}, \text{CH}_3\text{COONH}_4$
3. [A] (a-s), (b-q), (c-r), (d-p)
 [B] (a-r), (b-s), (c-p), (d-q)
 [C] (a-r), (b-p), (c-s), (d-q)
4. [A] (a-r, s), (b-q, s), (c-p, s), (d-p)
 [B] (a-p, s), (b-r), (c-q), (d-p, s, q)
 [C] (a-r, s), (b-p), (c-q, s), (d-q, s)
 [D] (a-r), (b-s), (c-q), (d-p)
 [E] (a-r), (b-q), (c-s), (d-p)
 [F] (a-p, q, r), (b-r), (c-p, q), (d-s)

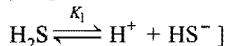
● PRACTICE PROBLEMS ●

1. Calculate the degree of ionisation of 0.1 M acetic acid. The dissociation constant of acetic acid is 1.8×10^{-5} .
 [Ans. $\alpha = 1.34 \times 10^{-2}$]
2. Calculate the concentration of OH^- ions of 0.01 M NH_4OH solution. The equilibrium constant of NH_4OH is 1.8×10^{-5} .
 [Ans. $4.24 \times 10^{-4} \text{ mol L}^{-1}$]
3. At 15°C , 0.05 N solution of a weak monobasic acid is 3.5% ionised. Calculate the ionisation constant of acid.
 [Ans. 6.125×10^{-5}]
4. 0.02 M solution of NH_4OH is 3% dissociated. Calculate the dissociation constant of NH_4OH .
 [Ans. 1.8×10^{-5}]
5. A solution contains 0.4 M CH_3COOH and 0.2 M CH_3COONa . Calculate the concentration of H^+ ions. The ionisation constant of acetic acid is 1.8×10^{-5} .
 [Ans. $3.6 \times 10^{-5} \text{ mol L}^{-1}$]
6. The dissociation constant of hydrocyanic acid (HCN) is 4×10^{-8} . Calculate the H^+ ion concentration of 0.01 M HCN solution.
 [Ans. $2 \times 10^{-5} \text{ mol L}^{-1}$]
7. The degree of dissociation of a weak electrolyte in 0.1 M aqueous solution is 0.0114 at 298 K . Calculate the degree of dissociation of the same electrolyte at 298 K in 0.001 M solution.
 [Ans. 0.114]
8. Calculate K_a for a dibasic acid if its concentration is 0.05 N and hydrogen ion concentration is $1 \times 10^{-3} \text{ mol L}^{-1}$.
 [Ans. 2×10^{-8}]
 [Hint: Conc. = 0.025 M , $[\text{H}^+] = 2C \times \alpha = 1 \times 10^{-3}$, i.e., $\alpha = 0.02$, $K_a = 4 \times C^2 \times \alpha^3$]
9. K_a for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} . What concentration of the acid must be taken so that it is 1% dissociated?
 [Ans. 0.18 mol L^{-1}]
10. Calculate the degree of ionisation and hydroxyl ion concentration in 0.2 M NH_3 solution. ($K_b = 1.85 \times 10^{-5}$ at 298 K).
 [Ans. $\alpha = 0.962 \times 10^{-2}$, $[\text{OH}^-] = 1.924 \times 10^{-3} \text{ M}$]
11. The dissociation constant of acetic acid at 18°C is 1.8×10^{-5} . Calculate the pH of 0.1 N and 0.001 N solution of acetic acid.
 [Ans. 2.873, 3.726]

12. Calculate the approximate pH of 0.1 M aqueous H₂S solution. K₁ and K₂ for H₂S are 1.0×10^{-7} and 1.3×10^{-13} respectively at 25°C.

[Ans. pH = 4]

[Hint: Second dissociation constant is very small. H⁺ ion concentration mainly depends on the first dissociation constant.]



13. The pH of a soft drink is 4.4. Calculate [H₃O⁺] and [OH⁻] of the drink.

[Ans. 3.98×10^{-5} mol L⁻¹, 2.5×10^{-10} mol L⁻¹]

14. Calculate the pH of a 0.001 M solution of Sr(OH)₂ assuming it to be completely ionised.

[Ans. 11.301]

[Hint: Sr(OH)₂ \rightleftharpoons Sr²⁺ + 2OH⁻;

$$[\text{OH}^-] = 2 \times 0.001 = 0.002 \text{ M}$$

15. The value of K_w is 9.55×10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

[Ans. 6.51]

[Hint: K_w = [H⁺][OH⁻], So, [H⁺] = $\sqrt{K_w}$]

16. 9.8 g of H₂SO₄ is present in 500 mL of the solution. Calculate the pH of the solution.

[Ans. 0.3979]

17. The pH of a 0.1 M solution of an organic acid is 4.0. Calculate the dissociation constant of the acid.

[Ans. 1×10^{-7}]

18. Calculate [H₃O⁺], [OH⁻] and pH of 0.2 M solution of HCN. (K_a = 7.2×10^{-10})

[Ans. [H₃O⁺] = 1.2×10^{-5} mol L⁻¹, [OH⁻] = 8.33×10^{-10} mol L⁻¹, pH = 4.92]

19. Calculate pH of 0.002 M CH₃COOH if it is 2.3% ionised at this concentration.

[Ans. 4.34]

20. Calculate the pH of the solution obtained by mixing 150 mL of 0.2 M HCl and 150 mL of 0.1 M NaOH.

[Ans. 1.30]

21. pH of a 0.1 M HCN solution is 5.2. What is the value of K_a for the acid?

[Ans. 3.97×10^{-10}]

22. The pH of a solution of B(OH)₂ is 10.6. Calculate the solubility and solubility product of hydroxide.

[Hint: pOH = 3.4, [OH⁻] = 3.98×10^{-4} mol L⁻¹

$$\text{Solubility} = \frac{1}{2}[\text{OH}^-] = 1.99 \times 10^{-4} \text{ mol L}^{-1}$$

$$K_{sp} = [\text{B}^+][\text{OH}^-]^2 = 3.15 \times 10^{-11}$$

23. Calculate the pH of a solution:

- (i) containing 2 g of sodium hydroxide in one litre;
(ii) made by mixing 50 mL of 0.01 M Ba(OH)₂ solution with 50 mL water.

[Ans. (i) pH = 12.7, (ii) pH = 12]

24. What happens to the pH of 500 mL of a solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 mL of 0.1 M sodium hydroxide is added?

[Ans. pH = 4.7447 and pH will increase]

25. What ratio of acetic acid to sodium acetate concentration is needed to achieve a buffer whose pH is 5.70? The dissociation constant of acetic acid is 1.8×10^{-5} .

[Ans. 1:9]

26. Find the concentration of H⁺, HCO₃⁻ and CO₃²⁻ in a 0.01 M solution of carbonic acid if the pH of the solution is 4.18, K₁ = 4.45×10^{-7} , K₂ = 4.69×10^{-11} .

[Ans. [H⁺] = 6.61×10^{-5} M, [HCO₃⁻] = 6.73×10^{-5} M, [CO₃²⁻] = 4.78×10^{-11} mol L⁻¹]

$$[\text{Hint}], K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.45 \times 10^{-7}$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}$$

$$[\text{H}^+] = 6.61 \times 10^{-5} \text{ M}, [\text{H}_2\text{CO}_3] = 0.01 \text{ M}$$

$$[\text{HCO}_3^-] = 6.73 \times 10^{-5} \text{ M}, [\text{CO}_3^{2-}] = 4.78 \times 10^{-11} \text{ mol L}^{-1}$$

27. What will be the pH value of a solution of 500 mL containing 5 g acetic acid and 7.2 g of sodium acetate? K_a = 1.8×10^{-5} at 25°C.

[Ans. 4.82]

28. The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10} .

(IIT 1991)

[Ans. [H⁺] = 7.2×10^{-10} M; [OH⁻] = 1.4×10^{-7} M]

[Hint: pH = log $\frac{[\text{Salt}]}{[\text{Acid}]}$ - log K_a = -log [H⁺]]

29. A buffer solution of pH = 9 is to be prepared by mixing NH₄Cl and NH₄OH. Calculate the number of moles of NH₄Cl that should be added to one litre of 1.0 M NH₄OH solution. (K_b = 1.8×10^{-5})

(MLNR 1991)

[Ans. 1.8 mole]

30. Calculate the amount of (NH₄)₂SO₄ which must be added to 500 mL of 0.200 M NH₃ to yield a solution of pH 9.35. (K_b for NH₃ = 1.78×10^{-5})

(MLNR 1992)

[Ans. 10.494 g]

31. Calculate the pH of the buffer containing 1.0 mol L⁻¹ of weak acid HA and 0.1 mol L⁻¹ of its sodium salt NaA assuming K_a to be 10^{-6} .

(Dhanbad 1993)

[Ans. pH = 5]

32. Calculate K_b for a base whose 0.1 M solution has pH of 10.5.

[Ans. 10^{-6}]

33. What is the maximum pH of a solution 0.10 M in Mg²⁺ from which Mg(OH)₂ will not precipitate? Given, K_{sp} [Mg(OH)₂] = 1.2×10^{-11}

[Ans. pH = 9.4]

34. A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be the pH of the resulting solution?

[Ans. pH = 6.9586]

[Hint: pH = 5, $[\text{H}^+] = 10^{-5} M$. After dilution = $\frac{10^{-5}}{1000} = 10^{-8} M$

$$[\text{H}^+] = 10^{-8} + 10^{-7}$$

$$= 1.1 \times 10^{-7}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 1.1 \times 10^{-7} = 6.9586$$

35. Calculate the pH of the solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4 .

[Ans. pH = 0.4685]

[Hint: $[\text{H}^+] = \frac{10 \times 0.1 + 40 \times 0.4}{50} = 0.34$]

36. The degree of dissociation of a weak electrolyte in 0.1 M aqueous solution is 0.0114 at 298 K. Calculate the degree of dissociation of the same electrolyte at 298 K in 0.001 M solution.

[Ans. 0.114]

[Hint: α is proportional to $\sqrt{\frac{1}{C}}$

$$\frac{\alpha}{\alpha'} = \sqrt{\frac{C'}{C}} = \sqrt{\frac{0.001}{0.1}} = 0.1$$

$$\alpha' = \frac{\alpha}{0.1} = \frac{0.0114}{0.1} = 0.114$$

37. The degree of dissociation of water is 1.8×10^{-9} at 298 K. Calculate the ionisation constant and ionic product of water at 298 K.

[Hint: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$, $[\text{H}_2\text{O}] = \frac{1000}{18} = 55.56 \text{ mol L}^{-1}$,

$$[\text{H}^+] = [\text{OH}^-] = C \times \alpha = 55.56 \times 1.8 \times 10^{-9}$$

$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{55.56 \times 1.8 \times 10^{-9} \times 55.56 \times 1.8 \times 10^{-9}}{55.56} \\ = 1.8 \times 10^{-16}$$

$$K_w = [\text{H}^+][\text{OH}^-] = (55.56 \times 1.8 \times 10^{-9})^2 = 1 \times 10^{-14}$$

38. One litre of a buffer solution is prepared by dissolving 0.6 mole of NH_3 and 0.4 mole of NH_4Cl . What is the pH of the solution? For NH_3 , $K_b = 1.8 \times 10^{-5}$.

(i) What is the pH of the buffer after addition of 0.1 mole of HCl?

(ii) What is the pH of the buffer after addition of 0.1 mole of NaOH?

[Ans. 9.4314 (i) 9.2553 (ii) 9.6233]

39. One litre of a buffer contains 40 g of NH_4Cl and 20 g of NH_3 . Calculate the pH of the solution. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ at 298 K.

[Ans. 9.452]

40. A buffer solution is prepared by mixing 50 mL of 0.5 molar ammonia solution, 40 mL of 0.4 molar NH_4Cl solution and 10 mL of distilled water. Calculate the pH of the buffer.

$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ at 298 K.

[Ans. 9.45]

[Hint: Total volume = $50 + 40 + 10 = 100 \text{ mL}$

$$\text{Molarity of } \text{NH}_3 = \frac{0.5 \times 50}{100} = 0.25$$

$$\text{Molarity of } \text{NH}_4\text{Cl} = \frac{0.4 \times 40}{100} = 0.16$$

41. pK_a value of acetic acid is 4.76 at room temperature. How will you obtain buffers of 4.40 and 5.40 pH values from acetic acid and sodium acetate?

[Ans. $\frac{\text{Acetate}}{\text{Acid}} = 0.4365$ and $\frac{\text{Acetate}}{\text{Acid}} = 4.364$]

42. Calculate the ratio of pH of a solution containing 1 mole of $\text{CH}_3\text{COONa} + 1$ mole of HCl per litre and of the other solution containing 1 mole of $\text{CH}_3\text{COONa} + 1$ mole of CH_3COOH per litre.

[Hint: 1st case: $\text{CH}_3\text{COONa} + \text{HCl} \longrightarrow \text{CH}_3\text{COOH} + \text{NaCl}$

$$\text{pH}_1 = -\frac{1}{2} \log K_a$$

$$\text{2nd case: } \text{pH}_2 = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a$$

$$\frac{\text{pH}_1}{\text{pH}_2} = \frac{1}{2}$$

43. Calculate the composition of an acidic buffer solution ($\text{HA} + \text{NaA}$) of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.

[Ans. [Salt] = 0.09 M; [Acid] = 0.20 M]

[Hint: $\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$= -\log K_a + \log \frac{a}{(0.29-a)}$$

44. Calculate the pH of a solution obtained by mixing 100 mL of an acid of pH = 3 and 400 mL solution of pH = 1.

[Ans. 1.096]

45. The solubility product of AgCl in water is 1.5×10^{-10} . Calculate its solubility in 0.01 M NaCl aqueous solution.

(IIT 1995)

[Ans. $1.5 \times 10^{-8} \text{ mol L}^{-1}$]

46. Calculate the pH of a 0.02 M aqueous solution of NH_4Cl ? Given, $\text{pK}_{\text{NH}_4\text{OH}} = 4.73$.

[Ans. 3.78]

47. Determine the pH value of 0.1 M aqueous solution of ammonium cyanide ($\text{pK}_a = 9.04$, $\text{pK}_b = 4.73$).

[Ans. 9.15]

48. Calculate the pH of a 0.2 M solution of strychnine hydrochloride. ($K_b = 1 \times 10^{-7}$)

[Ans. 3.8494]

49. The dissociation constants of acetic acid and aniline are 1.8×10^{-5} and 4.2×10^{-10} respectively. What is the degree of hydrolysis of aqueous aniline acetate? What is the pH of the solution?

[Ans. 0.5348, pH = 4.684]

50. A weak acid HA after treatment with 12 mL of 0.1 M strong base has a pH of 5. At the end point, the volume of the same base required is 26.6 mL. Calculate the K_a of the acid.

[Ans. 8.219×10^{-6}]

[Hint: Applying $M_1V_1 = M_2V_2$
Acid Base
 $= 26.6 \times 0.1$
 $= 2.66 \text{ meq.}$



After the reaction 1.46 0 1.2 1.2

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \text{p}K_a$$

51. K_a for HCN is 1.4×10^{-9} . Calculate for 0.01 N KCN solution:

- (a) degree of hydrolysis
- (b) $[\text{OH}^-]$ and $[\text{CN}^-]$
- (c) pH

[Ans. (a) 2.67×10^{-2} (b) 2.67×10^{-4} , 9.73×10^{-3} (c) 10.4265]

52. What is the H^+ ion concentration in ammonium acetate solution?

$$K_a = 1.8 \times 10^{-5}, K_b = 1.8 \times 10^{-5} \text{ and } K_w = 1.0 \times 10^{-14}$$

[Ans. 1.0×10^{-7}]

53. A 40 mL sample of 0.1 M solution of nitric acid is added to 20 mL of 0.3 M aqueous ammonia. What is the pH of the resulting solution? Given, K_b for ammonia = 1.8×10^{-5} .

[Ans. 8.95]

54. Calculate the pH of 0.1 M solution of NH_4OCN . K_b for NH_3 is 1.75×10^{-5} and K_a for HOCN is 3.3×10^{-4} .

[Ans. 6.36]

55. Which of the two solutions 0.1 M HCN ($K_a = 4 \times 10^{-10}$) and 0.1 M HF ($K_a = 6.7 \times 10^{-4}$) will have greater degree of ionisation and to what extent?

[Ans. HF will have greater degree of dissociation.

$$\frac{\alpha(\text{HF})}{\alpha(\text{HCN})} = 1294$$

56. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.4 M HCl with 100.0 mL of 0.4 M NH_3 . Hydrolysis constant of ammonium chloride is 5.6×10^{-10} .

[Ans. pH = 4.96]

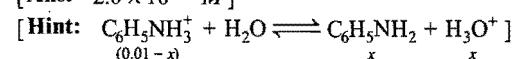
57. Calculate the per cent hydrolysis in 0.003 M aqueous solution of NaOCN.

(K_a for $\text{HOCN} = 3.33 \times 10^{-4} \text{ M}$) (IIT 1996)

[Ans. 0.01%]

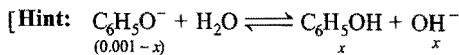
58. What is the $[\text{OH}^-]$ in a 0.01 M solution of aniline hydrochloride? K_b for aniline is 4.0×10^{-10} .

[Ans. $2.0 \times 10^{-11} \text{ M}$]



59. Calculate the pH of $1.0 \times 10^{-3} \text{ M}$ sodium phenolate NaOC_6H_5 . K_a for $\text{C}_6\text{H}_5\text{OH}$ is 1×10^{-10} .

[Ans. pH = 10.43]



$$K_h = \frac{K_w}{K_a} = 1 \times 10^{-4} = \frac{x^2}{(0.001 - x)}$$

$$x^2 + 1 \times 10^{-4}x - 1 \times 10^{-7} = 0, x = 2.7 \times 10^{-4}, \text{pOH} = 3.57$$

60. The dissociation constants of *m*-nitrobenzoic acid and acetic acid are 36.0×10^{-5} and 1.8×10^{-5} respectively. What are their relative strengths?

[Ans. 4.47 : 1]

61. Calculate the degree of hydrolysis of 0.10 solution of KCN. Dissociation constant of HCN = 7.2×10^{-10} at 25°C and $K_w = 10 \times 10^{-14}$.

[Ans. 1.18×10^{-2}]

62. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at $1 \times 10^{-8} \text{ M}$?

(K_a for $\text{C}_6\text{H}_5\text{NH}_3^+ = 2.4 \times 10^{-5} \text{ M}$) (IIT 1996)

[Ans. 0.01 M]

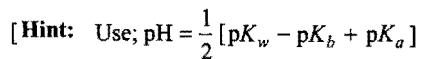
63. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. (IIT 1996)

[Ans. pH = 11.5]

64. Calculate the pH of an aqueous solution of 1 M ammonium formate, assuming complete dissociation.

($pK_a = 3.8, pK_b = 4.8$) (IIT 1995)

[Ans. 6.5]



65. Calculate the hydrolysis constant of the salt containing NO_2^- ions. Given, K_a for $\text{HNO}_2 = 4.5 \times 10^{-10}$. (MLNR 1996)

[Ans. 2.2×10^{-5}]

66. Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride $[\text{C}_6\text{H}_5\text{NH}_3]\text{Cl}$, a salt of aniline and HCl. Calculate the pH of 0.233 M solution of aniline.

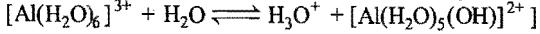
[K_b (aniline) = 4.6×10^{-10}]

[Ans. 2.64]

67. Calculate the pH of a 0.1 M solution of AlCl_3 that dissolves to give hydrated aluminium ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in solution. ($K_a = 1.4 \times 10^{-5}$)

[Ans. 2.92]

[Hint: Consider the equilibrium:



68. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH, when total concentration of buffering reagents is 0.6 mol litre $^{-1}$, pK_b for $\text{NH}_3 = 4.7, \log_{10} 2 = 0.30$. (IIT 1997)

[Ans. [Salt] = 0.4 M, [Base] = 0.2 M]

69. The solubility product of AgCl in water is 1.5×10^{-10} at 18°C . Calculate its solubility at the same temperature.

[Ans. $1.75 \times 10^{-3} \text{ g L}^{-1}$]

70. The solubility product of AgBr is 4×10^{-13} and the concentration of Ag^+ ions in it is $1 \times 10^{-6} \text{ mol L}^{-1}$. What is concentration of Br^- ions?

[Ans. $4 \times 10^{-7} \text{ mol L}^{-1}$]

71. A sample of hard water contains 0.005 mole of CaCl_2 per litre. What is the minimum concentration of Na_2SO_4 which must be exceeded for removing calcium ions from this water solution? The solubility product of CaSO_4 is 2.4×10^{-5} .

[Ans. $4.8 \times 10^{-3} \text{ mol L}^{-1}$]

72. Solubility of AgCl at 20°C is $1.435 \times 10^{-5} \text{ g L}^{-1}$. Calculate the solubility product of AgCl .

[Ans. 1×10^{-14}]

73. Given, that the solubility product of radium sulphate (RaSO_4) is 4×10^{-11} . Calculate its solubility in:

(a) pure water.

(b) $0.10 \text{ M Na}_2\text{SO}_4$.

(Dhanbad 1992)

[Ans. (a) $6.32 \times 10^{-6} \text{ mol L}^{-1}$ (b) $4 \times 10^{-10} \text{ mol L}^{-1}$]

74. Calculate the solubility of AgCl in 0.20 M AgNO_3 . K_{sp} AgCl is 1×10^{-10} .

[Ans. $5 \times 10^{-10} \text{ mol L}^{-1}$]

75. The values of K_{sp} for sparingly soluble AB and MB_2 are each equal to 4.0×10^{-18} . Which salt is more soluble?

[Ans. Solubility $AB = 2 \times 10^{-9}$; Solubility $MB_2 = 1.0 \times 10^{-6}$; MB_2 is more soluble]

76. The solubility of CaSO_4 at 25°C is 2.036 g L^{-1} and degree of dissociation of the saturated solution at this temperature is 52.25%. Compute K_{sp} for CaSO_4 . (Mol. mass of $\text{CaSO}_4 = 136$)

[Ans. 6.12×10^{-5}]

77. The concentration of the Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20°C is $1.5 \times 10^{-4} \text{ mol L}^{-1}$. Compute the solubility product constant of Ag_2CrO_4 at 20°C .

[Ans. 1.7×10^{-12}]

78. K_{sp} AgCl is 2.8×10^{-10} at 25°C . Calculate the solubility of AgCl in (a) pure water (b) 0.1 M AgNO_3 (c) 0.1 M KCl and (d) 0.1 M KNO_3 .

(MLNR 1994)

[Ans. (a) $1.673 \times 10^{-3} \text{ mol L}^{-1}$ (b) $2.8 \times 10^{-9} \text{ mol L}^{-1}$
(c) $2.8 \times 10^{-9} \text{ mol L}^{-1}$ (d) No common ion is present, so treat it like water $2.8 \times 10^{-9} \text{ mol L}^{-1}$]

79. A solution is saturated with respect to strontium fluoride and strontium carbonate. The fluoride ion concentration in the solution is found to be $3.7 \times 10^{-2} \text{ mol L}^{-1}$. What is the value of $[\text{CO}_3^{2-}]$?

$K_{sp} \text{ SrF}_2 = 7.9 \times 10^{-10}$ and $K_{sp} \text{ SrCO}_3 = 7.0 \times 10^{-10}$

[Ans. $1.2 \times 10^{-3} \text{ mol L}^{-1}$]

[Hint: $\frac{K_{sp} \text{ SrCO}_3}{K_{sp} \text{ SrF}_2} = \frac{[\text{Sr}^{2+}][\text{CO}_3^{2-}]}{[\text{Sr}^{2+}][\text{F}^-]^2} = \frac{[\text{CO}_3^{2-}]}{[\text{F}^-]^2}$]

80. A solution contains 0.01 mol L^{-1} of each Pb^{2+} and Zn^{2+} ions. The solution is saturated with H_2S when $[\text{S}^{2-}]$ is $1.0 \times 10^{-14} \text{ mol L}^{-1}$. Predict which one of the two ions will be precipitated from the solution? $K_{sp} \text{ PbS} = 2.4 \times 10^{-27}$ and $K_{sp} \text{ ZnS} = 1.0 \times 10^{-21}$.

[Ans. Both the ions will be precipitated as ionic products exceed the solubility products of both the sulphides.]

81. An acid type indicator, HIn , differs in colour from its conjugate base In^- . The human eye is sensitive to colour differences only when the ratio $[\text{In}^-]/[\text{HIn}]$ is greater than 10 or smaller than 0.1. What should be the minimum change in pH of solution to observe a complete colour change? ($K_a = 10^{-5}$)

(IIT 1997)

[Ans. 2]

[Hint: For calculation of pH we can use following relation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

(i) $\text{pH} = 5 + \log_{10} 10 = 6$

(ii) $\text{pH} = 5 + \log_{10} 0.1 = 4$

Thus, minimum pH change will be 2.]

82. A sample of AgCl was treated with 5 mL of $1.5 \text{ M Na}_2\text{CO}_3$ solution to give Ag_2CO_3 . The remaining solution contained 0.0026 g Cl^- per litre. Calculate the solubility product of AgCl . ($K_{sp} \text{ Ag}_2\text{CO}_3 = 8.2 \times 10^{-12}$)

(IIT 1997)

[Ans. $K_{sp} \text{ AgCl} = 1.71 \times 10^{-10}$]

83. Calculate the simultaneous solubility of CaF_2 and SrF_2 . K_{sp} for the two salts are 4×10^{-11} and 2.8×10^{-9} respectively.

[Ans. 1.25×10^{-5} and 8.75×10^{-4}]

84. The solubility product of Fe(OH)_3 is 1×10^{-36} . What is the minimum concentration of OH^- ions required to precipitate Fe(OH)_3 from 0.001 M solution of FeCl_3 ?

[Ans. $1 \times 10^{-11} \text{ mol L}^{-1}$]

85. The solubility product of AgCl is 1.5×10^{-10} . Predict whether there will be any precipitation by mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M AgNO_3 solution.

[Ans. Since, ionic product (2.5×10^{-5}) is greater than solubility product, precipitation will occur.]

86. A solution containing 0.1 M Zn^{2+} and 0.01 M Cu^{2+} is saturated with H_2S . The S^{2-} concentration is $8.1 \times 10^{-31} \text{ M}$. Will ZnS or CuS precipitate?

$K_{sp} \text{ ZnS} = 3.0 \times 10^{-23}$ and $K_{sp} \text{ CuS} = 8.0 \times 10^{-34}$

[Ans. CuS precipitates]

87. The precipitate of M_2S_3 is obtained on mixing equal volumes of solutions S_1 having $[\text{M}^{3+}] = 4 \times 10^{-5} \text{ M}$ and S_2 having $[\text{S}^{2-}] = 2 \times 10^{-3} \text{ M}$. Calculate its solubility product.

[Ans. 4×10^{-17}]

[Hint: Let 1 litre of both S_1 and S_2 be mixed; then their concentration in mixture will become half ($M_1V_1 = M_2V_2$).

$[\text{M}^{3+}] = 2 \times 10^{-4} \text{ M}; [\text{S}^{2-}] = 1 \times 10^{-3}$

$$K_{sp} \text{ M}_2\text{S}_3 = [\text{M}^{3+}]^2[\text{S}^{2-}]^3$$

$$= [2 \times 10^{-4}]^2[1 \times 10^{-3}]^3 = 4 \times 10^{-17} \text{ M}^5$$

88. Solubility products (K_{sp}) of two salts AB and A_2C are same where, ' A ' is mono cation and B and C are anions. Calculate the ratio of their solubilities.

[Ans. $(16 K_{sp})^{1/3}$]

[Hint: Use; $K_{sp} AB = x^2$

$$K_{sp} A_2 C = 4y^3]$$

89. Calculate the pH of a solution having 0.1 M formic acid and 0.2 M HCl. Also find the concentration of all the anions present in the solution.

[Ans. pH = 0.6989, $[\text{OH}^-] = 5 \times 10^{-14}$]

90. Calculate the accurate pH of 5×10^{-3} M formic acid solution. $K_a (\text{HCOOH}) = 2 \times 10^{-4}$.

[Ans. pH = 3.043]

[Hint: Use the quadratic equation:

$$[\text{H}^+]^2 + K_a [\text{H}^+] - CK_a = 0$$

$$[\text{H}^+] = \frac{-K_a + \sqrt{K_a^2 + 4CK_a}}{2} = 9.05 \times 10^{-4}$$

(On substituting the values of C and K_a)

$$\text{pH} = -\log_{10} [\text{H}^+]$$

$$= -\log_{10} [9.05 \times 10^{-4}]$$

$$= 3.043$$

91. Calculate the accurate pH of 5×10^{-6} M pyridine solution.

$K_b (\text{pyridine}) = 1.5 \times 10^{-9}$.

[Ans. 7.1215]

[Hint: Use; $[\text{OH}^-]^2 = CK_b + K_w$

$$[\text{OH}^-] = \sqrt{5 \times 10^{-6} \times 1.5 \times 10^{-9} + 10^{-14}} \\ = \sqrt{1.75 \times 10^{-14}}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$= -\log \sqrt{1.75 \times 10^{-14}} = 6.8785$$

$$\text{pH} = 7.1215]$$

92. Ionic product of water (K_w) at two different temperatures 25°C and 50°C are 1.08×10^{-14} and 5.474×10^{-14} respectively. Assuming ΔH of any reaction to be independent of temperature, calculate enthalpy of neutralisation of strong acid with strong base.

[Ans. 12.5 kcal]

[Hint: Use $\log \frac{K_{w2}}{K_{w1}} = \frac{\Delta H}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$]

93. The solubility product of PbI_2 is 7.47×10^{-9} at 15°C and 1.39×10^{-8} at 25°C . Calculate the molar heat of solution of PbI_2 .

[Ans. 44.318 kJ/mol]

[Hint: $\log \frac{(K_{sp})_2}{(K_{sp})_1} = \frac{\Delta H}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$]

$$\log \frac{[1.39 \times 10^{-8}]}{[7.47 \times 10^{-9}]} = \frac{\Delta H}{2.303 \times 8.314} \left(\frac{1}{288} - \frac{1}{298} \right)$$

$$\Delta H = 44318.4 \text{ J} = 44.318 \text{ kJ/mol}$$

94. Given, a solution of acetic acid. How many times of the acid concentration, acetate salt should be added to obtain a solution with pH = 7?

K_a for dissociation of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$.

[BCECE (Mains) 2007]

[Ans. 1.799×10^2]

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. A certain weak acid has a dissociation constant of 1×10^{-4} . The equilibrium for its reaction with a strong base is:

- (a) 1×10^{-4} (b) 1×10^{-10} (c) 1×10^{10} (d) 1×10^{14}

[Hint: $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}$;

$$K_{eq} = \frac{1}{K_h} = 1 \times 10^{10}$$

2. Which one of the following formulae represents Ostwald's dilution law for a binary electrolyte whose degree of dissociation is ' α ' and concentration C ?

$$(a) K = \frac{(1-\alpha)C}{\alpha} \quad (b) K = \frac{\alpha^2 C}{(1-\alpha)}$$

$$(c) K = \frac{(1-\alpha)C}{\alpha^2} \quad (d) K = \frac{\alpha^2}{(1-\alpha)C}$$

3. Which of the following is the correct quadratic form of the Ostwald's dilution law equation? [CET (J&F 2009)]

$$(a) \alpha^2 C + \alpha K - K = 0 \quad (b) \alpha^2 C - \alpha K - K = 0$$

$$(c) \alpha^2 C - \alpha K + K = 0 \quad (d) \alpha^2 C + \alpha K + K = 0$$

[Hint: According to Ostwald's dilution law :

$$K = \frac{C\alpha^2}{1-\alpha}$$

$$\text{or } C\alpha^2 + K\alpha - K = 0$$

4. A monoprotic acid in 1.00 M solution is 0.001% ionised. The dissociation constant of acid is:

- (a) 1.0×10^{-3} (b) 1.0×10^{-6}
(c) 1.0×10^{-8} (d) 1.0×10^{-10}

5. Formic acid is 4.5% dissociated in a 0.1 N solution at 20°C . The ionisation constant of formic acid is:

- (a) 21×10^{-4} (b) 21
(c) 0.21×10^{-4} (d) 2.1×10^{-4}

6. The fraction of total molecules which is ionised in a solution of an electrolyte is known as:

- (a) molecular velocity
(b) order of reaction
(c) degree of ionisation
(d) mole fraction of the electrolyte

77. One litre of water contains 10^{-7} mole of H^+ ions. Degree of ionisation of water is:

(a) $1.8 \times 10^{-7}\%$ (b) $0.8 \times 10^{-9}\%$
 (c) $3.6 \times 10^{-9}\%$ (d) $3.6 \times 10^{-7}\%$

[Hint: Since, 1 litre of water contains $1000/18$ mole, degree of ionisation = $10^{-7}/\frac{1000}{18}$]

78. The degree of dissociation in a weak electrolyte increases:
- (a) on increasing pressure (b) on decreasing dilution
 - (c) on increasing dilution (d) on increasing concentration

79. Which of the following is the weakest base?

(a) NaOH (b) $\text{Ca}(\text{OH})_2$
 (c) NH_4OH (d) KOH

80. Acetic acid is a weak electrolyte because:

- (a) its molecular mass is high
- (b) it is a covalent compound
- (c) it is highly unstable
- (d) it does not dissociate much or its ionisation is very small

81. When NH_4Cl is added to NH_4OH solution, the dissociation of ammonium hydroxide is reduced. It is due to:

[PMT (MP) 1993]

(a) common ion effect (b) hydrolysis
 (c) oxidation (d) reduction

82. The addition of HCl will not suppress the ionisation of:

[PMT (MP) 1993]

(a) acetic acid (b) sulphuric acid
 (c) H_2S (d) benzoic acid

83. H_2S in presence of HCl precipitates second group radicals but not fourth group radicals because:

(a) HCl activates H_2S
 (b) HCl decreases concentration of sulphide ions
 (c) HCl increases concentration of sulphide ions
 (d) sulphides of IV group are unstable in HCl

84. The solubility product of a salt AB is 1×10^{-8} . In a solution, in which concentration of A is 10^{-3} M , AB will precipitate when the concentration of B will be:

[PET (MP) 1990]

(a) 10^{-7} M (b) 10^{-4} M (c) 10^{-5} M (d) 10^{-6} M

85. The solubility product of BaSiO_4 is 1.5×10^{-9} . The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration:

(a) 10^{-9} M (b) 10^{-8} M
 (c) 10^{-7} M (d) 10^{-6} M

86. Solubility product of BaCl_2 is 4×10^{-9} . Its solubility would be:

[UGET (Manipal) 2006]

(a) 1×10^{-27} (b) 1×10^{-3} (c) 1×10^{-7} (d) 1×10^{-2}

87. Which pair will show common ion effect? [PMT (MP) 1990]

(a) $\text{BaCl}_2 + \text{Ba}(\text{NO}_3)_2$ (b) $\text{NaCl} + \text{HCl}$
 (c) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ (d) $\text{AgCN} + \text{KCN}$

88. What is the correct representation of solubility product of Ag_2CrO_4 ?

(a) $[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$ (b) $[\text{Ag}^+][\text{CrO}_4^{2-}]$
 (c) $[\text{Ag}^+][\text{CrO}_4^{2-}]$ (d) $[2\text{Ag}^+]^2[\text{CrO}_4^{2-}]$

19. Solubility product of silver bromide 5×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is : (AIEEE 2010)

(a) $6.2 \times 10^{-5} \text{ g}$ (b) $5.0 \times 10^{-8} \text{ g}$
 (c) $12 \times 10^{-10} \text{ g}$ (d) $12 \times 10^{-9} \text{ g}$

20. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

[JAMU (PMT) 2009]

(a) $10^{-4} \text{ M Ag}^+ + 10^{-4} \text{ M Cl}^-$
 (b) $10^{-5} \text{ M Ag}^+ + 10^{-5} \text{ M Cl}^-$
 (c) $10^{-6} \text{ M Ag}^+ + 10^{-6} \text{ M Cl}^-$
 (d) $10^{-10} \text{ M Ag}^+ + 10^{-10} \text{ M Cl}^-$

21. Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to:

(a) 1.0 (b) 100.0 (c) 10.0 (d) 0.1

22. Which hydroxide will have lowest value of solubility product at normal temperature (25°C)? (IIT 1996)

(a) $\text{Mg}(\text{OH})_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) $\text{Ba}(\text{OH})_2$ (d) $\text{Be}(\text{OH})_2$

23. The solubility of $\text{Al}(\text{OH})_3$ is ' S ' g mol L^{-1} . Its solubility product is:

(a) S^2 (b) S^3 (c) $27S^4$ (d) $27S^3$

24. The solubility products of $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ are 8.5×10^{-23} and 1.8×10^{-14} at room temperature. If the solution contains Al^{3+} and Zn^{2+} ions, the ion first precipitated by adding NH_4OH is:

(a) Al^{3+} (b) Zn^{2+}
 (c) both (d) none of these

25. The solubility product of CaSO_4 is 2.4×10^{-5} . When 100 mL of 0.01 M CaCl_2 and 100 mL of 0.02 M Na_2SO_4 are mixed, then:

(a) Na_2SO_4 will precipitate (b) both will precipitate
 (c) CaSO_4 will precipitate (d) none will precipitate

26. The solubility of AgCl in a solution of common salt is lower than in water. This is due to:

(a) salt effect (b) lowering of solubility effect
 (c) common ion effect (d) complex formation

27. The solubility products of AgCl and AgI are 1.1×10^{-10} and 1.6×10^{-16} respectively. If AgNO_3 is added drop by drop to the solution containing both chloride and iodide ions, the salt precipitated first is:

(a) AgI (b) AgNO_3
 (c) AgCl (d) both AgI and AgCl

28. Why is pure NaCl precipitated when HCl gas is passed in saturated solution of NaCl ? (PET (MP) 1993)

(a) Impurities dissolve in HCl
 (b) The value of $[\text{Na}^+]$ and $[\text{Cl}^-]$ product becomes smaller than K_{sp} of NaCl
 (c) The value of $[\text{Na}^+]$ and $[\text{Cl}^-]$ product becomes higher than K_{sp} of NaCl
 (d) HCl dissolves in water

29. On passing a current of HCl gas in saturated solution of NaCl , the solubility of NaCl :

- (a) increases (b) decreases
 (c) remains unchanged (d) NaCl decomposes
- 30.** In a saturated solution of electrolytes, the ionic products of their concentration are constant at a particular temperature. This constant for an electrolyte is known as:
 (a) ionic product (b) ionisation constant
 (c) dissociation constant (d) solubility product
- 31.** On addition of ammonium chloride to a solution of NH_4OH :
 (a) dissociation of NH_4OH increases
 (b) concentration of OH^- decreases
 (c) concentration of OH^- increases
 (d) concentration of both NH_4^+ and OH^- increases
- 32.** The solubility product of a salt A_2B is 4×10^{-9} . Its solubility would be:
 (a) $4 \times 10^{-2} M$ (b) $2 \times 10^{-4} M$
 (c) $1 \times 10^{-4} M$ (d) $1 \times 10^{-3} M$ (HT 1990)
- 33.** If the concentration of CrO_4^{2-} ions in a saturated solution of silver chromate is 2×10^{-4} , solubility product of silver chromate will be:
 [PET (MP) 1992]
 (a) 4×10^{-8} (b) 8×10^{-12}
 (c) 16×10^{-12} (d) 32×10^{-12}
- 34.** 50% neutralisation of a solution of formic acid ($K_a = 2 \times 10^{-4}$) with NaOH would result in a solution having a hydrogen ion concentration of:
 (a) 2×10^{-4} (b) 3.7 (c) 2.7 (d) 1.85
- 35.** The solubility product of BaCl_2 is 4×10^{-9} . Its solubility in mol L^{-1} would be:
 (a) 1×10^{-3} (b) 1×10^{-9}
 (c) 4×10^{-27} (d) 1×10^{-27}
- 36.** Addition of conc. HCl to saturated BaCl_2 solution precipitate BaCl_2 because:
 [BHU (Screening) 2010]
 (a) at constant temperature the product $[\text{Ba}^{2+}][\text{Cl}^-]^2$ remains constant in a saturated solution
 (b) ionic product of $[\text{Ba}^{2+}][\text{Cl}^-]$ remains constant in a saturated solution
 (c) of common ion effect
 (d) it follows Le-Chatelier's principle
- 37.** How many grams of CaC_2O_4 will dissolve in distilled water to make one litre of saturated solution? ($K_{sp} = 2.5 \times 10^{-9}$ and its molecular mass is 128)
 [PMT (MP) 1993]
 (a) 0.0064 g (b) 0.0128 g (c) 0.0032 g (d) 0.0640 g
- 38.** On the addition of a solution containing CrO_4^{2-} ions to the solution of Ba^{2+} , Sr^{2+} and Ca^{2+} ions, the precipitate obtained first will be of:
 [PET (MP) 1993]
 (a) CaCrO_4 (b) SrCrO_4
 (c) BaCrO_4 (d) a mixture of all the three
- 39.** Ostwald's dilution law is applicable in the case of the solution of:
 (a) NaCl (b) NaOH (c) H_2SO_4 (d) CH_3COOH
- 40.** What will be the solubility of AgCl in a 0.1 M NaCl solution?
 (K_{sp} $\text{AgCl} = 1.20 \times 10^{-10}$)
 [PMT (MP) 1992]
 (a) 0.1 M (b) $1.2 \times 10^{-4} M$
 (c) $1.2 \times 10^{-9} M$ (d) $1.2 \times 10^{-10} M$
- 41.** Which of the following metal sulphides has maximum solubility in water?
 (a) CdS ($K_{sp} = 36 \times 10^{-30}$) (b) FeS ($K_{sp} = 11 \times 10^{-20}$)
 (c) HgS ($K_{sp} = 32 \times 10^{-54}$) (d) ZnS ($K_{sp} = 11 \times 10^{-22}$)
- 42.** The ionisation constant of acetic acid is 1.8×10^{-5} . The concentration at which it will be dissociated to 2%, is:
 (a) 1 M (b) 0.045 M (c) 0.018 M (d) 0.45 M
- 43.** The solubility of PbSO_4 in 0.01 M Na_2SO_4 solution is:
 (K_{sp} for $\text{PbSO}_4 = 1.25 \times 10^{-9}$)
 (a) $1.25 \times 10^{-7} \text{ mol L}^{-1}$ (b) $1.25 \times 10^{-9} \text{ mol L}^{-1}$
 (c) $1.25 \times 10^{-10} \text{ mol L}^{-1}$ (d) $1.25 \times 10^{-18} \text{ mol L}^{-1}$
- 44.** The value of K_{sp} for HgCl_2 is 4×10^{-15} . The concentration of Cl^- ion in its aqueous solution at saturation point is:
 (a) $1 \times 10^{-5} M$ (b) $4 \times 10^{-15} M$
 (c) $8 \times 10^{-15} M$ (d) $2 \times 10^{-5} M$
- 45.** If the solubility of PbBr_2 is 'S' gram mol per litre, considering 80% ionisation, its ionic product is:
 (a) $2S^3$ (b) $4S^2$ (c) $4S^3$ (d) $2S^4$
- 46.** If the solubility of M_3N_2 is 'S' g mol L^{-1} , its solubility product is:
 (a) $2S^3$ (b) $8S^4$ (c) $108S^5$ (d) $27S^3$
- 47.** At 30 °C, the solubility of Ag_2CO_3 ($K_{sp} = 8 \times 10^{-12}$) would be greatest in one litre of:
 (a) 0.05 M Na_2CO_3 (b) 0.05 M AgNO_3
 (c) pure water (d) 0.05 M NH_3
- 48.** The following equilibrium exists in aqueous solution;

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$$

 If dilute HCl is added:
 (a) the equilibrium constant will increase
 (b) the equilibrium constant will decrease
 (c) acetate ion concentration will increase
 (d) acetate ion concentration will decrease
- 49.** According to Arrhenius concept, base is a substance that:
 (a) gives H^+ ions in solution
 (b) gives OH^- ions in solution
 (c) accepts electrons
 (d) donates electrons
- 50.** According to Bronsted-Lowry concept an acid is a substance which:
 (a) accepts proton (b) gives an electron pair
 (c) gives proton (d) combines with H_3O^+ ions
- 51.** According to Lewis concept, a base is a substance which:
 (a) donates an electron pair (b) accepts an electron pair
 (c) produces hydronium ions (d) combines with OH^- ions
- 52.** The strength of the acid depends on the:
 (a) number of hydrogen atoms present in the molecule
 (b) oxygen content
 (c) density
 (d) concentration of hydrogen ions furnished by ionisation
- 53.** Cl^- ion is the conjugate base of:
 (a) HCl (b) HOCl (c) HClO_3 (d) HClO_4

54. Which one of the following is the strongest acid?
 (a) CH_3COOH (b) CH_2ClCOOH
 (c) CHCl_2COOH (d) CCl_3COOH
55. Number of H^+ ions present in 250 mL of lemon juice of pH = 3 is:
 (a) 1.506×10^{22} (b) 1.506×10^{23}
 (c) 1.506×10^{20} (d) 3.012×10^{21}
 (e) 2.008×10^{23}
 [Hint: $[\text{H}^+] = 10^{-3} M$
 Number of moles of H^+ ions in 250 mL = $\frac{10^{-3}}{4} \times 6.023 \times 10^{23}$
 $= 1.506 \times 10^{20}$]
56. Conjugate acid of OH^- base is:
 (a) H_2 (b) H_2O (c) H^+ (d) H_3O^+
57. Which among the following qualifies as a Lewis acid?
 (a) NaF (b) NaCl (c) BF_3 (d) MgCl_2
58. Which of the following will qualify as Lewis base?
 (a) BCl_3 (b) CH_4 (c) Cl_2 (d) NH_3
59. NH_4^+ ion in an aqueous solution will behave as:
 (a) a base (b) an acid
 (c) both acid and base (d) neutral
60. In the dissociation of bicarbonate ion, the conjugate base involved is:
 (a) CO_3^{2-} (b) CO_2 (c) H_2CO_3 (d) CO
61. Which one of the following is an acidic salt?
 (a) NaHSO_4 (b) Na_2SO_4 (c) Na_2SO_3 (d) Na_2SO_4
62. The conjugate acid of NH_2^- is:
 (a) NH_4^+ (b) NH_3 (c) NH_2OH (d) N_2H_4
63. The correct increasing order of strengths of following acids is:
 (a) $\text{H}_2\text{SO}_4, \text{CH}_3\text{COOH}, \text{H}_2\text{CO}_3$
 (b) $\text{CH}_3\text{COOH}, \text{H}_2\text{SO}_4, \text{H}_2\text{CO}_3$
 (c) $\text{H}_2\text{CO}_3, \text{CH}_3\text{COOH}, \text{H}_2\text{SO}_4$
 (d) $\text{CH}_3\text{COOH}, \text{H}_2\text{CO}_3, \text{H}_2\text{SO}_4$
64. The decreasing order of strength of following bases is:
 (a) $\text{Cl}^-, \text{CH}_3\text{COO}^-, \text{NH}_3$ (b) $\text{CH}_3\text{COO}^-, \text{NH}_3, \text{Cl}^-$
 (c) $\text{CH}_3\text{COO}^-, \text{Cl}^-, \text{NH}_3$ (d) $\text{NH}_3, \text{CH}_3\text{COO}^-, \text{Cl}^-$
65. Which one of the following does not act as a Bronsted acid?
 (a) NH_4^+ (b) HCO_3^- (c) HSO_3^- (d) CH_3COO^-
66. Of the given anions, the strongest Bronsted base is:
 (a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-
67. The compound that is not a Lewis acid is:
 (a) BaCl_2 (b) AlCl_3 (c) BCl_3 (d) SnCl_4
68. The dissociation constants of two acids H_A_1 and H_A_2 are 3.0×10^{-4} and 1.8×10^{-5} respectively. The relative strengths of the acids will be:
 (a) 1:4 (b) 4:1 (c) 1:16 (d) 16:1
69. In the acid-base relation;

$$\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$$
 the conjugate acid of acetic acid is:
 (a) Cl^- (b) HCl
 (c) $\text{CH}_3\text{COOH}_2^+$ (d) H_3O^+
70. The numerical value of negative power to which 10 must be raised in order to express hydrogen ion concentration, is equal to:
 (a) strength of the solution
 (b) pH of the solution
 (c) degree of hydrolysis
 (d) solubility product of the electrolyte
71. Which one of the following solutions will have pH close to unity?
 [HIT 1992; PMT(Kerala) 2008]
 (a) 100 mL of $M/10 \text{ HCl}$ + 100 mL of $M/10 \text{ NaOH}$
 (b) 55 mL of $M/10 \text{ HCl}$ + 45 mL of $M/10 \text{ NaOH}$
 (c) 10 mL of $M/10 \text{ HCl}$ + 90 mL of $M/10 \text{ NaOH}$
 (d) 75 mL of $M/5 \text{ HCl}$ + 25 mL of $M/5 \text{ NaOH}$
 (e) 50 mL of $M/5 \text{ HCl}$ + 50 mL of $M/5 \text{ NaOH}$
 [Hint: $M_{\text{mix}} V_{\text{mix}} = M_{\text{HCl}} V_{\text{HCl}} + M_{\text{NaOH}} V_{\text{NaOH}}$
 $M_{\text{mix}}(100) = \frac{1}{5} \times 75 + \frac{1}{5} \times 25 = 20$
 $M_{\text{mix}} = 0.2$
 $[\text{H}^+] = 0.2 M$
 $\text{pH} = -\log 0.2 = 0.7 \approx \text{close to unity}]$
72. 0.1 M acetic acid solution is titrated against 0.1 M NaOH solution. What would be the difference in pH between 1/4 and 3/4 stages of neutralisation of acid?
 (a) $2 \log 3/4$ (b) $2 \log 1/4$ (c) $\log 1/3$ (d) $2 \log 3$
73. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be:
 (a) unionised in the small intestine and in the stomach
 (b) completely ionised in the small intestine and in the stomach
 (c) ionised in the stomach and almost unionised in the small intestine
 (d) ionised in the small intestine and almost unionised in the stomach
74. When 10^{-6} mole of a monobasic strong acid is dissolved in one litre of solvent, the pH of the solution is:
 (a) 6 (b) 7
 (c) less than 6 (d) more than 7
75. When pH of a solution is 2, the hydrogen ion concentration in mol litre $^{-1}$ is:
 (a) 1×10^{-12} (b) 1×10^{-2} (c) 1×10^{-7} (d) 1×10^{-4}
76. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6}$ mol litre $^{-1}$. The value of K_w at 90°C is:
 (a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}
77. The pH of 10^{-8} molar solution of HCl in water is:
 (CPMT 1990; MLNR 1992)
 (a) 8 (b) -8
 (c) between 7 and 8 (d) between 6 and 7
78. When pH of 0.001 M solution of HCl is:
 (a) 1.0 (b) 3 (c) 4.0 (d) 5.0
79. The pH of a solution containing 0.1 N NaOH solution is:
 (a) 1 (b) 10^{-1} (c) 13 (d) 10^{-13}
80. When 0.4 g of NaOH is dissolved in one litre of solution, the pH of the solution is:
 (a) 12 (b) 2 (c) 6 (d) 10

81. The pH of an aqueous solution of a 0.1 M solution of a weak monoprotic acid which is 1% ionised is:
 (a) 1 (b) 2 (c) 3 (d) 11
82. The pH of a 0.002 N acetic acid solution if it is 2.3% ionised at this dilution is: ($\log 4.6 = 0.6628$)
 (a) 4.3372 (b) 0.4337 (c) 3.4337 (d) 0.6628
83. 0.1 M HCl and 0.1 M H_2SO_4 each of volume 2 mL are mixed and the volume is made up to 6 mL by adding 2 mL of 0.01 N NaCl solution. The pH of the resulting mixture is:
 (a) 1.17 (b) 1.0
 (c) 0.3 (d) $\log 2 - \log 3$

[Hint: Number of millimoles of H^+ = $0.1 \times 2 + 0.1 \times 2 \times 2 = 0.6$

$$\text{Concentration of } [\text{H}^+] = \frac{0.6}{6} = 0.1\text{ M}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$= -\log 0.1 = 1$$

84. The pH and pOH of 0.1 M aqueous solution of HNO_3 are:
 (a) 0, 14 (b) 14, 0 (c) 13, 1 (d) 1, 13
85. The pH of a neutral solution at 50°C is: ($K_w = 10^{-13.26}$ at 50°C)
 (a) 7 (b) 6.0 (c) 7.23 (d) 6.63
86. The pH of 0.005 molar aqueous solution of sulphuric acid is approximately:
 (a) 0.005 (b) 1 (c) 0.1 (d) 2.0
87. 20 mL of 0.1 N HCl is mixed with 20 mL of 0.1 N KOH solution; the pH of the solution will be:
 (a) 0 (b) 2 (c) 7 (d) 9
88. When the pH changes from 4 to 2, the hydrogen ion concentration will increase by a factor:
 (a) 2 (b) 1/2 (c) 10^2 (d) $10^{0.5}$
89. 100 mL of 0.2 N HCl is added to 100 mL of 0.18 N NaOH and the whole volume is made one litre. The pH of the resulting solution is:
 (a) 1 (b) 2 (c) 3 (d) 4
90. 10 mL of 0.1 N HCl is added to 990 mL solution of NaCl. The pH of the resulting solution is:
 (a) zero (b) 3 (c) 7 (d) 10

91. Solutions with reserve acidity and alkalinity are called:
 (a) isohydric solutions (b) true solutions
 (c) normal solutions (d) buffer solutions
92. A solution which is resistant to changes of pH on dilution, or addition of small amounts of an acid or a base is known as:
 (a) buffer solution (b) true solution
 (c) isohydric solution (d) ideal solution
93. Which of the following is a buffer solution?
 (a) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 (b) $\text{NaCl} + \text{NaOH}$
 (c) $\text{HCl} + \text{NH}_4\text{Cl}$
 (d) $\text{CH}_3\text{COOH} + \text{HCl}$
94. The hydrogen ion concentration of a buffer solution consisting of a weak acid and its sodium salt is given by:
 (a) $[\text{H}^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$ (b) $[\text{H}^+] = K_a [\text{Salt}]$
 (c) $[\text{H}^+] = K_a [\text{Acid}]$ (d) $[\text{H}^+] = K_a \frac{[\text{Salt}]}{[\text{Acid}]}$

95. When a buffer solution of CH_3COOH and CH_3COONa is diluted with water:
 (a) CH_3COO^- ion concentration increases
 (b) $[\text{H}^+]$ ion concentration increases
 (c) OH^- ion concentration increases
 (d) H^+ ion concentration does not change
96. In a buffer solution consisting of a weak acid and its salt, the ratio of concentration of salt to acid is increased tenfold; then the pH of the solution will:
 (a) increase by one (b) increase tenfold
 (c) decrease by one (d) decrease tenfold
97. Acetic acid and propionic acid have K_a values 1.75×10^{-5} and 1.3×10^{-5} respectively at a certain temperature. An equimolar solution of a mixture of the two acids is partially neutralised by NaOH. How is the ratio of the contents of acetate and propionate ions related to the K_a values and the molarity?

- (a) $\left[\frac{\alpha}{1-\alpha} \right] = \frac{1.75}{1.3} \times \left[\frac{\beta}{1-\beta} \right]$, where, α and β are ionised fractions of the acids
 (b) The ratio is unrelated to the K_a values
 (c) The ratio is unrelated to the molarity
 (d) The ratio is unrelated to the pH of the solution

98. A weak acid of dissociation constant 10^{-5} is being titrated with aqueous NaOH solution. The pH at the point of one-third neutralisation of the acid will be: [JEE (WB) 2010]

- (a) $5 + \log 2 - \log 3$ (b) $5 - \log 2$
 (c) $5 - \log 3$ (d) $5 - \log 6$

[Hint: $pK_a = -\log 10^{-5} = 5$

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 5 + \log \frac{1/3}{2/3} = 5 - \log 2$$

99. Which of the following salts when dissolved in water will hydrolyse?
 (a) NaCl (b) KCl (c) NH_4Cl (d) Na_2SO_4
100. The aqueous solution of AlCl_3 is acidic due to:
 (a) cation hydrolysis
 (b) anion hydrolysis
 (c) hydrolysis of both the ions
 (d) dissociation

101. A certain buffer solution contains equal concentration of X^- and H_X . The K_b for X^- is 10^{-10} . The pH of the buffer is:
 (a) 4 (b) 7 (c) 10 (d) 14
102. An acidic buffer solution can be prepared by mixing the solutions of:
 (a) sodium acetate and acetic acid
 (b) ammonium chloride and ammonium hydroxide
 (c) sulphuric acid and sodium hydroxide
 (d) sodium chloride and sodium hydroxide

103. The compound whose aqueous solution has highest pH, is:
 (a) NaCl (b) NH_4Cl
 (c) $\text{CH}_3\text{COONH}_4$ (d) Na_2CO_3

104. The compound whose 0.1 M solution is basic, is:
 (a) ammonium chloride (b) ammonium acetate
 (c) ammonium sulphate (d) sodium acetate
105. Aqueous solution of copper sulphate:
 (a) turns blue litmus red
 (b) turns red litmus blue
 (c) does not affect litmus
 (d) affects both red and blue litmus
106. When an equivalent of a strong acid is added to one equivalent of a weak base, the resulting solution will be:
 (a) neutral (b) acidic
 (c) alkaline (d) coloured
107. Indicators used in acid-base titrations are:
 (a) strong organic acids
 (b) strong organic bases
 (c) weak organic acids or weak organic bases
 (d) non-electrolytes
108. For the titration between oxalic acid and sodium hydroxide, the indicator used is:
 (a) potassium permanganate (b) phenolphthalein
 (c) litmus (d) methyl orange
109. Phenolphthalein gives a pink colour in alkaline medium due to the fact that:
 (a) it is a coloured compound
 (b) it ionises to give coloured ions
 (c) it is decomposed by alkali
 (d) it forms a complex compound with alkali
110. Which is the best choice for weak base-strong acid titration?
 [JEE (Orissa) 2008]
- (a) Methyl red (b) Litmus
 (c) Phenol red (d) Phenolphthalein
111. Water is:
 (a) a base (b) an acid
 (c) non-electrolyte (d) an amphiprotic molecule
112. An aqueous solution, whose pH is zero, is:
 (a) alkaline (b) neutral
 (c) acidic (d) amphoteric
113. 0.1 N solution of Na_2CO_3 is being titrated with 0.1 N HCl . The best indicator to be used is:
 (a) potassium ferricyanide (b) phenolphthalein
 (c) methyl red (d) litmus
114. In the reaction, $\text{AlCl}_3 + \text{Cl}^- = \text{AlCl}_4^-$, AlCl_3 can be classified as:
 (a) a base (b) an acid
 (c) a salt (d) none of these
115. Sulphuric acid is a dibasic acid. Hence, it forms:
 (a) acidic salt (b) basic and acidic salt
 (c) acidic and normal salt (d) double salt
116. The buffer solutions play an important role in:
 (a) increasing the pH value (b) decreasing the pH value
 (c) keeping the pH constant (d) none of these
117. Which of the following will occur if 1.0 M solution of a weak acid is diluted to 0.01 M at constant temperature?
 (AHMS 1993)
- (a) $[\text{H}^+]$ will decrease to 0.01 M
 (b) pH will decrease by 2 units
- (c) K_a will increase
 (d) Percentage ionisation will increase
118. Which one of the following indicators works in the pH range $8 - 9.8$?
 (a) Litmus (b) Phenolphthalein
 (c) Methyl red (d) Methyl orange
119. What is $[\text{OH}^-]$ in the final solution prepared by mixing 20 mL of 0.05 M HCl with 30 mL of 0.10 M Ba(OH)_2 ?
 [CBSE (PMT) 2009]
- (a) 0.12 M (b) 0.10 M
 (c) 0.40 M (d) 0.005 M
- [Hint : $n_{\text{H}^+} = \frac{MV}{1000} = \frac{0.05 \times 20}{1000} = 10^{-3}\text{ mol}$
- $$\begin{aligned} n_{\text{OH}^-} &= 2 \times n_{\text{Ba(OH)}_2} \\ &= 2 \times \frac{MV}{1000} = 2 \times \frac{0.1 \times 30}{1000} = 6 \times 10^{-3}\text{ mol} \end{aligned}$$
- Remaining moles of OH^- after neutralization
 $= 6 \times 10^{-3} - 10^{-3}$
 $= 5 \times 10^{-3}\text{ mol}$
- Conc. of $[\text{OH}^-] = \frac{n_{\text{OH}^-}}{V} \times 1000 = \frac{5 \times 10^{-3}}{50} \times 1000 = 0.1\text{ M}$
120. The following reaction is known to occur in the human body;
 $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$
 If CO_2 escapes from the system:
 (a) pH will decrease
 (b) H^+ ion concentration will decrease
 (c) H_2CO_3 concentration will be unaltered
 (d) the forward reaction will be promoted
121. The pH of human blood is about:
 (a) 5.2 (b) 6.3 (c) 7.4 (d) 8.3
122. The dissociation constants of acids HA , HB , HC and HD are 2.6×10^{-3} , 5.3×10^{-9} , 1.1×10^{-2} and 7.5×10^{-5} respectively. The weakest acid amongst these acids is:
 (a) HA (b) HB (c) HC (d) HD
123. The addition of sodium carbonate in pure water causes:
 (a) an increase in the hydrogen ion concentration
 (b) a decrease in hydroxyl ion concentration
 (c) no change in pH
 (d) an increase in pH
124. The best indicator for titrating HCl against NH_4OH is:
 (a) litmus (b) phenolphthalein
 (c) phenol red (d) methyl orange
125. A buffer solution is used in:
 (a) preparation of potash alum
 (b) the removal of PO_4^{3-} ions
 (c) increasing the pH value of a solution
 (d) precipitation of Cr(OH)_3 from CrCl_3
126. A certain weak acid has a dissociation constant of 1.0×10^{-4} . The equilibrium constant for its reaction with a strong base is:
 (a) 1.0×10^{-4} (b) 1.0×10^{-10}
 (c) 1.0×10^{10} (d) 1.0×10^{-14}
- [Hint: $\text{HA} + \text{BOH} \rightleftharpoons \text{BA} + \text{H}_2\text{O}$. The equilibrium constn.
 $= 1/K_h$ and $K_h = K_w / K_a$]

127. Which one of the following statements is correct?

- CH_3COOH is a weak acid
- NH_4Cl gives an alkaline solution in water
- CH_3COONa gives an acidic solution in water
- NH_4OH is a strong base

128. In the hydrolytic equilibrium $A^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$, $K_a = 1.0 \times 10^{-5}$. The degree of hydrolysis of 0.001 M solution of the salt is:

- 10^{-3}
- 10^{-4}
- 10^{-5}
- 10^{-6}

129. The pH of an aqueous solution of 0.1 M solution of the salt of a weak base ($K_b = 1.0 \times 10^{-5}$) and a strong acid is:

- 4.5
- 5.0
- 5.5
- 6.0

[Hint: First calculate degree of hydrolysis;

$$\alpha^2 C = K_h, K_h = (K_w / K_b), [\text{H}^+] = \alpha C$$

130. The pH of the solution obtained by mixing equal volumes of solution of pH = 5 and pH = 3 of the same electrolyte is:

- 3.3
- 4.0
- 4.5
- 2.0

$$[\text{Hint: } [\text{H}^+] = \frac{10^{-3} + 10^{-5}}{2} = \frac{100 \times 10^{-5} + 10^{-5}}{2} = 50.5 \times 10^{-5}]$$

131. pK_a values of four acids are given below at 25°C. The strongest acid is: [PMT (MP) 1990]

- 2.0
- 2.5
- 3.0
- 4.0

132. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant of the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is $3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$. The rate constant for proton transfer from water to NH_3 is:

- $6.07 \times 10^5 \text{ s}^{-1}$
- $6.07 \times 10^{-10} \text{ s}^{-1}$
- $6.07 \times 10^{-5} \text{ s}^{-1}$
- $6.07 \times 10^{10} \text{ s}^{-1}$

133. The pH of a soft drink is 3.82. The hydrogen ion concentration will be: (given a antilog 0.18 = 1.5) [PET (MP) 1990]

- $1.96 \times 10^{-2} \text{ mol lit}^{-1}$
- $1.96 \times 10^{-5} \text{ mol lit}^{-1}$
- $1.5 \times 10^{-4} \text{ mol lit}^{-1}$
- $1.5 \times 10^{-2} \text{ mol lit}^{-1}$

134. 100 mL of 0.1 M HCl is mixed with 100 mL of 0.01 M HCl. The pH of the resulting solution is:

- 2.0
- 1.0
- 1.26
- none of these

135. How many times has a solution of pH 2 higher acidity than a solution of pH 6?

- 10,000
- 12
- 400
- 4

136. For a concentrated solution of a weak electrolyte A_xB_y of concentration 'C', the degree of dissociation ' α ' is given as: [PET (Kerala) 2008]

$$(a) \alpha = \sqrt{\frac{K_{\text{eq}}}{C(x+y)}} \quad (b) \alpha = \sqrt{\frac{CK_{\text{eq}}}{xy}}$$

$$(c) \alpha = \left[\frac{K_{\text{eq}}}{(C^{x+y-1} x^x y^y)} \right]^{1/x+y}$$

$$(d) \alpha = \frac{K_{\text{eq}}}{Cx}, \quad (e) \alpha = \frac{K_{\text{eq}}}{C^{xy}}$$

$$[\text{Hint: } A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}]$$

t_0	C	0	0
t_{eq}	$C(1-\alpha)$	$x\alpha C$	$y\alpha C$

$$\begin{aligned} K_{\text{eq.}} &= \frac{(x\alpha)^x (y\alpha)^y}{C (1-\alpha)} \\ &\approx \frac{(x\alpha)^x (y\alpha)^y}{C} \quad \because (1-\alpha) \approx 1 \\ \alpha &= \left[\frac{K_{\text{eq.}}}{C^{x+y-1} x^x y^y} \right]^{1/x+y} \end{aligned}$$

137. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid;



The set that characterises the conjugate acid-base pairs is:

(JNT 1992)

- (HCl, CH_3COOH) and ($\text{CH}_3\text{COOH}_2^+$, Cl^-)
- (HCl, H_3COO^+) and (CH_3COOH , Cl^-)
- ($\text{CH}_3\text{COOH}_2^+$, HCl) and (Cl^- , CH_3COOH)
- (HCl, Cl^-) and ($\text{CH}_3\text{COOH}_2^+$, CH_3COOH)

138. The pH of a 10^{-10} M NaOH solution is:

[PMT (Uttarakhand) 2006]

- 10
- 7.01
- 6.99
- 4

139. Which of the following is strongest Lewis base?

- CH_3^-
- Ag^+
- NH_3
- H_2

140. If the solubility of lithium sodium hexafluoro aluminate, $\text{Li}_3\text{Na}_3(\text{AlF}_6)_2$ is ' S ' mol L^{-1} , its solubility product is equal to: (CPMT 1992)

- S^8
- $12S^3$
- $18S^3$
- $2916S^8$

141. Given that the dissociation constant for water is $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$. The pH of a 0.001 molar KOH solution is: (MLNR 1991)

- 10^{-11}
- 10^{-3}
- 3
- 11

142. Which one of the following solutions will have the highest pH value? (CPMT 1992)

- 0.01 M NaOH
- 0.02 M CH_3COONa
- 0.10 M NaHCO_3
- 0.10 M H_2SO_4

143. In the titration of NH_4OH with HCl, the indicator which cannot be used is:

- phenolphthalein
- methyl orange
- methyl red
- both methyl orange and methyl red

144. pH of the buffer containing 0.6 g of acetic acid and 8.2 g of sodium acetate in 1 litre of water is: (pK_a of acetic acid = 4.5)

- 7.5
- 4.5
- 5.5
- 6.5

145. At 25°C, the dissociation constants of CH_3COOH and NH_4OH in aqueous solution are almost the same. The pH of a solution of 0.01 N CH_3COOH is 4.0 at 25°C. The pH of 0.01 N NH_4OH solution at the same temperature would be: (JNT 1990)

- 3.0
- 4.0
- 10.0
- 10.5

[Hint: $[\text{H}^+]$ in CH_3COOH soln. = 10^{-4} ,

Similarly $[\text{OH}^-]$ in NH_4OH soln. = 10^{-4} ;

$$\text{So, } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

146. The dissociation constant of acetic acid is 1.8×10^{-5} and that of ammonium hydroxide is also 1.8×10^{-5} at 25°C. Hence, an aqueous solution of ammonium acetate is:
 (a) acidic (b) basic
 (c) neutral (d) slightly acidic

147. The concentration of OH^- ions in neutral solution is:
 (a) 1×10^{-14} g ions/litre (b) 1×10^{14} g ions/litre
 (c) 1×10^7 g ions/litre (d) 1×10^{-7} g ions/litre

148. $10^{-6} M$ NaOH is diluted by 100 times. The pH of diluted base is:
 [PMT (Pb.) 1993]
 (a) between 6 and 7 (b) between 10 and 11
 (c) between 7 and 8 (d) between 5 and 6

149. Ionic dissociation of acetic acid is represented as:
 $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
 According to Lowry and Bronsted, the reaction possesses:
 [CEE (Bihar) 1992]
 (a) an acid and three bases (b) two acids and two bases
 (c) an acid and a base (d) three acids and a base

150. The concept of an acid as an acceptor of a pair of electrons was introduced by:
 (a) Lowry (b) Bronsted (c) Arrhenius (d) Lewis

151. The ionic product of water will increase if:
 (a) pressure is decreased (b) H^+ ions are added
 (c) OH^- ions are added (d) temperature is increased

152. One litre of a buffer solution containing $0.01 M$ NH_4Cl and $0.1 M$ NH_4OH having pK_b of 5 has pH of:
 (a) 10 (b) 9 (c) 4 (d) 6

153. An aqueous solution of ferric chloride would be:
 (a) acidic (b) neutral (c) basic (d) amphoteric

154. An acid solution of pH 6 is diluted hundred times. The pH of the solution becomes:
 (a) 6 (b) 6.95 (c) 4 (d) 8

155. The pH of a solution is 5.0. To this solution sufficient acid is added to decrease the pH to 2.0. The increase in hydrogen ion concentration is:
 (CPMT 1990)
 (a) 100 times (b) 10 times (c) 1000 times (d) 2.5 times

156. Conjugate base of HPO_4^{2-} is:
 [PMT (MP) 1991]
 (a) PO_4^{3-} (b) H_2PO_4^-
 (c) H_3PO_4 (d) H_4PO_3

157. The pH of a solution is 2. Its pH is to be changed to 4. Then the H^+ ion concentration of original solution has to be:
 (a) halved (b) doubled
 (c) increased 100 times (d) decreased 100 times

158. The pH value of 0.1 mol/litre HCl is approximately 1. The approximate pH value of 0.05 mol/litre H_2SO_4 is most likely to be:
 (a) 0.05 (b) 0.5
 (c) 1 (d) 2

159. The aqueous solution of a salt is alkaline. This shows that the salt is made from:
 [PMT (MP) 1991]
 (a) a weak acid and a weak base
 (b) a weak acid and a strong base
 (c) a strong acid and a strong base
 (d) a strong acid and a weak base

160. A semi-normal solution of sodium acetate in water has $[\text{H}^+]$:
 (a) less than $10^{-7} M$ (b) greater than $10^{-7} M$
 (c) equal to $10^{-7} M$ (d) none of these

161. The most important buffer in the blood consists of:
 (a) HCl and Cl^- (b) H_2CO_3 and HCO_3^-
 (c) H_2CO_3 and Cl^- (d) HCl and HCO_3^-

162. The pH of a buffer solution containing 25 mL of $1 M$ CH_3COONa and 25 mL of $1 M$ CH_3COOH will be appreciably affected by 5 mL of:
 (a) $1 M$ CH_3COOH (b) $5 M$ HCl
 (c) $5 M$ CH_3COOH (d) $1 M$ NH_4OH

163. 50 mL of $2 N$ acetic acid mixed with 10 mL of $1 N$ sodium acetate solution will have an approximate pH:
 (a) 7 (b) 6 (c) 5 (d) 4

164. The solution of which salt in water is acidic?
 (a) $\text{Na}_2\text{B}_4\text{O}_7$ (b) NaHCO_3 (c) KCl (d) FeCl_3

165. Which of the following expressions is not true?
 (a) $[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w}$ for a neutral solution
 (b) $[\text{H}^+] > \sqrt{K_w}$ and $[\text{OH}^-] < \sqrt{K_w}$ for an acidic solution
 (c) $[\text{H}^+] < \sqrt{K_w}$ and $[\text{OH}^-] > \sqrt{K_w}$ for an alkaline solution
 (d) $[\text{H}^+] = [\text{OH}^-] = 10^{-7} M$ for a neutral solution at all temperatures

166. Ammonia gas dissolves in water to give NH_4OH . In this reaction water acts as:
 [PMT (MP) 1990]
 (a) an acid (b) a base
 (c) a salt (d) a conjugate base

167. What is the decreasing order of strength of the bases OH^- , NH_2^- , $\text{H}-\text{C}\equiv\text{C}^-$ and CH_3CH_2^- ?
 (IIT 1993)
 (a) $\text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{OH}^-$
 (b) $\text{H}-\text{C}\equiv\text{C}^- > \text{CH}_3-\text{CH}_2^- > \text{NH}_2^- > \text{OH}^-$
 (c) $\text{OH}^- > \text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{CH}_3\text{CH}_2^-$
 (d) $\text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{OH}^- > \text{CH}_3\text{CH}_2^-$

168. The best explanation for the solubility of MnS in dil. HCl is that:
 (MLNR 1993)
 (a) solubility product of MnCl_2 is less than that of MnS
 (b) concentration of Mn^{2+} is lowered by the formation of complex ions
 (c) concentration of sulphide ions is lowered by oxidation to free sulphur
 (d) concentration of sulphide ions is lowered by the formation of weak acid H_2S

169. The correct order of increasing $[\text{H}_3\text{O}^+]$ in the following aqueous solution is:
 (MLNR 1993; AFMC 2009)
 (a) $0.001 M \text{H}_2\text{S} < 0.01 M \text{H}_2\text{SO}_4 < 0.01 M \text{NaCl} < 0.01 M \text{NaNO}_2$
 (b) $0.01 M \text{NaCl} < 0.01 M \text{NaNO}_2 < 0.01 M \text{H}_2\text{S} < 0.01 M \text{H}_2\text{SO}_4$
 (c) $0.01 M \text{NaNO}_2 < 0.01 M \text{NaCl} < 0.01 M \text{H}_2\text{S} < 0.01 M \text{H}_2\text{SO}_4$
 (d) $0.01 M \text{H}_2\text{S} < 0.01 M \text{NaCl} < 0.01 M \text{NaNO}_2 < 0.01 M \text{H}_2\text{SO}_4$

170. Which of the following statements/relationships is not correct?
 (a) Upon hydrolysis salt of strong base and weak acid gives a solution with pH > 7
 (b) $\text{pH} = \log \frac{1}{[\text{H}^+]}$
 (c) Only at 25°C, the pH of pure water is 7
 (d) The value of pK_w at 25°C is 7
171. Fear and excitement generally cause one to breathe rapidly and it results in the decrease of CO_2 concentration in blood. In what way will it change the pH of the blood? (IIT 1993)
 (a) pH will decrease (b) pH will increase
 (c) No change (d) pH will adjust to 7
172. Nucleophiles are:
 (a) Lewis acids (b) Lewis bases
 (c) Bronsted acids (d) none of these
173. Electrophiles are:
 (a) Lewis acids (b) Lewis bases
 (c) Bronsted acids (d) Bronsted bases
174. K_h (hydrolysis constant) of ammonium benzoate can be calculated by the formula:
 (a) $\sqrt{\frac{K_w}{K_a C}}$ (b) $\sqrt{\frac{K_w}{K_a \times K_b}}$ (c) $\sqrt{\frac{K_w}{K_b \times C}}$ (d) $\sqrt{\frac{K_h}{C}}$
175. The pH of a neutral water is 6.5. Then the temperature of water: [PET (Kerala) 2007]
 (a) is 25°C
 (b) is more than 25°C
 (c) is less than 25°C
 (d) can be more or less than 25°C
 (e) cannot be predicted
176. The buffer capacity of buffer containing acid with $\text{pK}_a = 4.0$ is highest when its pH is equal to:
 (a) 6.0 (b) 5.0
 (c) 4.0 (d) 3.0
177. $K_{\text{sp}}(\text{AgCl}) > K_{\text{sp}}(\text{AgBr}) > K_{\text{sp}}(\text{AgI})$. This means that:
 (a) AgCl is more ionised than AgBr and AgI
 (b) both AgBr and AgI are less soluble than AgCl
 (c) AgI is most soluble
 (d) AgBr is more soluble than AgCl but less soluble than AgI
178. In the hydrolytic equilibrium;

$$\text{B}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH} + \text{H}^+$$

$$K_b = 1 \times 10^{-5}$$
. The hydrolysis constant is:
 (a) 10^{-5} (b) 10^{-19} (c) 10^{-10} (d) 10^{-9}
179. The solution of a salt of a weak acid and weak base will have pH: ($K_b = 1.0 \times 10^{-6}$ and $K_a = 1.0 \times 10^{-4}$)
 (a) 7.0 (b) 8.0
 (c) 6 (d) 4.0
180. 0.1 N solution of sodium acetate will have pH: ($\text{pK}_a = 4.57$)
 (a) 8.78 (b) 11.57
 (c) 4.57 (d) 7.0
181. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order: (IIT 1996)
- ClOH (I) BrOH (II) IOH (III)
- (a) I > II > III (b) II > I > III
 (c) III > II > I (d) I > III > II
182. Which of the following statements is correct?
 (a) pK_w increases with increase of temperature
 (b) pK_w decreases with increase of temperature
 (c) $\text{pK}_w = 14$ at all temperatures
 (d) $\text{pK}_w = \text{pH}$ at all temperatures
183. For a concentrated solution of a weak electrolyte A_x and B_y , the degree of dissociation is given as:
 (a) $\alpha = \sqrt{K_{\text{eq}} / c(x+y)}$
 (b) $\alpha = \sqrt{K_{\text{eq}} c / (xy)}$
 (c) $\alpha = (K_{\text{eq}} / c^{x+y-1} x^x y^y)^{1/(x+y)}$
 (d) $\alpha = \sqrt{K_{\text{eq}} / xy c}$
184. A solution is saturated with respect to SrCO_3 and SrF_2 . The $[\text{CO}_3^{2-}]$ was found to be $1.2 \times 10^{-3} M$. The concentration of F^- in the solution would be:
 (a) $1.3 \times 10^{-3} M$ (b) $2.6 \times 10^{-2} M$
 (c) $3.7 \times 10^{-2} M$ (d) $5.8 \times 10^{-7} M$
 (Given: $K_{\text{sp}}(\text{SrCO}_3) = 7.0 \times 10^{-10} M^2$,
 $K_{\text{sp}}(\text{SrF}_2) = 7.9 \times 10^{-10} M^3$)
185. The solubility of sparingly soluble electrolyte $M_m A_a$ in water is given by the expression:
 (a) $S = \left[\frac{K_{\text{sp}}}{m^m a^a} \right]^{m+a}$ (b) $S = \left[\frac{K_{\text{sp}}}{m^m a^a} \right]^{1/(m+a)}$
 (c) $S = \left[\frac{K_{\text{sp}}}{m^a a^m} \right]^{m+a}$ (d) $S = \left[\frac{K_{\text{sp}}}{m^a a^m} \right]^{1/(m+a)}$
186. The solubility of mercurous chloride in water will be given as:
 (a) $S = K_{\text{sp}}$ (b) $S = K_{\text{sp}}/4$
 (c) $S = (K_{\text{sp}}/4)^{1/2}$ (d) $S = (K_{\text{sp}}/4)^{1/3}$
187. In the titration of acetic acid versus sodium hydroxide, the pH of the solution at equivalence point (when temperature is 25°C) is:
 (a) about 5.5 (b) about 6.5
 (c) about 7 (d) about 8.5
188. When K_2O is added to water, the solution is basic because it contains a significant concentration of:
 (a) K^+ (b) OH^-
 (c) O^{3-} (d) O_2^{2-}
189. The blood buffers are most often involved in stabilizing the pH in presence of metabolically produced:
 (a) acids (b) bases
 (c) salts (d) none of these
190. The colour of CuCr_2O_7 solution in water is green because:
 (a) Cu^{2+} ion is green
 (b) $\text{Cr}_2\text{O}_7^{2-}$ ions are green
 (c) both the ions are green
 (d) Cu^{2+} ion is blue and $\text{Cr}_2\text{O}_7^{2-}$ ion is yellow

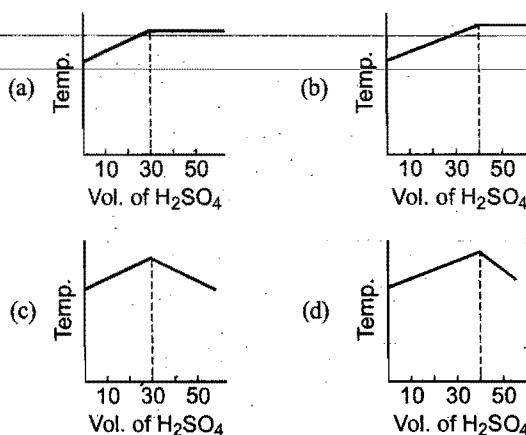
191. An acid with molecular formula $C_7H_6O_3$ forms three types of sodium salts, i.e., $C_7H_5O_3Na$, $C_7H_4O_3Na_2$ and $C_7H_3O_3Na_3$. The basicity of the acid is:

(a) one (b) two (c) three (d) four

192. If the salts M_2X , QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as:

(a) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$
 (b) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
 (c) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_3)$
 (d) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$

193. In an experiment to determine the enthalpy of neutralization of sodium hydroxide with sulphuric acid, 50 cm^3 of 0.4 M sodium hydroxide were titrated thermometrically with 0.25 M sulphuric acid. Which of the following plots gives the correct representation?



194. K_{sp} of CuS , Ag_2S and HgS are 10^{-31} , 10^{-44} and 10^{-54} respectively. Select the correct order for their solubility in water:

(a) $\text{Ag}_2\text{S} > \text{HgS} > \text{CuS}$ (b) $\text{HgS} > \text{CuS} > \text{Ag}_2\text{S}$
 (c) $\text{HgS} > \text{Ag}_2\text{S} > \text{CuS}$ (d) $\text{Ag}_2\text{S} > \text{CuS} > \text{HgS}$

[Hint: Solubility of Ag_2S ($4S^3 = K_{sp}$) and for CuS and HgS ($S^2 = K_{sp}$)]

195. If the K_b value in the hydrolysis reaction,



is 1.0×10^{-6} , then the hydrolysis constant of the salt would be:

(HT 1998)

(a) 1.0×10^{-6} (b) 1.0×10^{-7} (c) 1×10^{-8} (d) 1.0×10^{-9}

196. The concentration of $[\text{H}^+]$ and $[\text{OH}^-]$ of a 0.1 M aqueous solution of 2% ionised weak acid is: (ionic product of water $= 1 \times 10^{-14}$)

(CBSE 1999)

(a) $0.2 \times 10^{-3}\text{ M}$ and $5 \times 10^{-11}\text{ M}$
 (b) $1 \times 10^{-3}\text{ M}$ and $3 \times 10^{-11}\text{ M}$
 (c) $2 \times 10^{-3}\text{ M}$ and $5 \times 10^{-12}\text{ M}$
 (d) $3 \times 10^{-2}\text{ M}$ and $4 \times 10^{-13}\text{ M}$

[Hint: $[\text{H}^+] = C \times \alpha = 0.1 \times 0.02 = 2 \times 10^{-3}\text{ M}$;

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

197. The pH value of decinormal solution of NH_4OH , which is 20% ionised, is:

(CBSE 1998)

- (a) 13.30 (b) 14.70 (c) 12.30 (d) 12.95

[Hint: $[\text{OH}^-] = 0.1 \times 0.2 = 2 \times 10^{-3}$; $\text{pOH} = 1.7$ pH = 14 - pOH]

198. The pH of 0.1 M solution of the following salts increases in the order of:

(a) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
 (b) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
 (c) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
 (d) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$

199. A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resists a change in pH yet contains only small concentration of buffering agents. Which one of the following weak acids together with its sodium salt would be best to use?

(CBSE 1997)

(a) *m*-chlorobenzoic acid ($pK_a = 3.98$)
 (b) *p*-chlorobenzoic acid ($pK_a = 4.41$)
 (c) 2,5-dihydroxybenzoic acid ($pK_a = 2.97$)
 (d) Acetoacetic acid ($pK_a = 3.58$)

200. Which one does not give a buffer solution?

(a) Ammonia and sodium hydroxide in water
 (b) Sodium acetate and acetic acid in water
 (c) Ammonia and ammonium chloride in water
 (d) Sodium acetate and hydrochloric acid in water

201. Conjugate base of $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3]$ is:

(a) $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_2]^+$ (b) $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_2\text{O}]^-$
 (c) $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3]^-$ (d) $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$

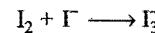
202. The solubility of calcium phosphate in water is $x\text{ mol h}^{-1}$ at 25°C . Its solubility product is equal to:

(a) $108x^2$ (b) $36x^3$
 (c) $36x^5$ (d) $108x^5$

203. K_{sp} values for silver bromide, silver chloride and silver iodide are $5 \times 10^{-13}\text{ mol}^2\text{ dm}^{-6}$, $2 \times 10^{-10}\text{ mol}^2\text{ dm}^{-6}$ and $8 \times 10^{-17}\text{ mol}^2\text{ dm}^{-6}$ respectively. The order of solubility of these silver salts is :

(a) $\text{AgCl} > \text{AgBr} > \text{AgI}$ (b) $\text{AgI} > \text{AgBr} > \text{AgCl}$
 (c) $\text{AgCl} > \text{AgI} > \text{AgBr}$ (d) $\text{AgI} > \text{AgCl} > \text{AgBr}$

204. In the reaction,



the Lewis base is:

(a) I_2 (b) I^-
 (c) I_3^- (d) none of these

205. Which of the following on reaction with H_2S does not produce metallic sulphide?

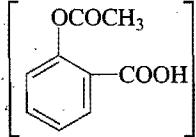
(a) CdCl_2 (b) ZnCl_2 (c) CoCl_2 (d) CuCl_2

206. A buffer solution of pH = 9 can be prepared by mixing:

(a) CH_3COONa and CH_3COOH
 (b) NaCl and NaOH
 (c) NH_4Cl and NH_4OH
 (d) KH_2PO_4 and K_2HPO_4

207. Which of the following is the strongest Lewis base?

(a) CH_3^- (b) NH_2^- (c) OH^- (d) F^-

- 208.** The monobasic acid among the following is : (ISAT 2010)
- H_3PO_3
 - $H_2S_2O_7$
 - H_3PO_2
 - $H_4P_2O_7$
- 209.** To Ag_2CrO_4 solution over its own precipitate, CrO_4^{2-} ions are added. This results in: [MEE (Kerala) 2000]
- increase in Ag^+ concentration
 - decrease in Ag^+ concentration
 - increase in solubility product
 - shifting of Ag^+ ions from the precipitate into the solution
- 210.** Aluminium chloride is: (KCET 2000)
- Bronsted Lowry acid
 - Arrhenius acid
 - Lewis acid
 - Lewis base
- 211.** A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. The pH of the mixture will be nearly: [IAS (Prelim.) 1995]
- 0.76
 - 1.26
 - 1.76
 - 2.26
- 212.** The $[Ag^+]$ in a saturated solution of Ag_2CrO_4 is $1.5 \times 10^{-4} M$. What is the solubility product of Ag_2CrO_4 ? (SCRA 2009)
- $3.375 \times 10^{-12} M^3$
 - $1.6875 \times 10^{-10} M^3$
 - $1.6875 \times 10^{-11} M^3$
 - $1.6875 \times 10^{-12} M^3$
- [Hint : $Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$
- $$[Ag^+] = 1.5 \times 10^{-4} M \quad \therefore [CrO_4^{2-}] = 0.75 \times 10^{-4} M$$
- $$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$
- $$= [1.5 \times 10^{-4}]^2 [0.75 \times 10^{-4}]$$
- $$= 1.6875 \times 10^{-12} M^3$$
- 213.** The pH of a buffer containing equal molar concentrations of a weak base and its chloride (K_b for weak base = 2×10^{-5} , $\log 2 = 0.3$) is:
- 5
 - 9
 - 4.7
 - 9.3
- 214.** The solubility product (K_{sp}) of $AgCl$ is 1.8×10^{-10} . Precipitation of $AgCl$ will occur only when equal volumes of solutions of: [IAS (Prelim.) 1997; PET (MP) 2007]
- $10^{-4} M Ag^+$ and $10^{-4} M Cl^-$ are mixed
 - $10^{-7} M Ag^+$ and $10^{-7} M Cl^-$ are mixed
 - $10^{-5} M Ag^+$ and $10^{-5} M Cl^-$ are mixed
 - $10^{-10} M Ag^+$ and $10^{-10} M Cl^-$ are mixed
- 215.** Solid $Ba(NO_3)_2$ is gradually dissolved in a $1 \times 10^{-4} M Na_2CO_3$ solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) (AIEEE 2009)
- $4.1 \times 10^{-5} M$
 - $5.1 \times 10^{-5} M$
 - $8.1 \times 10^{-8} M$
 - $8.1 \times 10^{-7} M$
- 216.** How many gram of CaC_2O_4 will dissolve in distilled water to make one litre of unsaturated solution of it? (K_{sp} for $CaC_2O_4 = 2.5 \times 10^{-9} \text{ mol}^2 \text{ lit}^{-2}$) [IPMT (MP) 2009]
- 0.0064 g
 - 0.1028 g
 - 0.1280 g
 - 0.2056 g
- 217.** When CO_2 dissolves in water, the following equilibrium is established,
- $$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$
- for which the equilibrium constant is 3.8×10^{-7} and pH = 6.0. The ratio of $[HCO_3^-]$ to $[CO_2]$ would be:
- 3.8×10^{-13}
 - 3.8×10^{-1}
 - 6.0
 - 13.4
- 218.** pH of a buffer solution decreases by 0.02 units when 0.12 g of acetic acid is added to 250 mL of a buffer solution of acetic acid and potassium acetate at 27°C. The buffer capacity of the solution is: (EAMCET 2009)
- 0.1
 - 10
 - 1
 - 0.4
- 219.** The dissociation constants of monobasic acids A, B, C and D are 6×10^{-4} , 5×10^{-5} , 3.6×10^{-6} and 7×10^{-10} respectively. The pH values of their 0.1 molar aqueous solutions are in the order:
- $A < B < C < D$
 - $A > B > C > D$
 - $A = B = C = D$
 - $A > B < C > D$
- 220.** If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9 , then pH in 0.1 M NaA is:
- 5
 - 9
 - 7
 - 8
- 221.** If the freezing point of 0.1 molal HA (aq.) is $-0.2046^\circ C$, then pH of the solution is: [$K_f (H_2O) = 1.86^\circ \text{ mol}^{-1} \text{ kg}$]
- 1
 - 2
 - 1.3
 - 1.7
- 222.** % ionisation of weak acid can be calculated as:
- $100 \sqrt{\frac{K_a}{c}}$
 - $\frac{100}{1 + 10^{(pK_a - pH)}}$
 - both correct
 - none is correct
- 223.** Assuming complete ionisation which will have maximum pH?
- $0.01 M NH_4Cl$
 - $0.01 M (NH_4)_2SO_4$
 - $0.01 M (NH_4)_3PO_4$
 - equal
- 224.** $H_2O + H_3PO_4 \rightleftharpoons H_3O^+ + H_2PO_4^-$; $pK_1 = 2.15$
 $H_2O + H_2PO_4^- \rightleftharpoons H_3O^+ + HPO_4^{2-}$; $pK_2 = 7.20$
Hence, pH of 0.01 M NaH_2PO_4 is:
- 9.35
 - 4.675
 - 2.675
 - 7.350
- 225.** Acetyl salicylic acid  called aspirin is a pain killer with $pK_a = 2$. If two tablets each of 0.09 g mass, containing aspirin are dissolved in 100 mL solution. Its pH will be:
- 0.5
 - 1.0
 - 0.0
 - 2.0
- 226.** If ionic product of water is $K_w = 10^{-16}$ at $4^\circ C$, then a solution with pH = 7.5 at $4^\circ C$ will:
- turn blue litmus red
 - turn red litmus blue
 - turn turmeric paper brown
 - be neutral to litmus
- 227.** How do we differentiate between Fe^{3+} and Cr^{3+} in group III? [AIEEE 2002]
- By taking excess of NH_4OH
 - By increasing NH_4^+ ion concentration
 - By decreasing OH^- ion concentration
 - Both (b) and (c)
- 228.** Which has the highest pH? [CBSE (PMT) 2002]
- CH_3COOK
 - Na_2CO_3
 - NH_4Cl
 - $NaNO_3$
- 229.** Water is a: (KCET 2002)
- protophobic solvent
 - protophilic solvent
 - amphiprotic solvent
 - aprotic solvent

230. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is:
 (AIEEE 2002)
 (a) not a buffer solution with pH < 7
 (b) not a buffer solution with pH > 7
 (c) a buffer solution with pH < 7
 (d) a buffer solution with pH = 7
231. Solution of 0.1 M NH₄OH and 0.1 M NH₄Cl has pH 9.25. Then pK_b of NH₄OH is:
 (CBSE (PMT) 2002)
 (a) 9.25
 (b) 4.75
 (c) 3.75
 (d) 8.25
232. Solubility of an MX₂ type electrolyte is 0.5×10^{-4} mol/litre, then K_{sp} of electrolyte is:
 (CBSE (PMT) 2002)
 (a) 5×10^{-12}
 (b) 25×10^{-10}
 (c) 1×10^{-13}
 (d) 5×10^{-13}
233. The concentration of KI and KCl in a certain solution containing both is 0.001 M each. If 20 mL of this solution is added to 20 mL of a saturated solution of AgI in water. What will happen?
 (K_{sp} AgCl = 10^{-10} ; K_{sp} AgI = 10^{-16}).
 (PET (MP) 2004)
 (a) AgI will be precipitated
 (b) AgCl will be precipitated
 (c) There will be no precipitate
 (d) Both AgCl and AgI will be precipitated
234. Degree of dissociation of NH₄OH in water is 1.8×10^{-5} , then hydrolysis constant of NH₄OH is:
 (CECE (Bihar) Pre. 2004)
 (a) 1.8×10^{-5}
 (b) 1.8×10^{-10}
 (c) 5.55×10^{-5}
 (d) 5.55×10^{-10}
235. What is the pH of 0.01 M glycine solution? For glycine $K_{a_1} = 4.5 \times 10^{-3}$; $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K.
 (AIIMS 2004)
 (a) 3.02
 (b) 6.94
 (c) 7.06
 (d) 10.02
236. The rapid change of pH near the stoichiometric point of an acid base titration is the basis of indicator detection. pH of the solution is related to the ratio of the concentrations of the conjugate acid HIn and base In⁻ forms of the indicator by the expression:
 (CBSE (PMT) 2004)
 (a) $\log \frac{[\text{In}^-]}{[\text{HIn}]} = pK_{\text{In}} - \text{pH}$
 (b) $\log \frac{[\text{HIn}]}{[\text{In}^-]} = pK_{\text{In}} - \text{pH}$
 (c) $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pH} - pK_{\text{In}}$
 (d) $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} - pK_{\text{In}}$
237. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is:
 (IIT (S) 2004)
 (a) 0.0001%
 (b) 0.01%
 (c) 0.1%
 (d) 0.15%
238. The molar solubility (in mol litre⁻¹) of a sparingly soluble salt MX₄ is S. The corresponding solubility product K_{sp} is given by the relation:
 (AIEEE 2004)
 (a) $S = (K_{sp}/128)^{1/4}$
 (b) $S = (218 K_{sp})^{1/4}$
 (c) $S = (256 K_{sp})^{1/5}$
 (d) $S = (K_{sp}/256)^{1/5}$
239. The K_{sp} of Mg(OH)₂ is 1×10^{-12} . 0.01 M Mg(OH)₂ will precipitate at the limiting pH:
 (DPMT 2005)
 (a) 3
 (b) 9
 (c) 5
 (d) 8
 [Hint: $[\text{Mg}^{2+}][\text{OH}^-]^2 = 10^{-12}$
 $0.01 \times [\text{OH}^-]^2 = 10^{-12}$

- $[\text{OH}^-] = 10^{-5} \text{ M}$
 $\therefore [\text{H}^+] = 10^{-9} \text{ M}$ and $\text{pH} = -\log[10^{-9}] = 9$
240. The correct expression for the solubility product of Ca₃(PO₄)₂ is:
 (JEE (Orissa) 2005)
 (a) $108S^5$
 (b) $27S^5$
 (c) $16S^4$
 (d) $81S^4$
241. The solubility product of a salt, having the general formula MX₂, in water is 4×10^{-12} . The concentration of M²⁺ ions in the aqueous solution of the salt is:
 (AIEEE 2005)
 (a) $2 \times 10^{-6} \text{ M}$
 (b) $1 \times 10^{-4} \text{ M}$
 (c) $1.6 \times 10^{-4} \text{ M}$
 (d) $4 \times 10^{-10} \text{ M}$
- [Hint: It is ternary electrolyte.
 $K_{sp} = 4S^3$
 $4 \times 10^{-12} = 4S^3$
 $S = 10^{-4} \text{ M}$
 $\therefore (M^{2+}) = 10^{-4} \text{ M}

242. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is:
 (CBSE (PMT) 2009)
 (a) 5.65×10^{-12}
 (b) 5.65×10^{-10}
 (c) 6.50×10^{-12}
 (d) 5.65×10^{-13}

[Hint: $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}

243. The K_a values of formic acid and acetic acid are respectively 1.77×10^{-4} and 1.75×10^{-5} . The ratio of the acid strength of 0.1 M acid is:
 (PMT (Kerala) 2005)
 (a) 10
 (b) 3.178
 (c) 0.3
 (d) 0.1
 (e) 100

244. Equal volumes of the following Ca²⁺ and F⁻ solutions are mixed. In which solution will the precipitation occur?
 K_{sp} of CaF₂ = 1.7×10^{-10}
 1. $10^{-2} \text{ M Ca}^{2+} + 10^{-5} \text{ M F}^-$
 2. $10^{-3} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
 3. $10^{-4} \text{ M Ca}^{2+} + 10^{-2} \text{ M F}^-$
 4. $10^{-2} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$

Select the correct answer using the codes given below:
 (PMT (Kerala) 2005)
 (a) in 4 only
 (b) in 1 and 2
 (c) in 3 and 4
 (d) in 2, 3 and 4
 (e) in all of these

245. Given, pH of a solution A is 3 and it is mixed with another solution B having pH 2. If both are mixed, then the resultant pH of the solution will be:
 (BHU (Pre.) 2005)
 (a) 3.2
 (b) 1.9
 (c) 3.4
 (d) 3.5

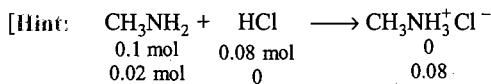
246. When 10 mL of 0.1 M acetic acid (pK_a = 5) is titrated against 10 mL of 0.1 M ammonia solution (pK_b = 5), the equivalent point will occur at pH:
 (AIIMS 2005)
 (a) 5
 (b) 6
 (c) 7
 (d) 9

247. On adding 0.1 M solution each of Ag⁺, Ba²⁺ and Ca²⁺ in an Na₂SO₄ solution, the species first precipitated is:
 (DCE 2005)
 $(K_{sp} \text{ BaSO}_4 = 10^{-11}, K_{sp} \text{ CaSO}_4 = 10^{-6}, K_{sp} \text{ Ag}_2\text{SO}_4 = 10^{-5})$
 (a) Ag₂SO₄
 (b) BaSO₄
 (c) CaSO₄
 (d) all of these$$

248. When 0.1 mole of CH_3NH_2 (ionization constant, $K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole HCl and the volume is made up to 1 litre, find the $[\text{H}^+]$ of resulting solution:

(IIT 2005)

- (a) 8×10^{-2} (b) 2×10^{-11}
 (c) 1.23×10^{-4} (d) 8×10^{-11}



$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log 5 \times 10^{-4} + \log \frac{0.08}{0.02} = 3.903$$

$$\text{pH} = 10.0967$$

$$[\text{H}^+] = \text{antilog}[-10.0967] = 8 \times 10^{-11}$$

249. At 25°C , the dissociation constant of a base BOH is 1×10^{-12} . The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be: [CBSE-PMT (Pre.) 2005]

- (a) $10^{-5} \text{ mol L}^{-1}$ (b) $10^{-6} \text{ mol L}^{-1}$
 (c) $2 \times 10^{-6} \text{ mol L}^{-1}$ (d) $10^{-7} \text{ mol L}^{-1}$

[Hint]: $[\text{OH}^-] = \sqrt{CK_b} = \sqrt{0.01 \times 10^{-12}} = 10^{-7} \text{ mol L}^{-1}$

250. Which of the following solutions has pH equal to 10? [UGET (Manipal) 2006]

- (a) 10^{-4} M KOH (b) 10^{-10} M KOH
 (c) 10^{-10} M HCl (d) 10^{-4} M HCl

251. A weak monobasic acid is half neutralised by a strong base. If the pH of the solution is 5.4; its $\text{p}K_a$ is: [JEE (Orissa) 2006]

- (a) 6.8 (b) 2.7 (c) 5.4 (d) 10.8

[Hint]: $[\text{Acid}] = [\text{Salt}]$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$5.4 = \text{p}K_a + \log_{10} 1$$

$$\therefore \text{p}K_a = 5.4$$

252. ZnS is not precipitated by passing H_2S in acidic medium but CuS precipitated. The reason for it is: [JEE (Orissa) 2006]

- (a) $K_{sp} \text{ CuS} \ll K_{sp} \text{ ZnS}$ (b) $K_{sp} \text{ CuS} >> K_{sp} \text{ ZnS}$
 (c) $K_{sp} \text{ CuS} = K_{sp} \text{ ZnS}$ (d) none of these

253. Solubility product of salt AB is $1 \times 10^{-8} \text{ M}^2$ in a solution, in which the concentration of A^+ ions is 10^{-3} M . The salt will precipitate when the concentration of B^- ions is kept:

(KCET 2006)

- (a) between 10^{-8} M to 10^{-7} M (b) between 10^{-7} M to 10^{-8} M
 (c) $> 10^{-5} \text{ M}$ (d) $< 10^{-8} \text{ M}$

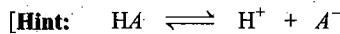
254. NaOH(*aq.*), HCl(*aq.*) and NaCl(*aq.*) have concentration of 10^{-3} M each. Their pH will be respectively:

(PMT (Uttarakhand) 2006)

- (a) 10, 6, 2 (b) 11, 3, 7
 (c) 10, 3, 7 (d) 10, 4, 7

255. The weak acid, HA, has a K_a of 1.00×10^{-5} . If 0.1 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to: [CBSE (Med.) 2007]

- (a) 1% (b) 99.9%
 (c) 0.1% (d) 99%



$$t=0 \quad C \quad 0 \quad 0$$

$$t_{eq.} \quad C - C\alpha \quad C\alpha \quad C\alpha$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{C^2\alpha^2}{C - C\alpha}$$

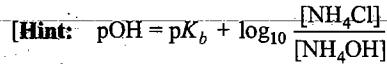
$$= \frac{C\alpha^2}{1 - \alpha} \approx C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.1}} = 10^{-2}$$

$$\% \text{ ionisation} = \alpha \times 100 = 1$$

256. At 25°C , the value of $\text{p}K_b$ (K_b being the dissociation constant as a base) for NH_3 in aqueous solution is 4.7. What is the pH of 0.1 M aqueous solution of NH_4Cl with 0.01 M NH_3 (approximately)? (SCRA 2007)

- (a) 8.3 (b) 9 (c) 9.5 (d) 10



$$= 4.7 + \log \left[\frac{0.1}{0.01} \right] = 5.7$$

$$\text{pH} = 14 - 5.7 = 8.3$$

257. The ionisation of strong electrolytes in acetic acid compared to that in water is: [CET (J&K) 2007]

- (a) weak, low (b) strong, more
 (c) medium, the same (d) no ionisation, 100%

258. By adding a little of acid or base, the change in pH of blood is not significant, because blood: [PET (Raj.) 2006]

- (a) has iron as a part of molecule
 (b) is a body fluid
 (c) has serum protein which works as buffer
 (d) is easily coagulated

259. 2.5 mL of $2/5 \text{ M}$ weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $2/15 \text{ M HCl}$ in water at 25°C . The concentration of H^+ ion at equivalence point is: ($K_w = 1 \times 10^{-14}$ at 25°C) (IIT 2008)

- (a) $3.7 \times 10^{-13} \text{ M}$ (b) $3.2 \times 10^{-7} \text{ M}$
 (c) $3.2 \times 10^{-2} \text{ M}$ (d) $2.7 \times 10^{-2} \text{ M}$



$$\frac{M_1 V_1}{1} (\text{Base}) = \frac{M_2 V_2}{1} (\text{Acid})$$

$$\frac{2}{5} \times 2.5 = \frac{2}{15} \times V_2$$

$$V_2 = 7.5 \text{ mL}$$

$$\text{Total volume} = 7.5 + 2.5 = 10 \text{ mL}$$

Concentration of salt in the mixture :

$$M_1 V_1 (\text{Base}) = M_2 V_2 (\text{Salt})$$

$$\frac{2}{5} \times 2.5 = M_2 \times 10$$

$$M_2 = 0.1$$

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$$

$$= \frac{1}{2} [14 - 12 - (-1)] = 1.5$$

$$[\text{H}^+] = \text{Antilog}(-1.5) = 0.032 \text{ M}$$

260. Solubility product constants (K_{sp}) of salts of types MX , MX_2 , M_3X at temperature T are 4×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol dm $^{-3}$) of the salts at temperature T are in the order: (IIT 2008)

- (a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$
 (c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

[Hint:

$$\text{Solubility } (S_1) \text{ of } MX = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4} M$$

Solubility (S_2) of

$$MX_2 = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}} = \left(\frac{3.2 \times 10^{-14}}{4} \right)^{\frac{1}{3}} = 2 \times 10^{-5} M$$

Solubility (S_3) of

$$M_3X = \left(\frac{K_{sp}}{27} \right)^{\frac{1}{4}} = \left(\frac{2.7 \times 10^{-15}}{27} \right)^{\frac{1}{4}} = 10^{-4} M$$

$$\therefore S_1 > S_3 > S_2$$

261. In aqueous solution, the ionization constants for carbonic acid are :

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid : (AIEEE 2010)

- (a) The concentrations of H^+ and HCO_3^- are approximately equal
 (b) The concentration of H^+ is double that of CO_3^{2-}
 (c) Concentration of CO_3^{2-} is 0.034 M
 (d) The concentration of CO_3^{2-} is greater than that of HCO_3^-

Set-2: The Questions given below may have more than one correct answers

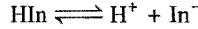
1. For dissociation constant (K) and ionic product (K_w) of water which is correct?
- (a) $K > K_w$ (b) $K_w > K$
 (c) $K_w = K$ (d) None of these
2. Which is an example of auto protolysis?
- (a) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
 (b) $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$
 (c) $H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$
 (d) All of the above
3. If concentrations of two acids are same, their relative strengths can be compared by:
- (a) α_1 / α_2 (b) K_1 / K_2
 (c) $[H^+]_1 / [H^+]_2$ (d) $\sqrt{K_1 / K_2}$
4. Three bases XOH , YOH and ZOH have pK_b values 2, 3 and 4 respectively; the strongest conjugate acid is:
- (a) XOH_2^+ (b) YOH_2^+
 (c) ZOH_2^+ (d) all are same
5. Aqueous solution of HNO_3 , KOH , CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is (are): (IIT 2010)
- (a) HNO_3 and CH_3COOH
 (b) KOH and CH_3COONa

- (c) HNO_3 and CH_3COONa
 (d) CH_3COOH and CH_3COONa
6. Four solutions of NH_4Cl are taken with concentrations 1 M, 0.1 M, 0.01 M and 0.001 M. Their degree of hydrolysis are h_1, h_2, h_3 and h_4 . What is the graduation of degree of hydrolysis?

- (a) $h_1 > h_2 > h_3 > h_4$ (b) $h_1 = h_2 = h_3 = h_4$
 (c) $h_4 > h_3 > h_2 > h_1$ (d) None of these
7. Which has maximum solubility AB , AB_2 , AB_3 and AB_4 if K_{sp} for all the salts are 10^{-10} ?

- (a) AB (b) AB_2 (c) AB_3 (d) AB_4

8. Dissociation of an indicator can be considered as,



Colours of HIn and In^- are different. Which statement is correct?

- (a) Solution assumes colours of HIn when $pH = P_{K-1}$

- (b) Solution assumes colours of In^- when $pH = P_{K+1}$

- (c) Solution assumes colours of HIn^- when $pH = P_{K+1}$

- (d) Solution assumes colours of In^- when $pH = P_{K-1}$

9. The % error in $[H^+]$ made by neglecting the ionisation of water in $10^{-6} M$ NaOH is:

- (a) 1% (b) 2% (c) 3% (d) 4%

10. 50 mL $N/10$ NaOH solution is mixed with 50 mL $N/20$ HCl solution. The resulting solution will:

- (a) turn phenolphthalein solution pink

- (b) turn blue litmus red

- (c) turn methyl orange red

- (d) $[H^+] < [OH^-]$

11. An acid indicator HIn has $K_a = 3 \times 10^{-5}$, the acid form is red and basic form is blue. Which is correct?

- (a) pH = 5 when indicator is 75% red

- (b) pH = 4.05 when indicator is 75% red

- (c) pH = 5 when indicator is 75% blue

- (d) pH = 4.05 when indicator is 75% blue

12. Which of the following will function as buffer?

[IAS (Pre.) 1997]

- (a) $NaCl + NaOH$ (b) Borax + boric acid

- (c) $NaH_2PO_4 + NaHPO_4$ (d) $NH_4Cl + NH_4OH$

13. Choose the correct statement(s):

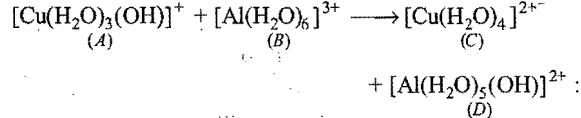
- (a) pH of an acidic buffer increases if more salt is added.

- (b) pH of a basic buffer decreases if more salt is added.

- (c) In a saturated solution, ionic product is equal to its solubility product.

- (d) The term solubility product is only for sparingly soluble salts.

14. In the following reaction,



- (a) (A) is an acid and (B) is a base

- (b) (A) is a base and (B) is an acid

- (c) (*C*) is the conjugate acid of (*A*) and (*D*) is the conjugate base of (*B*)
 (d) (*C*) is the conjugate base of (*A*) and (*D*) is the conjugate acid of (*B*)
15. Which among the following will not react with NaOH or which is not acid salt?
 (a) NaH_2PO_2 (b) Na_2HPO_3 (c) Na_2HPO_2 (d) NaHCO_3
- Direction:** In the following three questions, more than one of the answers given may be correct. Select the correct answers and mark it according to the codes. [BHU (Med.) 2007]
- Codes:**
 (a) 1, 2 and 3 are correct (b) 1 and 2 are correct
 (c) 2 and 4 are correct (d) 1 and 3 are correct
16. If equal volumes of 0.1 M HBr and 0.1 M KOH are mixed, then which of the following is/are correct about the resulting solution?

- (1) $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$
 (2) $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$
 (3) $[\text{K}^+] = 0.05 \text{ mol L}^{-1}$
 (4) $[\text{Br}^-] = 0.10 \text{ mol L}^{-1}$
17. Which of the following solutions will be acidic?
 (1) 0.1 M FeSO_4 (2) 0.1 M $(\text{NH}_4)_2\text{SO}_4$
 (3) 0.1 M CH_3COONa (4) 0.1 M NH_4OH
18. In a buffer solution consisting NaH_2PO_4 and Na_2HPO_4 : [BHU (Mains, 2013)]
 (1) NaH_2PO_4 is acid and Na_2HPO_4 is salt
 (2) The pH of solution can be calculated using the relation :

$$\text{pH} = \text{p}K_2 + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

 (3) The Na_2HPO_4 is acid and NaH_2PO_4 is salt
 (4) The pH can not be calculated

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as '**Assertion (A)**' and '**Reason (R)**'. While answering these questions you are required to choose any one of the following four responses:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 - (c) If (A) is correct, but (R) is incorrect.
 - (d) If both (A) and (R) are incorrect.
1. (A) A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.
(R) Solubility product of CdS is more than that of NiS .
 2. (A) In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of the acid required at the equivalence point is twice that of the acid required using phenolphthalein as indicator.
(R) Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3 . **(IIT 1991)**
 3. (A) The pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.
(R) The ionisation of acetic acid is suppressed by the addition of sodium acetate.
 4. (A) In acidic medium, Zn^{2+} is not precipitated by S^{2-} ions.
(R) Common ion effect reduces the concentration of S^{2-} ions to the minimum level.
 5. (A) In the acid-base titration involving a strong base and a weak acid, methyl orange can be used as an indicator.
(R) Methyl orange changes its colour in pH range 3 to 5.
 6. (A) A mixture of sodium acetate and sodium propionate forms a buffer solution.
(R) A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.
 7. (A) When small amount of an acid or base is added to pure water its pH undergoes a change.
(R) Addition of an acid or a base increases the degree of ionisation of water.
 8. (A) At $25^\circ C$, the pH of $10^{-8} M$ HCl is 8.
(R) pH of acidic solution is always below 7 at $25^\circ C$.
 9. (A) The addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution, will first precipitate $AgBr$ rather than $AgCl$.
(R) The value of K_{sp} of $AgCl < K_{sp}$ of $AgBr$. **(AIIMS 2004)**
 10. (A) Sb (III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
(R) Concentration of S^{2-} ions in alkaline medium is inadequate for precipitation. **(AIIMS 2004)**

11. (A) Sb_2S_3 is not soluble in yellow ammonium sulphide.
(R) The common ion effect due to S^{2-} ions reduces the solubility of Sb_2S_3 . **(AIIMS 2006)**
12. (A) H_2SO_4 acts as a base in presence of $HClO_4$.
(R) Perchloric acid is stronger acid than H_2SO_4 .
13. (A) pH of a neutral solution is always 7.
(R) pH of a solution does not depend upon temperature.
14. (A) pH of $10^{-8} M$ HCl is not equal to 8.
(R) HCl does not dissociate properly in very dilute solution.
15. (A) If a solution with pH = 2 is diluted to double the volume, the pH of the solution will fall to 1.
(R) pH is inversely proportional to the volume of the solution.
16. (A) If HCl gas is passed through saturated NaCl solution, solid NaCl starts separating out.
(R) HCl decreases the solubility product of NaCl.
17. (A) pH of a buffer changes with temperature.
(R) Ionic product of water (K_w) changes with temperature.
18. (A) $I_2 + I^- \longrightarrow I_3^-$
In above reaction, I_2 is Lewis base.
(R) Electron pair acceptor is Lewis base.
19. (A) Phenolphthalein is used as indicator during the titration of oxalic acid against sodium hydroxide.
(R) The pH range of phenolphthalein is from 8 to 9.6.
20. (A) If K_{sp} is less than K_{ip} , the precipitate is formed.
(R) Solubility product (K_{sp}) is the highest limit of ionic product of electrolyte solutions.
21. (A) H_3PO_3 is a dibasic acid.
(R) There are two hydrogen atoms directly attached to phosphorus. **(AIIMS 2007)**
22. (A) NaCl is precipitated when HCl gas is passed in a saturated solution of NaCl.
(R) HCl is a strong acid. **(AIIMS 2007)**
23. (A) On mixing 500 mL of $10^{-6} M$ Ca^{2+} ion and 500 mL of $10^{-6} M F^-$ ion, the precipitate of CaF_2 will be obtained.
 $K_{sp}(CaF_2) = 10^{-18}$.
(R) If K_{sp} is greater than ionic product, precipitate will be obtained. **(AIIMS 2007)**
24. (A) The aqueous solution of CH_3COONa is alkaline in nature.
(R) Acetate ion undergoes an ionic hydrolysis. **(EAMCET 2008)**
25. (A) An aqueous solution of ammonium acetate can act as a buffer.
(R) Acetic acid is a weak acid and NH_4OH is a weak base. **(EAMCET 2010)**
26. (A) $[Al(H_2O)_6]^{3+}$ is a stronger acid than $[Mg(H_2O)_6]^{2+}$.
(R) Size of $[Al(H_2O)_6]^{3+}$ smaller than $[Mg(H_2O)_6]^{2+}$ and possesses more effective nuclear charge. **(AIIMS 2010)**

Answers : OBJECTIVE QUESTIONS**• Set-1**

1. (c)	2. (b)	3. (a)	4. (d)	5. (d)	6. (c)	7. (a)	8. (c)
9. (c)	10. (d)	11. (a)	12. (b)	13. (b)	14. (b)	15. (d)	16. (b)
17. (c)	18. (a)	19. (d)	20. (a)	21. (a)	22. (d)	23. (c)	24. (a)
25. (c)	26. (c)	27. (a)	28. (c)	29. (b)	30. (d)	31. (b)	32. (d)
33. (d)	34. (c)	35. (a)	36. (c)	37. (a)	38. (c)	39. (d)	40. (c)
41. (b)	42. (b)	43. (a)	44. (d)	45. (a)	46. (c)	47. (d)	48. (d)
49. (b)	50. (c)	51. (a)	52. (d)	53. (a)	54. (d)	55. (c)	56. (b)
57. (c)	58. (d)	59. (b)	60. (a)	61. (a)	62. (b)	63. (c)	64. (d)
65. (d)	66. (a)	67. (a)	68. (b)	69. (c)	70. (b)	71. (d)	72. (d)
73. (d)	74. (a)	75. (b)	76. (b)	77. (d)	78. (b)	79. (c)	80. (a)
81. (c)	82. (a)	83. (b)	84. (d)	85. (d)	86. (d)	87. (c)	88. (c)
89. (b)	90. (b)	91. (d)	92. (a)	93. (a)	94. (a)	95. (d)	96. (a)
97. (a)	98. (b)	99. (c)	100. (a)	101. (a)	102. (a)	103. (d)	104. (d)
105. (a)	106. (b)	107. (c)	108. (b)	109. (b)	110. (a)	111. (d)	112. (c)
113. (c)	114. (b)	115. (c)	116. (c)	117. (d)	118. (b)	119. (b)	120. (b)
121. (c)	122. (b)	123. (d)	124. (d)	125. (b)	126. (c)	127. (a)	128. (a)
129. (b)	130. (a)	131. (a)	132. (a)	133. (c)	134. (c)	135. (a)	136. (c)
137. (d)	138. (b)	139. (a)	140. (d)	141. (d)	142. (c)	143. (a)	144. (b)
145. (c)	146. (c)	147. (d)	148. (c)	149. (b)	150. (d)	151. (d)	152. (a)
153. (a)	154. (b)	155. (c)	156. (a)	157. (d)	158. (c)	159. (b)	160. (a)
161. (b)	162. (b)	163. (d)	164. (d)	165. (d)	166. (a)	167. (a)	168. (d)
169. (c)	170. (d)	171. (b)	172. (b)	173. (a)	174. (b)	175. (b)	176. (c)
177. (b)	178. (d)	179. (c)	180. (a)	181. (a)	182. (b)	183. (c)	184. (c)
185. (b)	186. (d)	187. (d)	188. (b)	189. (a)	190. (d)	191. (c)	192. (a)
193. (b)	194. (d)	195. (c)	196. (c)	197. (c)	198. (b)	199. (c)	200. (a)
201. (d)	202. (d)	203. (a)	204. (b)	205. (c)	206. (c)	207. (d)	208. (c)
209. (b)	210. (c)	211. (b)	212. (d)	213. (d)	214. (a)	215. (b)	216. (a)
217. (b)	218. (d)	219. (d)	220. (b)	221. (b)	222. (c)	223. (c)	224. (b)
225. (d)	226. (a)	227. (d)	228. (b)	229. (c)	230. (a)	231. (b)	232. (d)
233. (a)	234. (d)	235. (c)	236. (c)	237. (b)	238. (d)	239. (b)	240. (a)
241. (b)	242. (b)	243. (b)	244. (d)	245. (b)	246. (c)	247. (a)	248. (d)
249. (d)	250. (a)	251. (c)	252. (a)	253. (c)	254. (b)	255. (a)	256. (a)
257. (a)	258. (c)	259. (c)	260. (d)	261. (b)			

• Set-2

1. (b)	2. (d)	3. (a, c, d)	4. (c)	5. (c, d)	6. (c)	7. (d)	8. (a, b)
9. (a)	10. (a, d)	11. (b, c)	12. (b, d)	13. (a, b, c)	14. (b, c)	15. (a, b, c)	16. (a)
17. (b)	18. (a)						

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c)	2. (b)	3. (d)	4. (a)	5. (d)	6. (b)	7. (c)	8. (d)
9. (c)	10. (c)	11. (d)	12. (a)	13. (d)	14. (c)	15. (d)	16. (c)
17. (a)	18. (d)	19. (a)	20. (b)	21. (c)	22. (b)	23. (d)	24. (a)
25. (c)	26. (a)						

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option:

1. The pH value of $10^{-3} M$ aqueous solution of NaCl is:
(a) 7 (b) 3 (c) 11 (d) 14
[Hint: NaCl is the salt of strong acid HCl and strong base NaOH. Its aqueous solution will be neutral with pH equal to seven.]
2. The acidic buffer solution can be prepared by mixing solutions of:
(a) sodium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide
3. Hydrolysis constants of two salts K_A and K_B of weak acids H_A and H_B are 10^{-8} and 10^{-6} . If the dissociation constant of third acid H_C is 10^{-2} . The order of acidic strengths of three acids will be:
(a) $H_A > HB > HC$ (b) $HB > HA > HC$
(c) $HC > HA > HB$ (d) $HA = HB = HC$

[Hint: $K_a(HA) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$

$$K_a(HB) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$$K_a(HC) = 10^{-2}$$

Greater the value of dissociation constant K_a , more is the acidic strength.]

4. Three sparingly soluble salts that have same solubility products are given below:

I. A_2X II. AX III. AX_3

Their solubilities in a saturated solution will be such that:

- (a) III > II > I (b) III > I > II (c) II > III > I (d) II > I > III

[Hint: $S = \sqrt{K_{sp}}$ for AX ; $S = \left[\frac{K_{sp}}{4} \right]^{1/3}$ for A_2X ;

$$S = \left[\frac{K_{sp}}{27} \right]^{1/4} \text{ for } AX_3$$

$$\therefore S_{II} > S_I > S_{III}$$

5. Consider the three solutions of 1 M concentration.

1. Sodium acetate (CH_3COONa)

2. Acetic acid + Sodium acetate
($CH_3COOH + CH_3COONa$)

3. Acetic acid (CH_3COOH)

The pH of these solutions will lie in the following sequence:

- (a) 3 < 2 < 1 (b) 2 < 1 < 3 (c) 1 < 2 < 3 (d) 3 < 1 < 2

[Hint: CH_3COOH (Acetic acid) < ($CH_3COO^- + CH_3COONa$)
pH < 7

CH₃COONa]
pH > 7
Salt of weak acid
with strong base

6. Glycine NH_2CH_2COOH behaves:
(a) as a Bronsted acid
(b) as a Bronsted base
(c) both as an acid and a base
(d) neither as an acid nor as a base
7. Solubility of Hg_2Cl_2 in a solvent is S moles/litre. Its solubility product will be:
(a) $16S^2$ (b) $8S^2$ (c) $16S^4$ (d) $4S^3$
[Hint: $Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$]
8. Arrange the following acids in increasing order of their acid strength:
I. $HClO_4$ II. H_2SO_4 III. H_3PO_4
(a) III < II < I (b) I < II < III (c) II < III < I (d) III < I < II
9. Select the anion which is the strongest bronsted base:
(a) ClO_4^- (b) ClO_3^- (c) ClO_2^- (d) ClO^-
[Hint: $HClO_4 > HClO_3 > HClO_2 > HClO$
(Decreasing acidic character)
 $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$
(Increasing basic strength)
(Conjugate base of strong acid is weak base)]
10. $M(OH)_x$ has a K_{sp} of 4×10^{-9} and its solubility is $10^{-3} M$. The value of x is:
(a) 4 (b) 1 (c) 3 (d) 2
11. What is the maximum possible concentration of Ni^{2+} ions in a solution containing 0.15 M HCl and 0.10 M H_2S ? [Given that, $K_{sp}(NiS) = 2 \times 10^{-21}$ and $[S^{2-}]_{H_2S} = 4 \times 10^{-21}$:]
(a) 0.65 M (b) 0.45 M (c) 0.10 M (d) 0.15 M
12. The pH of $10^{-10} M H_2SO_4$ will be almost:
(a) 4 (b) 7 (c) 6 (d) 0
13. Solubility of calcium phosphate (molecular mass, M) in water is W g per 100 mL at 25°C. Its solubility product at 25°C will be approximately:
(a) $10^9 \left(\frac{W}{M} \right)^5$ (b) $10^7 \left(\frac{W}{M} \right)^5$ (c) $10^5 \left(\frac{W}{M} \right)^5$ (d) $10^3 \left(\frac{W}{M} \right)^5$
[Hint: $S = \frac{10W}{M}$ mol litre
 K_{sp} of $Ca_3(PO_4)_2 = 108S^5$
 $= 108 \left(\frac{10W}{M} \right)^5$
 $= 10^7 \left(\frac{W}{M} \right)^5$ (approximately)]
14. When some amount of sodium acetate is further added to a mixture of acetic acid and sodium acetate, then pH of the solution:

- (a) increases
 (b) decreases
 (c) remains same
 (d) none of these can be predicted from given information

[Hint: $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$]

When the concentration of salt is increased, the value of pH will increase.]

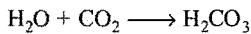
15. When strong base (NaOH) is added to the weak acid (acetic acid, CH_3COOH), then dissociation of acetic acid increases; this effect is known as:

- (a) common ion effect (b) reverse ion effect
 (c) saltation effect (d) solubility effect

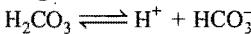
[Hint: $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

Ionization of acetic acid will increase with the progress of its neutralization. This effect is called reverse ion effect.]

16. In our body, carbon dioxide (CO_2) combines with water (H_2O) to form carbonic acid.



Carbonic acid undergoes dissociation as,



During the physical and mental stress, the rate of respiration increases, which results in the decrease in concentration of CO_2 in the blood. What will be the effect on pH of human blood during the stress?

- (a) Decreases (b) Remains same
 (c) Increases (d) Cannot be predicted

17. The correct order of basic strength is: (AIIMS 2007)

- (a) $\text{H}_2\text{O} < \text{OH}^- < \text{CH}_3\text{OH} < \text{CH}_3\text{O}^-$
 (b) $\text{CH}_3\text{OH} < \text{H}_2\text{O} < \text{CH}_3\text{O}^- < \text{OH}^-$
 (c) $\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{OH}^- < \text{CH}_3\text{O}^-$
 (d) $\text{OH}^- < \text{H}_2\text{O} < \text{CH}_3\text{O}^- < \text{CH}_3\text{OH}$

18. Which of the following orders is expected to be correct?

- (a) $pK_a(\text{ClCH}_2\text{COOH}) > pK_a(\text{CH}_3\text{COOH})$
 $> pK_a(\text{CH}_3\text{CH}_2\text{COOH})$
 (b) $pK_a(\text{ClCH}_2\text{COOH}) < pK_a(\text{CH}_3\text{COOH})$
 $< pK_a(\text{CH}_3\text{CH}_2\text{COOH})$
 (c) $pK_a(\text{ClCH}_2\text{COOH}) > pK_a(\text{CH}_3\text{COOH})$
 $< pK_a(\text{CH}_3\text{CH}_2\text{COOH})$
 (d) $pK_a(\text{ClCH}_2\text{COOH}) < pK_a(\text{CH}_3\text{COOH})$
 $> pK_a(\text{CH}_3\text{CH}_2\text{COOH})$

19. The concentration of H_3O^+ ions in pure water is $10^{-7} \text{ mol dm}^{-3}$. The corresponding concentration of OH^- ions will be:

- (a) $10^{-14} \text{ mol dm}^{-3}$ (b) $10^{-8} \text{ mol dm}^{-3}$
 (c) $10^{-6} \text{ mol dm}^{-3}$ (d) $10^{-7} \text{ mol dm}^{-3}$

[Hint: In water, $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$]

20. What will be the pH of a solution formed by mixing 40 cm^3 of 0.1 M HCl with 10 cm^3 of 0.45 M NaOH ?

- (a) 10 (b) 8 (c) 5 (d) 12

[Hint: Number of moles of HCl = $\frac{MV}{1000} = \frac{0.1 \times 40}{1000} = 0.004$

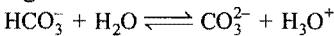
Number of moles of NaOH = $\frac{MV}{1000} = \frac{0.45 \times 10}{1000} = 0.0045$

Remaining moles of NaOH after neutralization = 0.0005

$$\text{Molarity of OH}^- = \frac{0.0005}{50} \times 1000 = 0.01 \text{ M}$$

$$\text{pOH} = 2 \quad \therefore \quad \text{pH} = 14 - 2 = 12$$

21. In the following reaction:



which two substances are Bronsted bases?

- (a) CO_3^{2-} and H_3O^+ (b) HCO_3^- and H_3O^+
 (c) HCO_3^- and CO_3^{2-} (d) CO_3^{2-} and H_2O

22. Which are strong acids?

- I. HClO_3 II. H_2SeO_3 III. H_3AsO_4
 (a) I only (b) III only
 (c) I and III only (d) II and III only

23. $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$; $K_a = 1.7 \times 10^{-4}$

The ionization of formic acid is represented above. Calculate $[\text{H}^+]$ of a solution initially containing 0.1 M HCOOH and 0.05 M HCOONa :

- (a) $8.5 \times 10^{-5} \text{ M}$ (b) $3.4 \times 10^{-4} \text{ M}$
 (c) $4.1 \times 10^{-3} \text{ M}$ (d) $1.8 \times 10^{-2} \text{ M}$

24. Carbonic acid, H_2CO_3 , is a diprotic acid for which $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$. Which solution will produce a pH closest to 9?

- (a) $0.1 \text{ M H}_2\text{CO}_3$
 (b) $0.1 \text{ M Na}_2\text{CO}_3$
 (c) 0.1 M NaHCO_3
 (d) 0.1 M NaHCO_3 and $0.1 \text{ M Na}_2\text{CO}_3$

25. What is the conjugate acid of HPO_4^{2-} ?

- (a) H_3PO_4 (b) H_2PO_4^- (c) H_3O^+ (d) PO_4^{3-}

26. What is the K_b of a weak base that produces one OH^- per molecule if a 0.05 M solution is 2.5% ionized?

- (a) 7.8×10^{-8} (b) 1.6×10^{-6} (c) 3.2×10^{-5} (d) 1.2×10^{-3}

[Hint: $K_b = C\alpha^2$

$$= 0.05 \times \left(\frac{2.5}{100} \right)^2 = 3.1 \times 10^{-5}$$

27. The amount of sodium hydrogen carbonate, NaHCO_3 , in an antacid tablet is to be determined by dissolving the tablet in water and titrating the resulting solution with hydrochloric acid. Which indicator is the most appropriate for this titration?

Acid	K_a
H_2CO_3	2.5×10^{-4}
HCO_3^-	2.4×10^{-8}

- (a) Methyl orange, $pK_{\text{In}} = 3.7$

- (b) Bromothymol blue, $pK_{\text{In}} = 7.0$

- (c) Phenolphthalein, $pK_{\text{In}} = 9.3$

- (d) Alizarin yellow, $pK_{\text{In}} = 12.5$

28. If equal volumes of BaCl_2 and NaF solutions are mixed, which of these combinations will not give a precipitate?

Substance	K_{sp}
BaF_2	1.7×10^{-7}

- (a) 0.004 M BaCl_2 and 0.02 M NaF

- (b) 0.010 M BaCl_2 and 0.015 M NaF

- (c) 0.015 M BaCl_2 and 0.010 M NaF

- (d) 0.020 M BaCl_2 and 0.002 M NaF

[Hint: In the mixture of 0.02 M BaCl_2 and 0.002 M NaF , the ionic product is less than the solubility product, hence there will be no precipitation of BaF_2 .]

29. HCN is a weak acid ($K_a = 6.2 \times 10^{-10}$). NH_4OH is a weak base ($K_b = 1.8 \times 10^{-5}$). A 1 M solution of NH_4CN would be:

(a) strongly acidic (b) weakly acidic
(c) neutral (d) weakly basic

[Hint: Since, $K_b > K_a$, hence the medium will be weakly basic.]

30. How many moles of HCOONa must be added to 1 L of 0.1 M HCOOH to prepare a buffer solution with a pH of 3.4?

Given: K_a for $\text{HCOOH} = 2 \times 10^{-4}$

(a) 0.01 (b) 0.05 (c) 0.1 (d) 0.2

31. Silver ions are added to the solution with:

$$[\text{Br}^-] = [\text{Cl}^-] = [\text{CO}_3^{2-}] = [\text{AsO}_4^{3-}] = 0.1\text{ M}$$

Which compound will precipitate at the lowest $[\text{Ag}^+]$?

(a) AgBr ($K_{sp} = 5 \times 10^{-13}$)

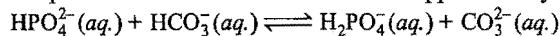
(b) AgCl ($K_{sp} = 1.8 \times 10^{-10}$)

(c) Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$)

(d) Ag_3AsO_4 ($K_{sp} = 10^{-22}$)

[Hint: In case of AgBr , the ionic product will exceed the solubility product before AgCl , Ag_2CO_3 and Ag_3AsO_4 . Thus, AgBr will start precipitation before other salts.]

32. The equilibrium constant for this reaction is approximately 10^{-3} .



Which is the strongest conjugate base in this reaction?

(a) HPO_4^{2-} (aq.) (b) HCO_3^- (aq.)

(c) H_2PO_4^- (aq.) (d) CO_3^{2-} (aq.)

[Hint: Conjugate base of weak acid is strong base.]

33. Which mixture forms a buffer when dissolved in 1 L of water?

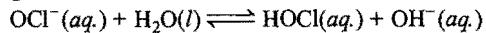
(a) 0.2 mol NaOH + 0.2 mol HBr

(b) 0.2 mol NaCl + 0.3 mol HCl

(c) 0.4 mol HNO_2 + 0.2 mol NaOH

(d) 0.5 mol NH_3 + 0.5 mol HCl

34. The equilibrium constant for this reaction is 3.6×10^{-7} .



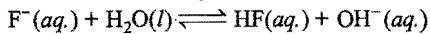
What is K_a for HOCl ?

(a) 2.8×10^{-8} (b) 3.6×10^{-7} (c) 6×10^{-4} (d) 2.8×10^{-6}

35. What is the concentration of H^+ in a solution that is prepared by mixing 50 mL of 0.5 M HCl and 200 mL of 0.25 M HCl ?

(a) 0.30 M (b) 0.35 M (c) 0.40 M (d) 0.45 M

36. K_a for hydrofluoric acid is 6.9×10^{-4} . What is the equilibrium constant K for the following reaction?



(a) 6.9×10^{-11} (b) 1.4×10^{-11} (c) 2.6×10^{-9} (d) 8.3×10^{-6}

37. A solution of 2 M formic acid (HCOOH) is 0.95% ionized. What is the K_a of formic acid?

(a) 1.9×10^{-2} (b) 1.8×10^{-4} (c) 9×10^{-5} (d) 4.5×10^{-5}

[Hint: $K_a = \text{Ca}^2 = 2 \times \left(\frac{0.95}{100}\right)^2$]

38. If 0.1 mol of salt is added to 1 L water, which of these salts is expected to produce the most acidic solution?

- (a) $\text{NaC}_2\text{H}_3\text{O}_2$ (b) NH_4NO_3
(c) CuSO_4 (d) AlCl_3

39. A sample of hard water contains 0.005 mole of calcium chloride per litre. What is the minimum concentration of sodium sulphate which must be added for removing the Ca^{2+} ions from this water sample? K_{sp} of $\text{CaSO}_4 = 2.4 \times 10^{-5}$.

(a) 4.8×10^{-2} (b) 4.8×10^{-3}
(c) 2.4×10^{-2} (d) 2.4×10^{-3}

40. Match the List-I and List-II:

- | List-I | List-II |
|--|-------------------------|
| (A) The limits of pH values of buffer | (i) 5×10^{-12} |
| solution | |
| (B) Concentration of $[\text{H}_3\text{O}^+]$ in | (ii) Equal |
| 0.001 M $\text{Ba}(\text{OH})_2$ | |

- | | |
|---------------------------------------|-------------------|
| (C) The buffer capacity of a solution | (iii) 10^{-14} |
| is maximum when concentration | |
| of salt to that of acid is | |
| (D) Ionic product of water is | (iv) $pK_a \pm 1$ |

- | Codes: A | B | C | D |
|----------|----|-----|-----|
| (a) iv | ii | i | iii |
| (b) iv | i | iii | ii |
| (c) i | iv | ii | iii |
| (d) iv | i | ii | iii |

41. Match the List-I and List-II:

- | List-I | List-II |
|--|-----------------------|
| (A) Degree of ionization of weak electrolytes increases | (i) Common ion effect |
| (B) pH of water decreases on | (ii) $\text{pH} = 4$ |
| (C) The solution has hydronium ion concentration of 0.0001 mol/litre | (iii) Heating |
| (D) The addition of NaOH to $\text{Ca}(\text{OH})_2$ solution precipitates $\text{Ca}(\text{OH})_2$ | (iv) On dilution |

- | Codes: A | B | C | D |
|----------|-----|-----|----|
| (a) iv | iii | i | ii |
| (b) iii | iv | ii | i |
| (c) iv | iii | ii | i |
| (d) iv | ii | iii | i |

42. Which of the following is not correct about the percentage ionization of BOH?

- | | |
|---|--|
| (a) $\frac{K_w[\text{H}^+]}{K_b + K_w}$ | (b) $100 \times \sqrt{\frac{K_b}{C}}$ |
| (c) $\frac{100}{1 + 10^{(pK_b - pOH)}}$ | (d) $\frac{K_b \times 100}{K_b + \text{OH}^-}$ |

[Hint: $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$

$$\begin{array}{cccc} t_0 & C & 0 & 0 \\ t_{eq.} & C - C\alpha & C\alpha & C\alpha \\ & & & \\ K_b & \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} & = \frac{C^2\alpha^2}{C(1 - \alpha)} \\ & & = C\alpha^2 & (\alpha \ll 1) \end{array}$$

$$\alpha = \sqrt{\frac{K_b}{C}} \quad \% \text{ ionization} = 100 \times \sqrt{\frac{K_b}{C}} \quad \dots(1)$$

$$\alpha = \frac{[B^+]}{[B^+] + [BOH]} = \frac{1}{1 + \frac{[BOH]}{[B^+]}} = \frac{1}{1 + \frac{[OH^-]}{[K_b]}}$$

$$\alpha = \frac{K_b}{K_b + OH^-} \quad \dots(2)$$

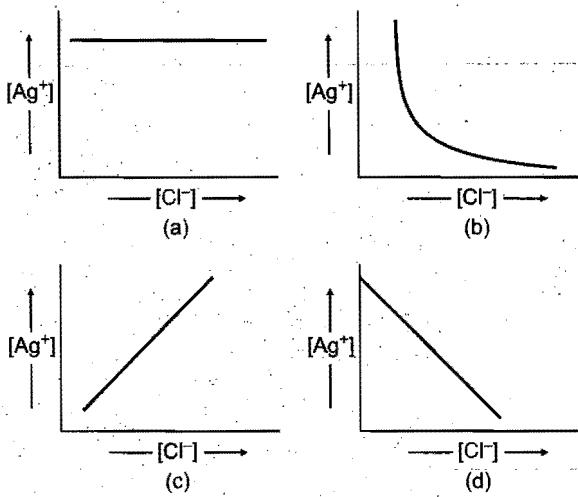
$$\text{Percentage ionization} = \frac{100 K_b}{K_b + OH^-}$$

$$\alpha = \frac{1}{1 + \frac{[OH^-]}{K_b}} = \frac{1}{1 + \frac{10^{-pOH}}{10^{-pK_b}}}$$

$$\alpha = \frac{1}{1 + 10^{(pK_b - pOH)}}$$

$$\therefore \text{Percentage ionization} = \frac{100}{1 + 10^{(pK_b - pOH)}}$$

43. When NaCl is added gradually to the saturated solution of AgCl then which of the following plot is correct?



The following questions may have more than one correct options:

1. Which of the following statements is/are correct about the ionic product of water?
- (a) K (equilibrium constant of water) $< K_w$ (ionic product of water)
 - (b) $pK > pK_w$
 - (c) At 300 K, K_w of water becomes 10^{-12}
 - (d) Ionic product of water at 25°C is 10^{-14}

2. Which among the following statements is/are correct?

- (a) $\text{pH} = -\log_{10}(\text{H}_3\text{O}^+)$
- (b) pH decreases with increase of temperature
- (c) pH cannot be zero, negative or more than 14
- (d) If a solution is diluted ten times, its pH increases by 1

3. Which among the following statements is/are correct?

- (a) pH of $10^{-8} M$ HCl is equal to 8
- (b) Conjugate base of H_2PO_4^- is HPO_4^{2-}
- (c) pH of $0.1 M$ NaCl (aqueous solution) = $\frac{1}{2} \text{p}K_w$
- (d) Ionization of water increases with decrease in temperature

4. Let us consider the ionization of HCl in the aqueous solution of CH_3COOH .



Select the correct statement(s) among the following:

- (a) Cl^- is the conjugate base of HCl
- (b) CH_3COOH is the conjugate base of $\text{CH}_3\text{COOH}_2^+$
- (c) $\text{CH}_3\text{COOH}_2^+$ is the conjugate base of CH_3COOH
- (d) Cl^- is the conjugate base of CH_3COOH

5. Which among the following species act both as an acid as well as a base?

- | | |
|------------------------|----------------------|
| (a) SO_4^{2-} | (b) HSO_4^- |
| (c) PO_4^{3-} | (d) NH_3 |

6. Which among the following salts will give basic solution on hydrolysis? [PET (MP) 2008]

- | | |
|-------------------------------|-----------------------------|
| (a) NaH_2PO_4 | (b) NH_4Cl |
| (c) NaCl | (d) K_2CO_3 |

7. Which among the following represent the conjugate acid/base pairs?

- (a) $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$
- (b) $\text{H}_2\text{SO}_4 / \text{SO}_4^{2-}$
- (c) $\text{HCO}_3^- / \text{CO}_3^{2-}$
- (d) All are conjugate acid/base pairs

8. If you have saturated solution of CaF_2 then:

- | | |
|--|---|
| (a) $[\text{Ca}^{2+}] = \sqrt{K_{sp}}$ | (b) $[\text{Ca}^{2+}] = 2[\text{F}^-]$ |
| (c) $2[\text{Ca}^{2+}] = [\text{F}^-]$ | (d) $[\text{Ca}^{2+}] = [K_{sp/4}]^{1/3}$ |

9. The relative strength of two weak bases at same concentration may be given as:

- | | |
|---------------------------------|---|
| (a) $\frac{K_{b_1}}{K_{b_2}}$ | (b) $\frac{[\text{OH}^-]_1}{[\text{OH}^-]_2}$ |
| (c) $\frac{\alpha_1}{\alpha_2}$ | (d) $\frac{\sqrt{K_{b_1}}}{\sqrt{K_{b_2}}}$ |

Answers

● Single correct option

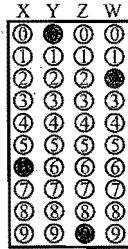
- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (a) | 3. (c) | 4. (d) | 5. (a) | 6. (c) | 7. (d) | 8. (a) |
| 9. (d) | 10. (d) | 11. (b) | 12. (b) | 13. (b) | 14. (a) | 15. (b) | 16. (c) |
| 17. (c) | 18. (b) | 19. (c) | 20. (d) | 21. (d) | 22. (a) | 23. (b) | 24. (c) |
| 25. (b) | 26. (c) | 27. (a) | 28. (d) | 29. (d) | 30. (b) | 31. (a) | 32. (d) |
| 33. (c) | 34. (a) | 35. (a) | 36. (b) | 37. (b) | 38. (b) | 39. (b) | 40. (d) |
| 41. (c) | 42. (c) | 43. (b) | | | | | |

● One or more than one correct options

- | | | | | | | | |
|-----------------|--------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1. (a, b, c, d) | 2. (a, b, d) | 3. (b, c) | 4. (a, b) | 5. (b, d) | 6. (a, d) | 7. (a, c) | 8. (c, d) |
| 9. (b, c, d) | | | | | | | |

Integer Answer TYPE QUESTIONS

This section contains 13 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



- What will be the pH of 0.1 M $\text{CH}_3\text{COONH}_4$? Dissociation constants of CH_3COOH and NH_4OH are $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$ respectively.
- Ionic product of water is 1×10^{-12} . pH of water will be :
- Calculate the pH at which an acid indicator HIn with concentration 0.1 M changes its colour. (K_a for $\text{HIn} = 1 \times 10^{-5}$)
- Sum of basicity of H_3PO_4 , H_3PO_3 , H_3PO_2 is equal to :
- A given weak acid (0.01 M) has $\text{p}K_a = 6$. The pH of this solution is :
- Solubility product of an electrolyte is $6912S^7$. How many ions will be obtained by the ionization of one molecule of electrolyte?
- The solubility product of Mg(OH)_2 is 5×10^{-19} at 25°C . pH of saturated solution of Mg(OH)_2 will be :
- pH of 10^{-x} M HCl is 6.9586. The value of x will be :
- If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9 , then the pH of 0.1 M NaA solution will be :

- Consider the titration of 50 mL of 0.1 M HBr with 0.1 M KOH. Calculate pH after 49 mL of the base has been added to the 50 mL of HBr.

- The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4} . The pH of a 0.01 M solution of its sodium salt is: (IIT 2009)

[Hint : pH of salt after hydrolysis may be calculated as,

$$\begin{aligned}\text{pH} &= \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C] \\ &= \frac{1}{2}[14 + (-\log 10^{-4}) + \log 0.01] \\ &= \frac{1}{2}[14 + 4 - 2] = 8\end{aligned}$$

- The total number of diprotic acids among the following is: H_3PO_4 , H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_2BO_3 , H_3PO_2 , H_2CrO_4 , H_2SO_3 (IIT 2010)

[Hint : H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_2CrO_4 , H_2SO_3 are diprotic acid.]

- Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is: KCN , K_2SO_4 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NaCl , $\text{Zn}(\text{NO}_3)_2$, FeCl_3 , K_2CO_3 , NH_4NO_3 , LiCN (IIT 2010)

[Hint : Salts of weak acid and strong base will give basic solution on hydrolysis and will turn red litmus to blue KCN , K_2CO_3 and LiCN are such type of salts.]

Answers

- | | | | | | | | |
|--------|---------|---------|---------|---------|--------|--------|--------|
| 1. (7) | 2. (6) | 3. (5) | 4. (6) | 5. (4) | 6. (7) | 7. (8) | 8. (8) |
| 9. (9) | 10. (3) | 11. (8) | 12. (6) | 13. (3) | | | |

LINKED COMPREHENSION TYPE QUESTIONS

● Passage 1

Higher the amount of acid or base used to produce a definite change of pH in a buffer solution, higher will be its buffer capacity. Buffer capacity of solution is maximum under the following conditions:

$$[\text{Salt}] = [\text{Acid}] \text{ (in acid buffer)}$$

$$[\text{Salt}] = [\text{Base}] \text{ (in base buffer)}$$

pH of a buffer solution lies in the range given below:

$$\text{pH} = \text{p}K_a \neq 1$$

In other words, any buffer solution can be used as buffer up to two pH units only, depending upon the value of $\text{p}K_a$ or $\text{p}K_b$. A buffer is said to be efficient when $\text{pH} = \text{p}K_a$ or $\text{pOH} = \text{p}K_b$.

Answer the following questions:

1. Any buffer can be used as a buffer up to:
(a) 10 pH units (b) 5 pH units (c) 2 pH units (d) 1 pH unit
2. Which among the following solutions will be the most efficient buffer?
(a) 0.1 M CH_3COONa + 0.01 M CH_3COOH
(b) 0.1 M NH_4Cl + 0.1 M NH_4OH
(c) 0.001 M HCOOH + 0.002 M HCOONa
(d) All of the above
3. The buffer capacity is equal to:
(a) $\frac{\Delta n}{\Delta \text{pH}}$ (b) $\frac{\text{pH}}{\Delta n}$ (c) $\pm 1 \text{p}K_a$ (d) none of these
4. A buffer of acetic acid ($\text{p}K_a \approx 4.8$) with sodium acetate will be, when CH_3COOH and CH_3COONa are present in equivalent amounts has pH limits equal to:
(a) 0 to 4.8 (b) 3.8 to 5.8 (c) 4.3 to 5.3 (d) 4.8
5. Buffer capacity is maximum when:
(a) one mole of NH_4Cl is added to two moles of NH_4OH
(b) one mole of NH_4Cl is added to one mole of NH_4OH
(c) one mole of NH_4Cl is added to one mole of NaOH
(d) one mole of NaCl is added to one mole of NaOH
6. A buffer solution is prepared by mixing equal concentration of acid (ionisation constant K_a) and a salt. The pH of buffer is:
[JEE (Orissa) 2008]
(a) $\text{p}K_a + 7$ (b) $14 - \text{p}K_a$ (c) $\text{p}K_a$ (d) $\text{p}K_a + 1$

● Passage 2

When a salt reacts with water to form acidic or basic solution, the process is called hydrolysis. The pH of salt solution can be calculated using the following relations:

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

(for salt of weak acid and strong base.)

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$$

(for salt of weak base and strong acid.)

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$$

(for salt of weak acid and weak base.)

where, 'C' represents the concentration of salt.

When a weak acid or a weak base is not completely neutralized by strong base or strong acid respectively, then formation of buffer takes place. The pH of buffer solution can be calculated using the following relation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} ; \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Answer the following questions using the following data:

$$\text{p}K_a = 4.7447, \text{p}K_b = 4.7447, \text{p}K_w = 14$$

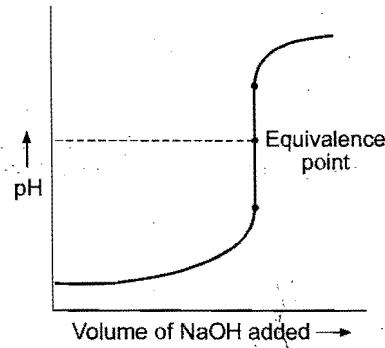
1. When 50 mL of 0.1 M NH_4OH is added to 50 mL of 0.05 M HCl solution, the pH is:
(a) 1.6021 (b) 12.3979 (c) 4.7447 (d) 9.2553
2. 0.001 M NH_4Cl aqueous solution has pH:
(a) 6.127 (b) 7.126 (c) 2.167 (d) 1.267
3. 50 mL 0.1 M NaOH is added to 50 mL of 0.1 M CH_3COOH solution, the pH will be:
(a) 4.7447 (b) 9.2553 (c) 8.7218 (d) 1.6021
4. 1 mole CH_3COOH and 1 mole CH_3COONa are dissolved in water to form 1 litre aqueous solution. The pH of the resulting solution will be:
(a) 9.2553 (b) 4.7447 (c) 14 (d) 7
5. When 50 mL of 0.1 M NaOH is added to 50 mL of 0.05 M CH_3COOH solution. The pH of the solution is:
(a) 1.6021 (b) 12.3979 (c) 4.7447 (d) 8.7218

● Passage 3

An acid-base titration consists of the controlled addition of a dissolved base to a dissolved acid (or the reverse). Acid-base react rapidly to neutralize each other. At the equivalence point, enough titrant, the solution being added, has gone into make the chemical amounts of the acid and base exactly equal. The pH of a titration changes every time a drop of titrant is added, but the rate of this change varies enormously. A titration curve, graph of pH as a function of the volume of titrant, displays in detail how the pH changes over the course of an acid-base titration. Significantly, the pH changes most rapidly near the equivalence point. The exact shape of a titration curve depends on the K_a and K_b acid and base.

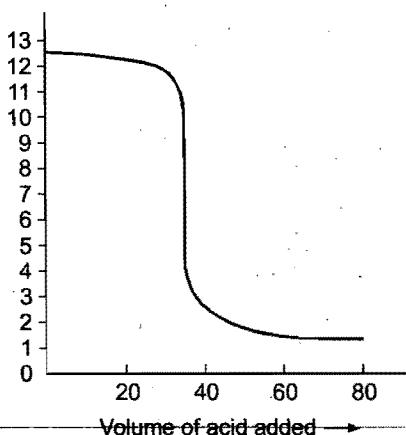
Answer the following questions:

1. The following figure represents titration curve of HCl against NaOH. The pH at equivalence point will be:



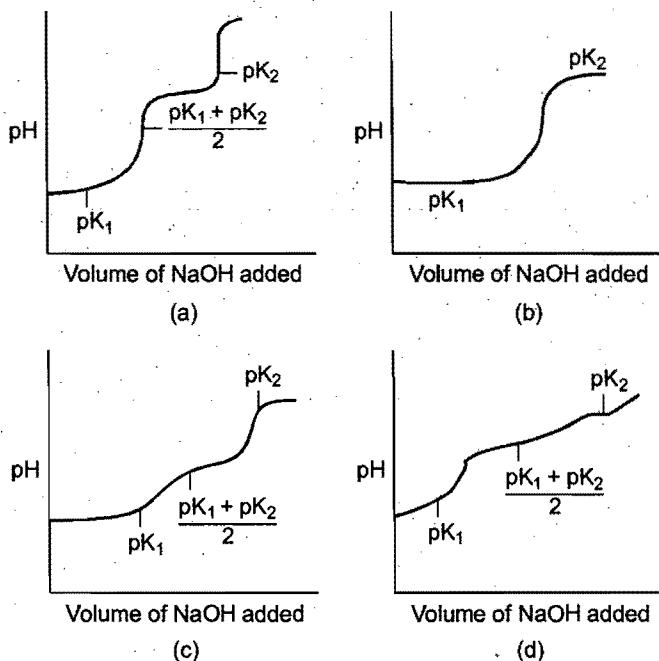
- (a) 7 (b) 6 (c) 8 (d) 3

Examine the titration curve below:



Answer the questions 2, 3 and 4 on the above curve.

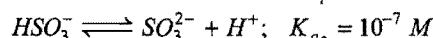
2. Which of the titrations could it represent?
 - (a) HCl by KOH (b) RbOH by HBr
 - (c) HCl by NaOH (d) NH₃ by HNO₃
3. The suitable indicator for this titration will be:
 - (a) bromothymol blue (b) methyl orange
 - (c) methyl red (d) all of these
4. The pH at equivalence point is:
 - (a) 11 (b) 7 (c) 3 (d) 2
5. Which of the following curves indicates the titration of a weak diprotic acid by NaOH of equivalent strength?



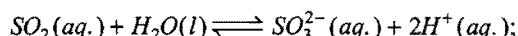
● Passage 4

Acid rain takes place due to combination of acidic oxides with water. In atmosphere, sulphur dioxide and nitrogen monoxide are oxidised to sulphur trioxide and nitrogen dioxide respectively, which react with water to give sulphuric and nitric acid. The resultant

solution so called is acid rain. Sulphur dioxide dissolves in water to form diprotic acid in aqueous solution.



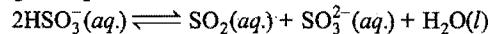
and for equilibrium,



$$K_a = K_{a_1} \times K_{a_2} = 10^{-9} \text{ at } 300 K \text{ at } 27^\circ C$$

Answer the following questions:

1. Which of the following reagents will give white precipitate with the aqueous solution of sulphurous acid?
 - (a) NaCl (b) KCl (c) BaCl₂ (d) HCl
2. The pH of 0.01 M aqueous solution of sodium sulphite will be:
 - (a) 8.5 (b) 9 (c) 4.5 (d) 9.5
3. The dominant equilibrium in an aqueous solution of sodium hydrogen sulphite is:



The equilibrium constant for the above reaction is:

$$(a) 10^{-6} \quad (b) 10^{-9} \quad (c) 10^{-5} \quad (d) 10^{-3}$$

4. Which among the following statements is correct?
 - (a) CO₂ gas develops more acidity in rain-water than SO₂
 - (b) H₂SO₃ is less acidic than H₂SO₄
 - (c) HNO₃ is less acidic than HNO₂
 - (d) SO₂(g) is reduced in the atmosphere during thunderstorm

● Passage 5

The product of the concentrations of the ions of an electrolyte raised to power of their coefficients in the balanced chemical equation in the solution at any concentration. Its value is not constant and varies with change in concentration. Ionic product of the saturated solution is called solubility product K_{sp}.

- (i) When K_{ip} = K_{sp}, the solution is just saturated and no precipitation takes place.
- (ii) When K_{ip} < K_{sp}, the solution is unsaturated and precipitation will not take place.
- (iii) When K_{ip} > K_{sp}, the solution is supersaturated and precipitation takes place.

Answer the following questions:

1. The solubility product, K_{sp}, of sparingly soluble salt MX at 25°C is 2.5×10^{-9} . The solubility of the salt in mol L⁻¹ at this temperature is:
 - (a) 1×10^{-14} (b) 5×10^{-8} (c) 1.25×10^{-9} (d) 5×10^{-5}
2. Which of the following is most soluble?
 - (a) Bi₂S₃ ($K_{sp} = 1 \times 10^{-70}$) (b) MnS ($K_{sp} = 7 \times 10^{-16}$)
 - (c) CuS ($K_{sp} = 8 \times 10^{-37}$) (d) Ag₂S ($K_{sp} = 6 \times 10^{-51}$)
3. The concentration of Ag⁺ ions in a given saturated solution of AgCl at 25°C is 1.06×10^{-5} g ion per litre. The solubility product of AgCl is:
 - (a) 0.353×10^{-10} (b) 0.530×10^{-10}
 - (c) 1.12×10^{-10} (d) 2.12×10^{-10}
4. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

- (a) $10^{-4} M \text{Ag}^+ + 10^{-4} M \text{Cl}^-$
 (b) $10^{-5} M \text{Ag}^+ + 10^{-5} M \text{Cl}^-$
 (c) $10^{-6} M \text{Ag}^+ + 10^{-6} M \text{Cl}^-$
 (d) $10^{-10} M \text{Ag}^+ + 10^{-10} M \text{Cl}^-$
5. When HCl gas is passed through saturated NaCl solution, the ionic product of NaCl is exceeded because of:
 (a) increase in Cl^- ion concentration
 (b) increase in Na^+ ion concentration
 (c) decrease in the NaCl concentration
 (d) decrease in Cl^- ion concentration
6. If the solubility of $\text{Li}_3\text{Na}_3(\text{AlF}_6)_2$ is $x \text{ mol L}^{-1}$, then its solubility product is equal to:
 (a) $12x^3$ (b) $18x^3$ (c) x^8 (d) $2916x^8$

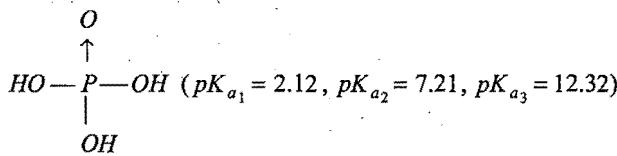
Passage 6

The dissociation of weak electrolyte (weak acid) is expressed in terms of Ostwald dilution law. Stronger is the acid, weaker is its conjugate base. The dissociation constants of an acid (K_a) and its conjugate base (K_b) are related by the given relation:

$$K_w = K_a \times K_b$$

At 25°C , K_w (Ionic product of water) = 10^{-14} .

Phosphoric acid is a weak acid. It is used in fertilizer, food, detergent and toothpaste. Structure of phosphoric acid is:

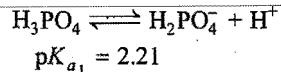


Aqueous solution of phosphoric acid with a density of 1 g mL^{-1} containing 0.05% by weight of phosphoric acid is used to impart tart taste to many soft drinks.

Phosphate ion is an interfering radical in qualitative analysis. It should be removed for analysis beyond third group of qualitative analysis.

Answer the following questions:

- The basicity of phosphoric acid is:
 (a) 1 (b) 2 (c) 3 (d) 4
- The state of hybridization of phosphorous in phosphoric acid is:
 (a) sp (b) sp^2 (c) sp^3 (d) sp^3d
- The removal of PO_4^{3-} in qualitative analysis of basic radicals is made by using a buffer solution of:
 (a) HCO_3^- and CO_3^{2-} (b) CH_3COO^- and CH_3COOH
 (c) NH_4^+ and NH_4OH (d) none of these
- What is the molarity of phosphoric acid used in soft drinks?
 (a) 5.1×10^{-3} (b) 1.5×10^{-3} (c) 3.1×10^{-3} (d) 2.1×10^{-3}
- Which among the following relations is correct?
 (a) $K_{a_1} < K_{a_2} < K_{a_3}$ (b) $K_{a_1} > K_{a_2} > K_{a_3}$
 (c) $K_{a_1} = K_{a_2} = K_{a_3}$ (d) $K_{a_1} > K_{a_3} > K_{a_2}$
- First ionization of phosphoric acid is:



The dissociation constant of conjugate base of H_3PO_4 will be:

- (a) 6.45×10^{-9} (b) 1.62×10^{-12}
 (c) 3.48×10^{-11} (d) 4.62×10^{-2}

[Hint: $\text{p}K_{a_1} = 2.21$

$$K_{a_1} = \text{antilog}(-2.21)$$

$$= 6.165 \times 10^{-3}$$

$$K_b \text{ (of conjugate base)} = \frac{K_w}{K_{a_1}}$$

$$= \frac{10^{-14}}{6.165 \times 10^{-3}}$$

$$= 1.62 \times 10^{-12}]$$

Answers

Passage 1.	1. (c)	2. (b)	3. (a)	4. (b)	5. (b)	6. (c)
Passage 2.	1. (d)	2. (a)	3. (c)	4. (b)	5. (b)	
Passage 3.	1. (a)	2. (b)	3. (d)	4. (b)	5. (a)	
Passage 4.	1. (c)	2. (d)	3. (c)	4. (b)		
Passage 5.	1. (d)	2. (b)	3. (c)	4. (a)	5. (a)	6. (d)
Passage 6.	1. (c)	2. (c)	3. (b)	4. (a)	5. (b)	6. (b)

SELF ASSESSMENT

ASSIGNMENT NO. 10

SECTION-I

Straight Objective Type Questions

This section contains 7 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. When 50 mL of 0.1 M NaOH is mixed with 50 mL of 0.05 M CH₃COOH solution, pH becomes:

(a) 1.602 (b) 12.39
 (c) 4.74 (d) 8.72
2. If the degree of dissociation of water at 90°C is 1.28×10^{-8} then the ionisation constant of water at 90°C is:

(a) $7.52 \times 10^{-12} M$ (b) $9.07 \times 10^{-15} M$
 (c) $1.28 \times 10^{-14} M$ (d) $1.38 \times 10^{-14} M$
3. How much water from 5 litre of 10⁻³ M HCl should be evaporated to change its pH by 2 units?

(a) 1.5 litre (b) 0.5 litre (c) 2.54 litre (d) 4.95 litre
4. Which among the following cannot exist in an aqueous solution?

(a) NH₄⁺ (b) NO₃⁻
 (c) NO₂⁻ (d) NH₂⁻
5. The pH of an HCl solution is 2. Sufficient water is added to make the pH of new solutions. The hydrogen ion concentration is reduced:

(a) ten fold (b) seven fold
 (c) thousand fold (d) hundred fold
6. Consider the following statements:

I. HNO₃ (strong acid) behaves as a base in HF.
 II. H₂SO₄ dissociates to a small extent in glacial acetic acid.
 III. CH₃COOH (a weak acid) behaves as strong acid in NH₃(l). Select the correct alternate for these statements:

(a) I, II, and III (b) I and III
 (c) II and III (d) I and II
7. The solubility of A₂X₅ is x mol dm⁻³. Its solubility product is:

(a) $36x^6$ (b) $64 \times 10^4 x^7$
 (c) $126x^7$ (d) $1.25 \times 10^4 x^7$

SECTION-II

Multiple Answers Type Objective Questions

8. During the titration of mixture of NaOH, Na₂CO₃ and an inert substance against hydrochloric acid:

(a) phenolphthalein is used to detect the end point when NaOH is completely neutralized and half of Na₂CO₃ is neutralized
 (b) methyl orange is used to detect the final end point
 (c) methyl orange is used to detect the first end point
 (d) phenolphthalein is used to detect the final end point
9. Solubility product of the hydroxide M(OH)₂ is 4×10^{-12} . Select the correct statement(s) among the following:

- (a) the pH of its saturated solution will be 10.3
 (b) its solubility will decrease in a buffer medium of pH = 9
 (c) its solubility will increase in a buffer medium of pH = 1
 (d) its solubility is unaffected by pH of the medium

10. Which of the following salt solutions will be basic?

(a) NaCl (b) NaCN (c) K₂CO₃ (d) NH₄NO₃
11. Which of the following salts will not undergo hydrolysis?

(a) NaCl (b) KCl (c) NH₄Cl (d) CH₃COONa
12. Which of the following mixtures will be buffer?

(a) CH₃COOH + CH₃COONH₄
 (b) HCl + NaCl
 (c) Borax ± boric acid
 (d) CH₃COOH + CH₃COONa

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
 (c) Statement-1 is true; statement-2 is false.
 (d) Statement-1 is false; statement-2 is true.
13. Statement-1: Mixture of CH₃COOH and CH₃COONH₄ is not a buffer solution.

Because

Statement-2: Acid buffer contains the mixture of weak acid and its salt with strong base.

14. Statement-1: Addition of NH₄OH to an aqueous solution of BaCl₂ in the presence of excess NH₄Cl, precipitates Ba(OH)₂.

Because

Statement-2: Ba(OH)₂ is soluble in water.

15. Statement-1: pH of blood does not change inspite of taking acidic foods.

Because

Statement-2: Blood behaves as buffer solution.

16. Statement-1: Borax forms alkaline aqueous solution.

Because

Statement-2: Borax is the salt of a weak acid (H₃BO₃) and a strong base (NaOH).

17. Statement-1: When the aqueous solution of CH₃COONH₄ is diluted, then its degree of hydrolysis does not change.

Because

Statement-2: It is the salt of a weak acid and a weak base hence its degree of hydrolysis does not depend on the concentration.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4×4 matrix should be as given:

	p	q	r	s
a	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
b	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
c	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>

18. Match the Column-I with Column-II:

Column-I (Salt solution in water)	Column-II (Nature of hydrolysis)
(a) NaCl	(p) Cationic hydrolysis
(b) CH ₃ COONa	(q) Anionic hydrolysis
(c) NH ₄ CN	(r) Both cationic and anionic hydrolysis
(d) NH ₄ Cl	(s) Does not undergo hydrolysis

19. Match the Column-I with Column-II:

Column-I	Column-II
(a) H ₃ PO ₂	(p) Dibasic
(b) H ₃ PO ₄	(q) Monobasic
(c) H ₃ PO ₃	(r) Tribasic
(d) H ₃ BO ₃	(s) Aprotic

20. Match the Column-I with Column-II:

Column-I (Salt)	Column-II (Degree of hydrolysis)
(a) NH ₄ Cl	(p) No hydrolysis
(b) NaCl	(q) $h = \sqrt{\frac{K_h}{C}}$
(c) CH ₃ COONa	(r) $h = \sqrt{\frac{K_w}{CK_b}}$
(d) CH ₃ COONH ₄	(s) $h = \sqrt{K_h}$

Answers

- | | | | | | | | |
|--------------|-----------------------------|------------|--------------------------------|---------|--------------------------------|---------|-----------|
| 1. (b) | 2. (a) | 3. (a) | 4. (d) | 5. (c) | 6. (a) | 7. (d) | 8. (a, b) |
| 9. (a, b, c) | 10. (b, c) | 11. (a, b) | 12. (c, d) | 13. (d) | 14. (d) | 15. (a) | 16. (a) |
| 17. (a) | 18. (a-s) (b-q) (c-r) (d-p) | | 19. (a-q) (b-r) (c-p) (d-q, s) | | 20. (a-q, r) (b-p) (c-q) (d-s) | | |



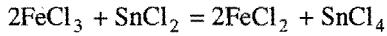
CHAPTER 11

OXIDATION AND REDUCTION (Redox Reactions)

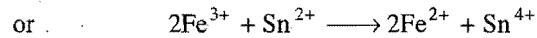
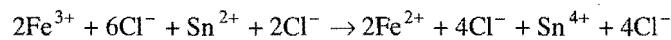
Several chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed **oxidation-reduction** or **redox reactions**. Redox reactions play a vital role in our daily life. These reactions are accompanied by energy changes in the form of heat, light, electricity, etc. Generation of electricity in batteries, production of heat energy by burning chemical substances, extraction of metals such as sodium, aluminium, iron, etc., manufacture of a number of useful products such as caustic soda, potassium permanganate, etc.; electrodeposition or electroplating are common examples of redox reactions. Before we discuss the application of redox reactions in the production of electricity in different cells and the electrolysis phenomenon, it will be proper to study first the basic concepts of oxidation-reduction. The present chapter deals with the basic fundamentals of oxidation-reduction.

11.1 MOLECULAR AND IONIC EQUATIONS

Consider the reaction between solutions of ferric chloride and stannous chloride. When they are mixed, ferrous chloride and stannic chloride are formed. The chemical change can be represented by the following equation:



The reactants and products have been written in molecular forms; thus, the equation is termed as **molecular equation**. Since, the reactants and products involved in the chemical change are ionic compounds, these will be present in the form of ions in the solution. So, the above chemical change can be written in the following manner also:



The ferric ions combine with stannous ions to form ferrous

ions and stannic ions. This is an **ionic equation** for the above chemical change.

Ionic equations represent chemical changes in terms of ions which actually undergo reaction. The ions which do not undergo any electronic change during a chemical change are termed **spectator ions**. The spectator ions are not included in the final balanced equations.

The rules to be followed for writing ionic equations are:

(i) All soluble ionic compounds involved in a chemical change are expressed in ionic symbols and covalent substances are written in molecular form. H_2O , NH_3 , NO_2 , NO , SO_2 , CO , CO_2 , etc., are expressed in molecular form.

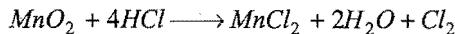
(ii) The ionic compound which is highly insoluble is expressed in molecular form.

(iii) The ions which are common and equal in number on both sides, i.e., spectator ions, are cancelled.

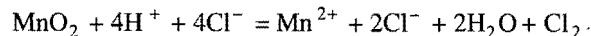
(iv) Besides the atoms, the ionic charges must also be balanced on both the sides.

Some Solved Examples

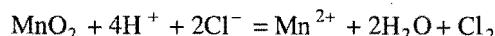
Example 1. Write the following equation in ionic form.



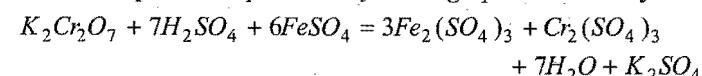
Solution: In this equation HCl and MnCl_2 are ionic in nature. Writing these compounds in ionic form,



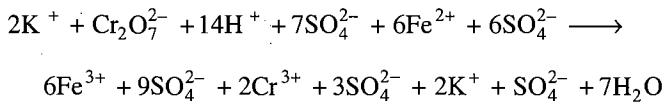
2Cl^- ions are common on both sides; so these are cancelled. The desired ionic equation reduces to,



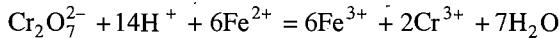
Example 2. Represent the following equation in ionic form.



Solution: In this equation except H_2O , all are ionic in nature. Representing these compounds in ionic forms,



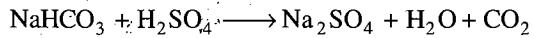
$2K^+$ ions and $13SO_4^{2-}$ ions are common on both sides, so these are cancelled. The desired ionic equation reduces to,



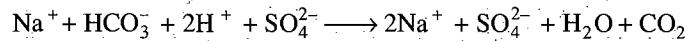
Total charges are equal on both sides; thus, the balanced ionic equation is the same as above.

Example 3. Write the balanced ionic equation for the reaction of sodium bicarbonate with sulphuric acid.

Solution: The molecular equation for the chemical change is:



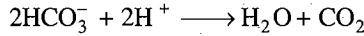
$NaHCO_3$, H_2SO_4 and Na_2SO_4 are ionic compounds; so these are written in ionic forms.



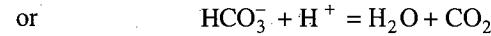
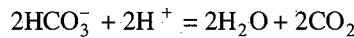
Na^+ and SO_4^{2-} ions are spectator ions; hence these shall not appear in the final equation.



To make equal charges on both sides, HCO_3^- should have a coefficient 2.

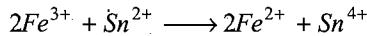


In order to balance the hydrogen and carbon on both sides, the molecules of H_2O and CO_2 should have a coefficient 2 respectively.

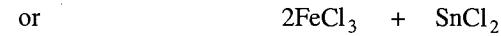
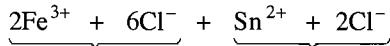


This is the balanced ionic equation.

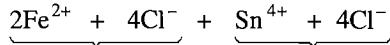
Example 4. Write the following ionic equation in the molecular form if the reactants are chlorides.



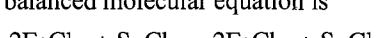
Solution: For writing the reactants in molecular forms, the requisite number of chloride ions are added.



Similarly 8 Cl^- ions are added on RHS to neutralise the charges.



Thus, the balanced molecular equation is

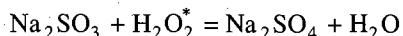
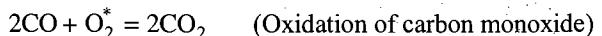


11.2 OXIDATION AND REDUCTION

Early Ideas of Oxidation and Reduction: The term oxidation was first used to describe chemical reactions in which oxygen was added to an element or a compound. The phenomenon of combustion was the earliest example of oxidation. Later on the term oxidation was extended to describe many more reactions which occurred without the use of even oxygen.

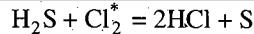
Oxidation is a process which involves:

(a) Addition of oxygen:

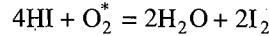


(Oxidation of sodium sulphite)

(b) Removal of hydrogen:



(Oxidation of hydrogen sulphide)

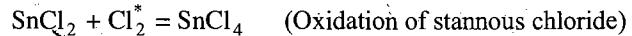


(Oxidation of hydrogen iodide)

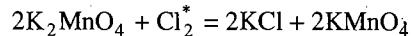


(Oxidation of hydrogen chloride)

(c) Addition of an electronegative element:



(d) Removal of an electropositive element:



(Oxidation of potassium manganate)

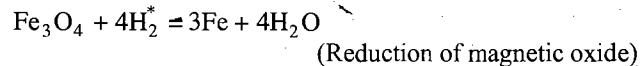
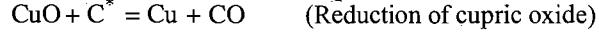


A substance which brings oxidation is known as **oxidising agent**. The substances marked with asterisk sign (*) in above equations are oxidising agents.

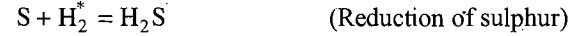
Reduction is just the reverse of oxidation.

Reduction is a process which involves:

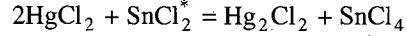
(a) Removal of oxygen:



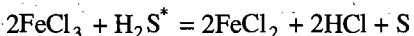
(b) Addition of hydrogen:



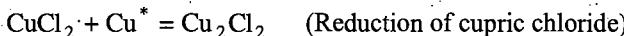
(c) Removal of an electronegative element:



(Reduction of mercuric chloride)



(Reduction of ferric chloride)

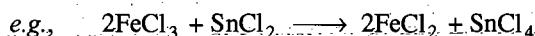
(d) Addition of an electropositive element:

The substance which brings reduction is known as **reducing agent**. The substances marked with asterisk sign (*) in the above equations are reducing agents.

A substance, which undergoes oxidation, acts as a reducing agent while a substance, which undergoes reduction, acts as an oxidising agent.

Mg, S, Cu, Na₂SO₃, H₂S, HI, H₂, C, KI are reducing agents, while O₂, Cl₂, F₂, H₂O₂, MnO₂, FeCl₃, CuCl₂, Fe₃O₄, CuO, etc., are oxidising agents in the above examples.

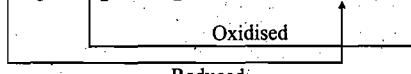
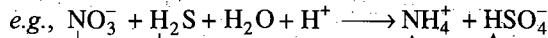
All oxidation and reduction reactions are complimentary of one another and occur simultaneously, one cannot take place without the other. No single oxidation and no single reduction process is known. The simultaneous oxidation and reduction reactions are generally termed as redox reactions.



In above example iron undergoes reduction from +3 to +2 and tin undergoes oxidation from +2 to +4.

Redox reactions are divided into two main types:

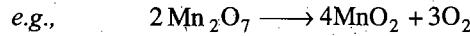
(i) Intermolecular redox: In such redox reactions, one molecule of reactant is oxidised whereas molecule of other reactant is reduced.



Reduced

Oxidised

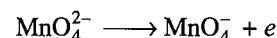
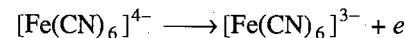
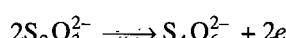
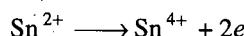
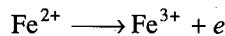
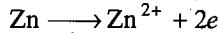
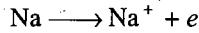
(ii) Intramolecular redox: One atom of a molecule is oxidised and other atom of same molecule is reduced then it is intramolecular redox reaction.



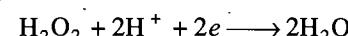
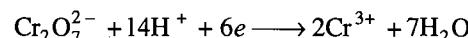
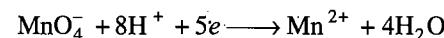
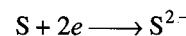
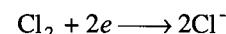
11.3 MODERN CONCEPT OF OXIDATION AND REDUCTION

According to the modern concept, loss of electrons is oxidation whereas gain of electrons is reduction.

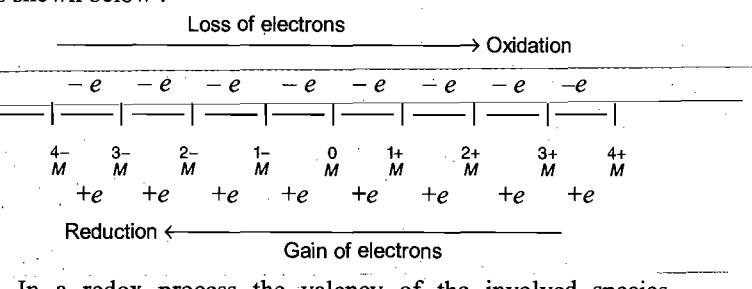
Examples of oxidation reactions are:



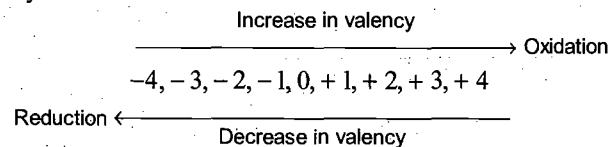
Examples of reduction reactions are:



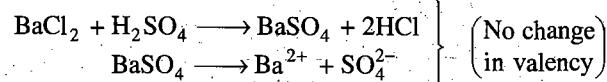
Oxidation and reduction can be represented in a general way as shown below :



In a redox process the valency of the involved species changes. The valency of a reducing agent increases while the valency of an oxidising agent decreases in a redox reaction. The valency of a free element is taken as zero.



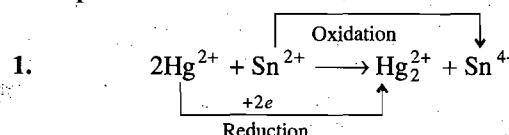
When there is no change in valency it means there is no oxidation or reduction, e.g., in

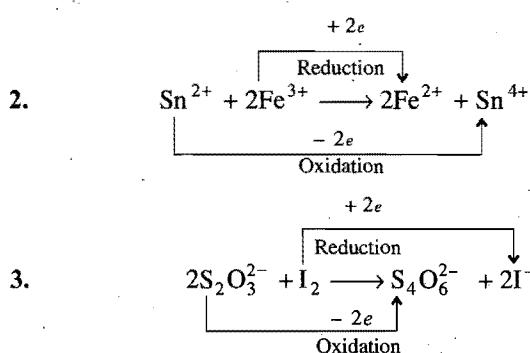


Conclusions

- Oxidation is a process in which one or more electrons are lost or valency of the element increases.
- Reduction is a process in which one or more electrons are gained or valency of the element decreases.
- Oxidising agent is a material which can gain one or more electrons, i.e., valency decreases.
- Reducing agent is a material which can lose one or more electrons, i.e., valency increases.
- Redox reaction involves two half reactions, one involving loss of electron or electrons (oxidation) and the other involving gain of electron or electrons (reduction).

Examples:





11.4 ION-ELECTRON METHOD FOR BALANCING REDOX REACTIONS

The method for balancing redox reactions by ion electron method was developed by Jette and LaMev in 1927. It involves the following steps:

- Write down the redox reaction in ionic form.
- Split the redox reaction into two half reactions, one for oxidation and the other for reduction.
- Balance each half reaction for the number of atoms of each element. For this purpose:
 - Balance the atoms other than H and O for each half reaction using simple multiples.
 - Add water molecules to the side deficient in oxygen and H⁺ to the side deficient in hydrogen. This is done in acidic or neutral solutions.
 - In alkaline solution, for each excess of oxygen, add one water molecule to the same side and two OH⁻ ions to the other side. If hydrogen is still unbalanced, add one OH⁻ ion for each excess hydrogen on the same side and one water molecule to the other side.
 - Add electrons to the side deficient in electrons as to equalise the charge on both sides.
 - Multiply one or both the half reactions by a suitable number so that the number of electrons become equal in both the equations.
 - Add the two balanced half reactions and cancel any term common to both sides.

The following solved problems illustrate the various steps of ion electron method:

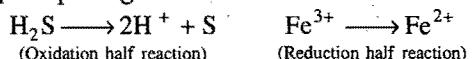
Example 5. Balance the following equations by ion electron method.

- $\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow \text{FeCl}_2 + \text{HCl} + \text{S}$
- $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
- $\text{KI} + \text{Cl}_2 \longrightarrow \text{KCl} + \text{I}_2$
- $\text{MnO}_2 + \text{HCl} \longrightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2$
- $\text{H}_2\text{S} + \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O}$

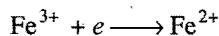
Solution: (a) $\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow \text{FeCl}_2 + \text{HCl} + \text{S}$

Ionic equation, $\text{Fe}^{3+} + \text{H}_2\text{S} \longrightarrow \text{Fe}^{2+} + \text{H}^+ + \text{S}$

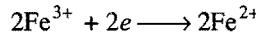
1st step. Splitting the redox reaction into two half reactions,



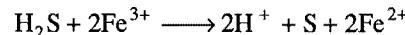
2nd step. Adding electrons to the side deficient in electrons,



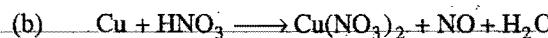
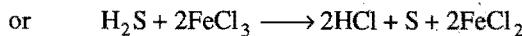
3rd step. Balancing electrons in both the half reactions,



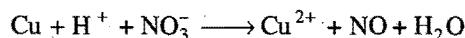
4th step. Adding both the half reactions,



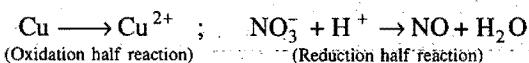
Converting it into molecular form,



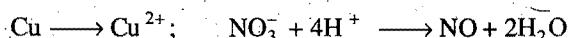
Ionic equation,



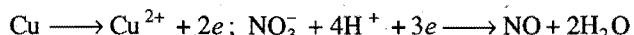
1st step. Splitting into two half reactions,



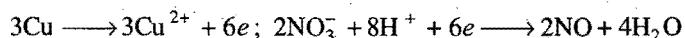
2nd step. Adding H⁺ ions to the side deficient in hydrogen,



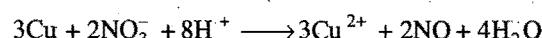
3rd step. Adding electrons to the side deficient in electrons,



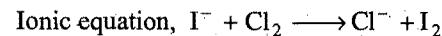
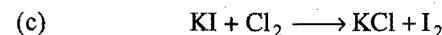
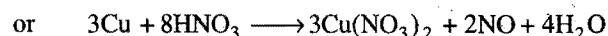
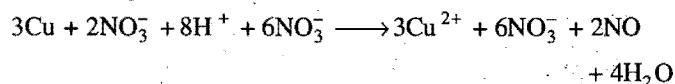
4th step. Balancing electrons in both half reactions,



5th step. Adding both the half reactions,



Converting it into molecular form,



Splitting into two half reactions,



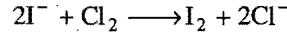
Making number of atoms equal,



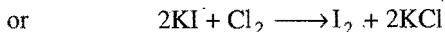
Adding electrons to the sides deficient in electrons,



Adding both the half reactions,



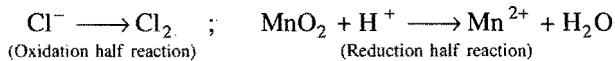
Converting it into molecular form,



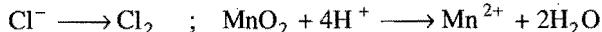
Ionic equation,



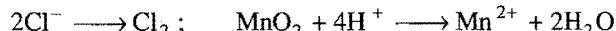
1st step. Splitting into two half reactions,



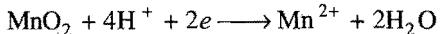
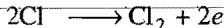
2nd step. Adding H^+ ions to the side deficient in hydrogen,



3rd step. Making atoms equal on both sides,



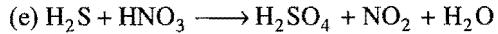
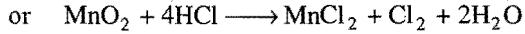
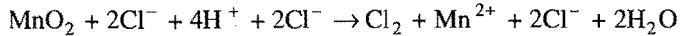
4th step. Adding electrons to the side deficient in electrons,



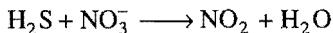
5th step. Adding both the half reactions,



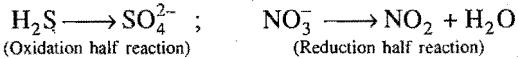
Converting it into molecular form,



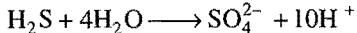
Ionic equation,



1st step. Splitting into two half reactions,



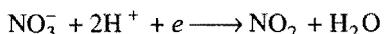
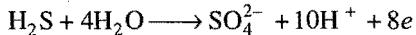
2nd step. Add water to the side deficient in oxygen,



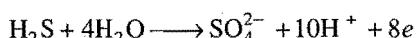
3rd step. Add H^+ ions to the side deficient in hydrogen,



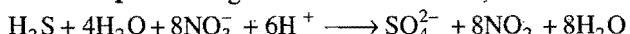
4th step. Add electrons to the side deficient in electrons,



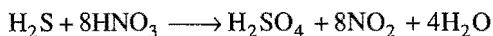
5th step. Balancing electrons in both the half reactions,



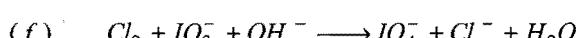
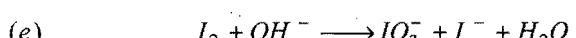
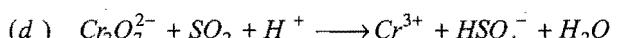
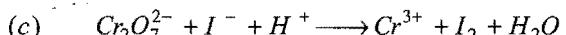
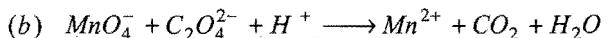
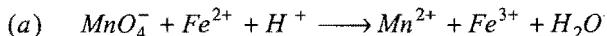
6th step. Adding both the half reactions,



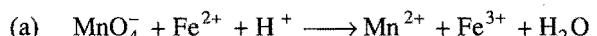
Converting it into molecular form,



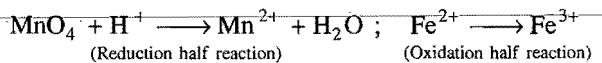
Example 6. Balance the following equations by ion electron method:



Solution:



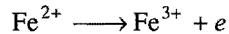
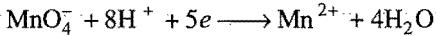
1st step. Splitting into two half reactions,



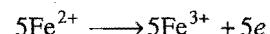
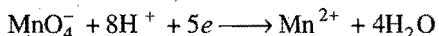
2nd step. Adding hydrogen ions to the side deficient in hydrogen,



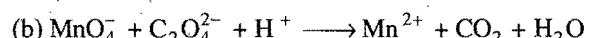
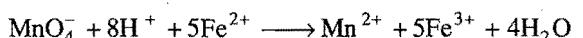
3rd step. Adding electrons to the sides deficient in electrons,



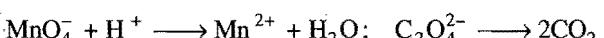
4th step. Balancing electrons in both half reactions,



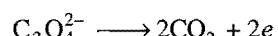
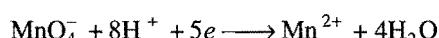
5th step. Adding both the half reactions,



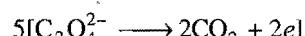
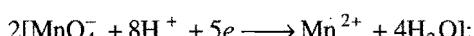
Splitting into two half reactions,



Balanced as in Question (a),

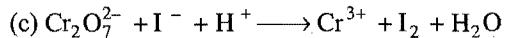


Balancing electrons in both half reactions,

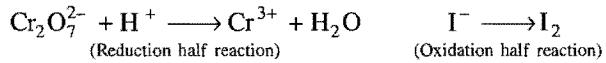


Adding both the half reactions,





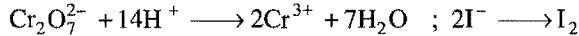
1st step. Splitting into two half reactions,



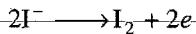
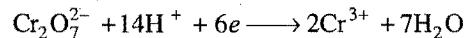
2nd step. Adding hydrogen ions to the side deficient in hydrogen,



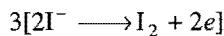
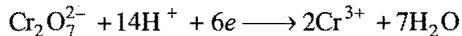
3rd step. Making atoms equal on both sides,



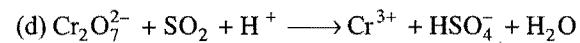
4th step. Adding electrons to the sides deficient in electrons,



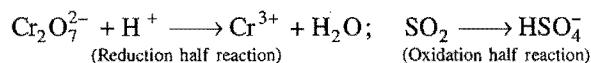
5th step. Balancing electrons,



6th step. Adding both the half reactions,



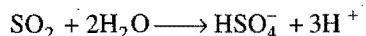
1st step. Splitting into two half reactions,



2nd step. Adding H⁺ ions to side deficient in hydrogen,



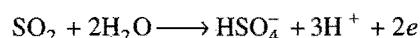
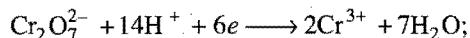
3rd step. Adding water to the side deficient in oxygen,



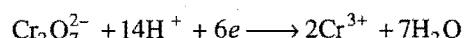
4th step. Making atoms equal on both sides,



5th step. Adding electrons to the sides deficient in electrons,



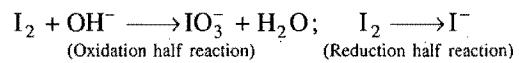
6th step. Balancing electrons in both the half reactions,



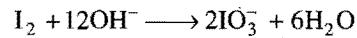
7th step. Adding both the half reactions,



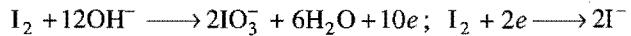
1st step. Splitting into two half reactions,



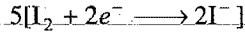
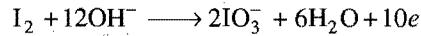
2nd step. Adding OH⁻ ions,



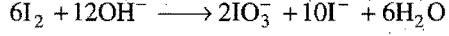
3rd step. Adding electrons to the sides deficient in electrons,



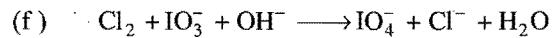
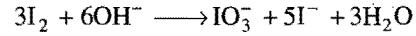
4th step. Balancing electrons in both the half reactions,



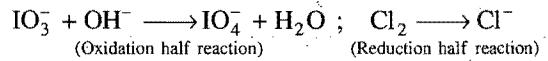
5th step. Adding both the half reactions,



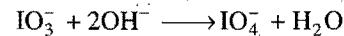
Dividing by 2,



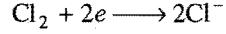
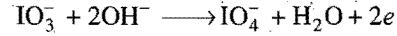
1st step. Splitting into two half reactions,



2nd step. Adding QH⁻ ions,



3rd step. Adding electrons to the sides deficient in electrons,



4th step. Adding both the half reactions,

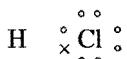


11.5 OXIDATION NUMBER (Oxidation State)

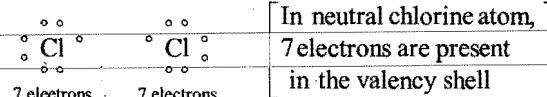
It is defined as the charge (real or imaginary) which an atom appears to have when it is in combination. In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion. This is the real charge and is developed by the loss and gain of electron or electrons. For example, in the electrovalent compound, sodium chloride (NaCl), the charge on sodium and chlorine is +1 and -1, respectively. The charges have been developed by the transfer of one electron from Na-atom to Cl-atom. Thus, in NaCl (Na⁺Cl⁻), the oxidation number of sodium is +1 and that of chlorine is -1.

The oxidation numbers of atoms in covalent compounds can be derived by assigning the electrons of each bond to the more electronegative atom of the bonded atoms. For a molecule of HCl

both the electrons of the covalent bond are assigned to the chlorine atom since it is more electronegative than hydrogen.



Thus, chlorine atom has one more electron than the neutral chlorine atom which brings one unit negative charge on chlorine. The oxidation number of chlorine in this compound is -1 . The hydrogen atom has lost the only electron possessed by it, thus acquiring one unit positive charge. The oxidation number of hydrogen is, therefore, $+1$ in this compound. In the case of covalent bond between two identical atoms, i.e., electronegativity difference is zero, the bonding electrons are shared equally between the bonded atoms, i.e., no charge is developed on any of the atoms. Thus, the oxidation numbers of both chlorine atoms are zero in the molecule of chlorine.



Counting of electrons in this fashion is not convenient in many molecules and therefore the following operational rules are followed which are helpful and convenient in determining the oxidation numbers:

- (i) The oxidation number (Ox.no.) of an atom in free elements is zero, no matter how complicated the molecule is, hydrogen in H_2 , sulphur in S_8 , phosphorus in P_4 , oxygen in O_2 or O_3 , all have zero value of oxidation numbers.
- (ii) The fluorine, which is the most electronegative element, has oxidation number -1 in all of its compounds.
- (iii) Oxidation number of oxygen is -2 in all compounds except in peroxides, superoxides and oxygen fluorides. In peroxides (O_2^{2-}), oxygen has oxidation number -1 ; in superoxides (O_2^-), oxygen has oxidation number $-1/2$; and in OF_2 , the oxygen has an oxidation number $+2$.
- (iv) The oxidation number of hydrogen is $+1$ in all of its compounds except in metallic hydrides like NaH , BaH_2 , etc. Hydrogen is in -1 oxidation state in these hydrides.
- (v) The oxidation number of an ion is equal to the electrical charge present on it.
- (vi) The oxidation number of IA elements (Li, Na, K, Rb, Cs and Fr) is $+1$ and the oxidation number of IIA elements (Be, Mg, Ca, Sr, Ba and Ra) is $+2$.
- (vii) For complex ions, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.
- (viii) In the case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecule is zero.

The following solved examples illustrate the application of the above rules for finding out the oxidation number of an element in particular species:

Example 7. What is the oxidation number of Mn in KMnO_4 and of S in $\text{Na}_2\text{S}_2\text{O}_3$?

Solution: Let the Ox.no. of Mn in KMnO_4 be x .

We know that, Ox.no. of K = $+1$
Ox.no. of O = -2

$$\begin{aligned} \text{So, } & \text{Ox.no. K} + \text{Ox.no. Mn} + 4(\text{Ox.no. O}) = 0 \\ \text{or } & +1 + x + 4(-2) = 0 \\ \text{or } & +1 + x - 8 = 0 \\ \text{or } & x = +8 - 1 = +7 \end{aligned}$$

Hence, Ox.no. of Mn in KMnO_4 is $+7$.

Similarly, for S in $\text{Na}_2\text{S}_2\text{O}_3$,

$$\begin{aligned} 2(\text{Ox.no. Na}) + 2(\text{Ox.no. S}) + 3(\text{Ox.no. O}) &= 0 \\ 2 \times (+1) + 2x + 3(-2) &= 0 \\ x &= +2 \end{aligned}$$

Hence, Ox.no. of S in $\text{Na}_2\text{S}_2\text{O}_3$ = $+2$.

Example 8. What is the oxidation number of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$? (Ranchi 1996)

Solution: Let the Ox.no. of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ be x .

We know that, Ox.no. of K = $+1$

Ox.no. of O = -2

$$\begin{aligned} \text{So, } & 2(\text{Ox.no. K}) + 2(\text{Ox.no. Cr}) + 7(\text{Ox.no. O}) = 0 \\ & 2(+1) + 2(x) + 7(-2) = 0 \\ \text{or } & +2 + 2x - 14 = 0 \\ \text{or } & 2x = +14 - 2 = +12 \\ \text{or } & x = +\frac{12}{2} = +6 \end{aligned}$$

Hence, oxidation number of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ is $+6$.

Example 9. What is the oxidation number of Fe in $\text{K}_4\text{Fe}(\text{CN})_6$?

Solution: Let the oxidation number of Fe be x .

We know that, Ox.no. of K = $+1$

Ox.no. of $(\text{CN})^-$ = -1

$$\begin{aligned} \text{So, } & 4(\text{Ox.no. K}) + \text{Ox.no. Fe} + 6(\text{Ox.no. CN}^-) = 0 \\ & 4(+1) + x + 6(-1) = 0 \\ \text{or } & +4 + x - 6 = 0 \\ \text{or } & x = +6 - 4 = +2 \end{aligned}$$

The oxidation number of iron in $\text{K}_4\text{Fe}(\text{CN})_6$ is $+2$.

Example 10. Find the oxidation number of

- (a) S in SO_4^{2-} ion
- (b) S in HSO_3^- ion
- (c) Pt in $(\text{PtCl}_6)^{2-}$ ion
- (d) Mn in $(\text{MnO}_4)^-$ ion

Solution: (a) Let the oxidation number of S be x .

We know that, Ox.no. of O = -2

$$\begin{aligned} \text{So, } & \text{Ox.no. S} + 4(\text{Ox.no. O}) = -2 \\ \text{or } & x + 4(-2) = -2 \\ \text{or } & x - 8 = -2 \\ \text{or } & x = +8 - 2 = +6 \end{aligned}$$

The oxidation number of S in SO_4^{2-} ion is $+6$.

(b) Let the oxidation number of S be x in HSO_3^- ion.

We know that, Ox.no. of H = $+1$

Ox.no. of O = -2

So, Ox. no. H + Ox. no. S + 3(Ox. no. O) = -1
 $+1 + x + 3(-2) = -1$
 or $+1 + x - 6 = -1$
 or $x - 5 = -1$
 or $x = +5 - 1 = +4$

The oxidation number of S in HSO_3^- ion is +4.

(c) Let oxidation number of Pt be x.

We know that Ox.no. of Cl = -1.

So, Ox. no. Pt + 6(Ox. no. Cl) = -2
 $x + 6(-1) = -2$
 or $x - 6 = -2$
 or $x = +6 - 2 = +4$

The oxidation number of Pt in $[\text{Pt}(\text{Cl})_6]^{2-}$ ion is +4.

(d) Let oxidation number of Mn be x.

We know that, Ox.no. of O = -2.

So, Ox. no. Mn + 4(Ox. no. O) = -1
 $x + 4(-2) = -1$
 or $x - 8 = -1$
 or $x = +8 - 1 = +7$

The oxidation number of Mn in $[\text{MnO}_4]^-$ ion is +7.

Example 11: Which compound amongst the following has the highest oxidation number for Mn?

KMnO_4 , K_2MnO_4 , MnO_2 and Mn_2O_3 .

Solution:

KMnO_4	$+1 + x - 8 = 0$	Ox.no. of Mn
	$x = +7$	+7
K_2MnO_4	$+2 + x - 8 = 0$	
	$x = +6$	+6
MnO_2	$x - 4 = 0$	
	$x = +4$	+4
Mn_2O_3	$2x - 6 = 0$	
	$x = +3$	+3

Thus, the highest oxidation number for Mn is in KMnO_4 .

Sometimes, oxidation numbers have such values which at first sight appear strange. For example, the oxidation number of carbon in cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), dichloromethane, etc., is zero.

Cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)
 $12 \times x + 22 \times 1 + 11(-2) = 0$ $6 \times x + 12 \times 1 + 6(-2) = 0$
 $12x + 22 - 22 = 0$ $6x + 12 - 12 = 0$
 So, $x = 0$ So, $x = 0$

Dichloromethane (CH_2Cl_2)
 $x + 2 \times 1 + 2(-1) = 0$
 $x + 2 - 2 = 0$
 So, $x = 0$

- ILLUSTRATIONS OF OXIDATION AND REDUCTION**
- Oxidation state of S in SO_4^{2-} : [BCECE (Medical) 2005]
 (a) +6 (b) +3
 (c) +2 (d) -2

[Ans. (a)]

[Hint: Let oxidation state of S is x.

$$\therefore x + 4(-2) = -2$$

$$x = +6]$$

- Arrange the following in the increasing order of oxidation state of Mn: (JCECE 2004)

$$(i) \text{Mn}^{2+} \quad (ii) \text{MnO}_2 \quad (iii) \text{KMnO}_4 \quad (iv) \text{K}_2\text{MnO}_4$$

$$(a) (i) > (ii) > (iii) > (iv) \quad (b) (i) < (ii) < (iv) < (iii)$$

$$(c) (ii) < (iii) < (i) < (iv) \quad (d) (iii) < (i) < (iv) < (ii)$$

[Ans. (b)]

[Hint: $\text{Mn}^{2+} < \text{MnO}_2 < \text{K}_2\text{MnO}_4 < \text{KMnO}_4$]
 $(+2) \quad (+4) \quad (+6) \quad (+7)$

- Which of the following has least oxidation state of Fe? (JCECE 2005)

$$(a) \text{K}_3[\text{Fe}(\text{OH})_6]$$

$$(b) \text{K}_2[\text{FeO}_4]$$

$$(c) \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$$

$$(d) [\text{Fe}(\text{CN})_6]^{3-}$$

[Ans. (c)]

[Hint: In mohr salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, oxidation state of iron is +2 which is least.

$$\text{K}_3[\text{Fe}(\text{OH})_6] \quad +3 + x - 6 = 0 \quad x = +3$$

$$\text{K}_2[\text{FeO}_4] \quad +2 + x - 8 = 0 \quad x = +6$$

$$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \quad +2 \text{ state in } \text{FeSO}_4 \quad (x - 2 = 0)$$

$$\text{Fe}(\text{CN})_6^{3-} \quad x - 6 = -3 \quad x = +3]$$

- Oxidation state of carbon in HCOOH will be:

$$(a) +1 \quad (b) +2 \quad (c) -4 \quad (d) 0$$

[Ans. (b)]

[Hint: Let the oxidation state of carbon be x.

$$2 + x - 4 = 0$$

$$x = 2]$$

- Oxidation states of chlorine in HClO_4 and HClO_3 are:

$$(a) +4, +3 \quad (b) +7, +5 \quad (c) +3, +4 \quad (d) +5, +7$$

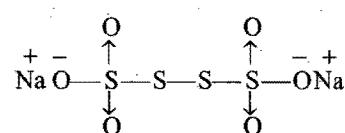
[Ans. (b)]

$$[\text{Hint: } \text{HClO}_4: +1 + x - 8 = 0, x = +7$$

$$\text{HClO}_3: +1 + x - 6 = 0, x = +5]$$

11.6: SPECIAL EXAMPLES OF OXIDATION STATE DETERMINATION

- Oxidation state of sulphur in $\text{Na}_2\text{S}_4\text{O}_6$:** It is only average oxidation number of sulphur. Let us see the structure of $\text{Na}_2\text{S}_4\text{O}_6$.



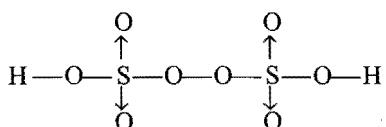
From the structure, it is clear that the sulphur atoms acting as donor atoms have +5 oxidation number (each). On the other hand, the sulphur atom involved in pure covalent bond formation has zero oxidation number.

2. Oxidation number of sulphur in $(CH_3)_2SO$ (dimethyl sulphoxide): Here, oxidation number O = -2, oxidation number of each CH_3 group is +1.

$$+2 + x - 2 = 0 \text{ or } x = 0$$

Thus, sulphur lies in zero oxidation state.

3. Oxidation number of sulphur in perdisulphuric acid $H_2S_2O_8$: It may be done only when the structure is drawn.



Oxidation number of S = x; oxidation number of H = +1; oxidation number of oxygen in peroxo linkage = -1; oxidation number of other six oxygen atoms = -2 each.

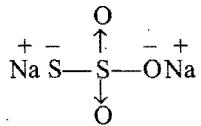
$$+2 + (-12) + 2x - 2 = 0$$

$$\therefore x = +6 \quad (\text{oxidation number of sulphur})$$

4. Oxidation number of sulphur in hypo, $Na_2S_2O_3$: Let the average oxidation number of sulphur be 'x'.

$$+2 + 2x - 6 = 0 \quad \therefore x = +2$$

Structure of hypo may be drawn as—

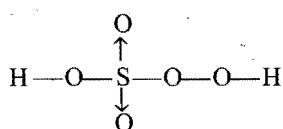


Here, the two sulphur atoms have different oxidation states:

- (i) Oxidation number of donor sulphur atom is +5. It gives up four electrons in coordination and one electron in covalent bond formation with oxygen.
- (ii) Sulphur, bonded with Na, lies in -1 state since one electron of Na lies towards the sulphur. Electrons of S-S bond are equally shared between two sulphur atoms.

Thus +5 and -1 are two oxidation states of the two sulphur atoms.

5. Oxidation number of sulphur in peroxy monosulphuric acid (H_2SO_5): Let us draw its structure.



Here, we have to consider Ox.no. of H = +1

Ox.no. of oxygen in peroxy linkage = -1

Ox.no. of rest of oxygen = -2

$$+2 + x - 6 - 2 = 0 \text{ or } x = +6$$

Thus, sulphur in H_2SO_5 lies in +6 oxidation state.

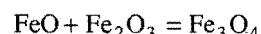
6. Fe in its oxides, FeO , Fe_2O_3 and Fe_3O_4 :

In $FeO \rightarrow x - 2 = 0, x = +2$

In $Fe_2O_3 \rightarrow 2x - 6 = 0, x = +3$

In $Fe_3O_4 \rightarrow 3x - 8 = 0, x = +8/3$ (fractional)

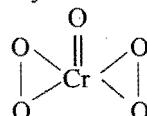
Here, in Fe_3O_4 , oxidation number is the average of those in FeO and Fe_2O_3 .



Average oxidation number of Fe in

$$Fe_3O_4 = \frac{+2 + 2(+3)}{3} = +\frac{8}{3}$$

7. Oxidation state of chromium in CrO_5 : CrO_5 has butterfly structure having two peroxy bonds



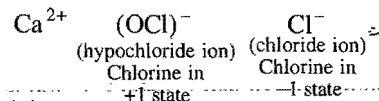
Peroxo oxygen has (-1) oxidation state.

Let oxidation state of chromium be 'x'.

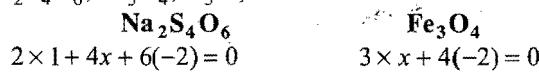
$$x + 4(-1) + (-2) = 0$$

$$x = +6$$

8. Oxidation state of chlorine in bleaching powder : Bleaching powder has two chlorine atoms having different oxidation states.



9. Fractional values of oxidation numbers are possible as in $Na_2S_4O_6$, Fe_3O_4 , N_3H , etc.



$$2 + 4x - 12 = 0 \quad 3x - 8 = 0$$

$$4x = +10 \quad 3x = 8$$

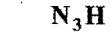
$$x = +\frac{10}{4} = +2.5 \quad x = +\frac{8}{3} \text{ or } +2\frac{2}{3}$$

Oxidation number of

S is +2.5

Oxidation number of

is $+2\frac{2}{3}$



$$3x + 1 = 0$$

$$3x = -1$$

$$x = -1/3$$

Oxidation number of
nitrogen is $-1/3$

10. Oxidation state of carbon and nitrogen in HCN and HNC: We should take into consideration the following fundamental aspects of bonding while counting the oxidation state of covalently bonded molecules:

(a) Single covalent bond contributes one unit for oxidation number.

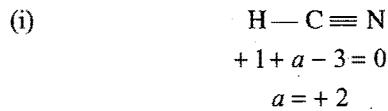
(b) Negative oxidation number is assigned to more electronegative atom and positive oxidation number to less electronegative atom.

(c) Coordinate bond is represented by an arrow from donor atom to acceptor atom.



If donor atom is less electronegative and acceptor is more, then +2 state is given to donor and -2 state is given to acceptor.

But it should be noted that if the donor is more electronegative than the acceptor, then contribution of coordinate bond for both atoms regarding oxidation state is neglected, e.g.,



Carbon is in +2 state and nitrogen is in -3 state. Each bond contributes -1 state to more electronegative atom.



Oxidation state of H = +1

Oxidation state of nitrogen = (-1) + (-2) + (0) = -3

Covalent bond with hydrogen contributes (-1) and covalent bond with carbon contributes (-2) and there is zero contribution of coordinate bond. Let the oxidation state of carbon be 'x'.

$$+1 - 3 + x = 0; x = +2$$

11. $\text{Fe}_{0.94}\text{O}$ (Oxidation state of iron is to be determined):

$$0.94x - 2 = 0 \\ x = 2 / 0.94 = 200 / 94$$

12. $\text{NH}_2 - \text{NH}_2$ (Oxidation state of nitrogen is to be determined):

$$2x + 4 = 0 \\ x = -2$$

13. KI_3 (Oxidation state of iodine is to be determined):

$$+1 + 3x = 0 \\ x = -1 / 3$$

KI_3 is mixture of K I and I_2 . Thus, two iodine atoms lie in zero state and one lies in -1 state.

14. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$: In iron complex NO lies in NO^+ state; thus oxidation state of 'Fe' may be determined as:

$$+2 + x - 5 + 1 = 0 \\ x = +2$$

15. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$:

$$x + 1 + 5(0) - 2 = 0 \\ x = +1$$

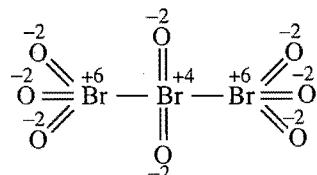
16. NOCl or $\text{Cl} - \text{N} = \text{O}$:

Oxidation state of chlorine = -1

Oxidation state of oxygen = -2

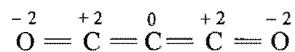
Thus, Oxidation state of nitrogen

17. Br_3O_8 (Tribromo octa-oxide):



$$\text{Average oxidation state} = \frac{(+6) + (4) + (+6)}{3} = \frac{16}{3}$$

18. C_3O_2 (Carbon sub-oxide):



$$\text{Average oxidation state} = \frac{+4}{3}$$

11.7 OXIDATION NUMBERS (States) IN DIFFERENT TYPES OF ELEMENTS

Zero group elements have zero oxidation number (state) as they do not show chemical activity while other elements have at least two oxidation states: zero when they exist in free state and positive or negative when they exist in compounds. Many elements show different oxidation states in different compounds. In the case of representative elements, the highest positive oxidation number (state) of an element is the same as its group number while the highest negative oxidation state is equal to (8 - group number) with negative sign with a few exceptions.

- (i) Alkali metals (IA) show uniformly +1 oxidation state, as they have ns^1 configuration and have only a tendency to lose this electron.
- (ii) Alkaline earth metals (IIA) show a common oxidation state of +2 as they have ns^2 configuration.
- (iii) Elements of group IIIA have $ns^2 np^1$ outer shell configuration, suggesting +1 and +3 oxidation states corresponding to use of np or $ns np$ electrons.
- (iv) Elements of group IVA have $ns^2 np^2$ outer shell configuration. They show oxidation states +4 (maximum) and -4 (minimum). However, Sn and Pb show either +2 or +4 oxidation states being metallic in nature.
- (v) VB elements have outer shell configuration $ns^2 np^3$. They show oxidation states between +5 and -3.
- (vi) The elements of VIA (with the exception of oxygen) show maximum oxidation state +6 and minimum oxidation state -2.
- (vii) The elements of VIIA (with the exception of fluorine) show maximum +7 and minimum -1 oxidation state.
- (viii) Transition metals exhibit a large number of oxidation states due to involvement of $(n-1)d$ electrons besides ns electrons.

The most common oxidation states of the representative elements are shown in the following table:

Group	Outer shell configuration	Common oxidation numbers (states) except zero in free state
IA	ns^1	+1
IIA	ns^2	+2
IIIA	$ns^2 np^1$	+3, +1
IV A	$ns^2 np^2$	+4, +3, +2, +1, -1, -2, -3, -4
V A	$ns^2 np^3$	+5, +3, +1, -1, -3
VIA	$ns^2 np^4$	+6, +4, +2, -2
VIIA	$ns^2 np^5$	+7, +5, +3, +1, -1

11.8 VALENCY AND OXIDATION NUMBER

Valecy of an element means the power or capacity of the element to combine with other elements. The valency of an element is numerically equal to the number of hydrogen atoms or chlorine atoms or twice the number of oxygen atoms that combine with one atom of that element. It is also equal to the number of electrons lost or accepted or shared by the atom of an element. In every case valency of an element is a pure number and has no plus or minus sign associated with it; while oxidation number (state) is an arbitrary number which can have positive, negative, zero or even fractional value. For example, in the following compounds of carbon, the oxidation number varies from -4 to +4 but valency of carbon is 4 in all the compounds:

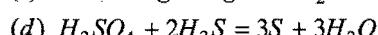
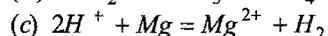
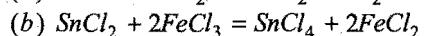
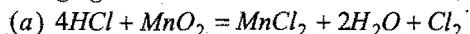
Compound	CH ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
Ox.no. of carbon	-4	-2	0	+2	+4

Thus, valency and oxidation number concepts are different. In some cases (mainly in the case of electrovalent compounds), valency and oxidation number are the same but in other cases they may have different values. Points of difference between the two have been tabulated below:

Valency	Oxidation number
1. It is the combining capacity of the element. No plus or minus sign is attached to it.	Ox.no. is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
2. Valency of an element is usually fixed.	Ox.no. of an element may have different values. It depends on the nature of the compound in which it is present.
3. Valency is always a whole number.	Ox.no. of the element may be a whole number or fractional.
4. Valency of the element is never zero except of noble gases.	Ox.no. of the element may be zero.

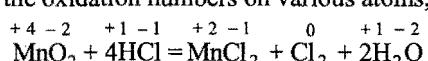
Term	Oxidation number
Oxidation	Increases
Reduction	Decreases
Oxidising agent	Decreases
Reducing agent	Increases

Example 12. In the following reactions, identify the species oxidised, the species reduced, the oxidising agent and the reducing agent:



Solution: (a) MnO₂ + 4HCl = MnCl₂ + Cl₂ + 2H₂O

Writing the oxidation numbers on various atoms,

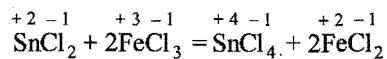


Ox.no. of Mn changes from +4 to +2, i.e., decrease in oxidation number. MnO₂ is thus reduced. It acts as an oxidising

agent. Ox.no. of Cl changes from -1 to 0, i.e., increase in oxidation number. HCl is thus oxidised. It acts as a reducing agent.

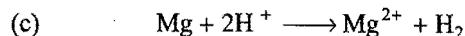


Writing the oxidation numbers on various atoms,

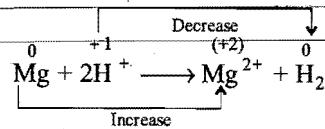


Ox.no. of Sn changes from +2 to +4, i.e., increase in oxidation number. SnCl₂ is thus oxidised or it acts as a reducing agent.

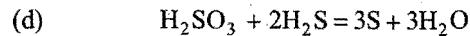
Ox.no. of Fe changes from +3 to +2, i.e., decrease in oxidation number. FeCl₃ is thus reduced or it acts as an oxidising agent.



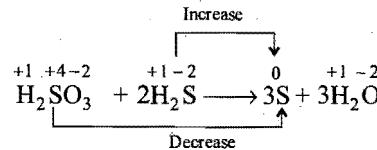
Writing oxidation numbers of various atoms,



Mg is oxidised, i.e., it acts as a reducing agent. H⁺ is reduced, i.e., it acts as an oxidising agent.

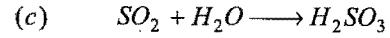
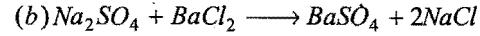
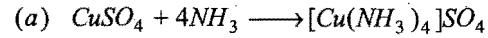


Writing oxidation numbers on various atoms,

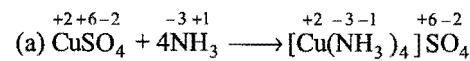


H₂SO₃ is reduced, i.e., it acts as oxidising agent. H₂S is oxidised, i.e., it acts as reducing agent.

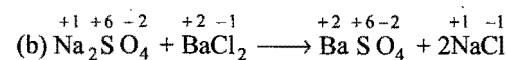
Example 13. Which one of the following reactions is a redox reaction?



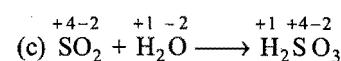
Solution: The reaction in which change in oxidation numbers of some of the atoms takes place is termed as a redox reaction.



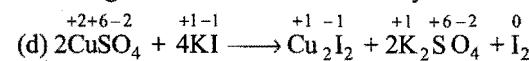
No change in oxidation number of any of the atoms.



No change in oxidation number of any one of the atoms.



No change in oxidation number of any one of the atoms.



Oxidation number of Cu decreases from +2 to +1 and oxidation number of iodine increases from -1 to 0.

Thus, out of the above four reactions, the reaction (d) is a redox reaction.

Example 14. Explain why HNO_3 acts only as oxidising agent while HNO_2 can act both as a reducing agent and an oxidising agent?

Solution: Nitrogen can have oxidation numbers from -3 to +5. The oxidation number of nitrogen in HNO_3 is +5. Thus, increase in oxidation number beyond +5 cannot occur. Hence, HNO_3 cannot act as reducing agent. The oxidation number of nitrogen in HNO_3 can only decrease; thus it acts as an oxidising agent. In HNO_2 , the oxidation number of nitrogen is +3. Thus, it can increase or decrease within the range -3 to +5. Hence, it can act as an oxidising as well as a reducing agent.

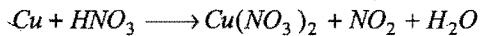
11.9 BALANCING OXIDATION-REDUCTION REACTIONS BY OXIDATION NUMBER METHOD

In a balanced redox reaction, total increase in oxidation number must be equal to the total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions. This method is applicable to both molecular and ionic equations. The general procedure involves the following steps:

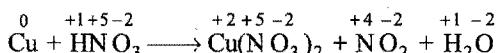
- (i) Write the skeleton equation (if not given, frame it) representing the chemical change.
- (ii) Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.
- (iii) Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.
- (iv) Complete the balancing by inspection. First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting H_2O molecules wherever needed.
- The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.
- (v) In ionic equations the net charges on both sides of the equation must be exactly the same. Use H^+ ion/ions in acidic reactions and OH^- ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

The following examples illustrate the above rules:

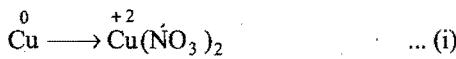
Example 15. Balance the following equation by oxidation number method:



Solution: Writing the oxidation numbers of all the atoms.



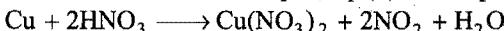
Change in Ox.no. has occurred in copper and nitrogen.



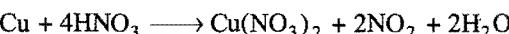
Increase in Ox.no. of copper = 2 units per molecule Cu

Decrease in Ox.no. of nitrogen = 1 unit per molecule HNO_3

To make increase and decrease equal, eq. (ii) is multiplied by 2.



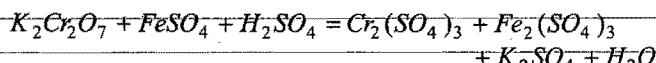
Balancing nitrate ions, hydrogen and oxygen, the following equation is obtained:



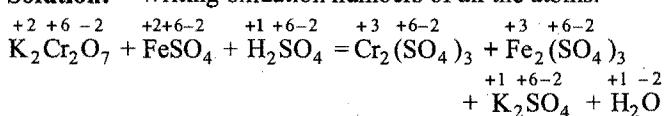
This is the balanced equation.

SOME SOLVED EXAMPLES

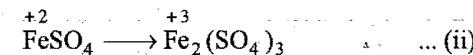
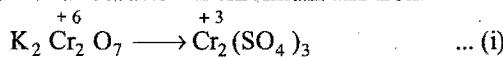
Example 16. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all the atoms.



Change in Ox.no. has occurred in chromium and iron.

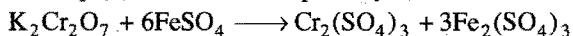


Decrease in Ox.no. of Cr per molecule

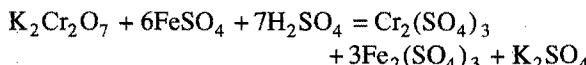
$$= (2 \times 6 - 2 \times 3) = 6 \text{ units}$$

Increase in Ox.no. of Fe per molecule = 1 unit

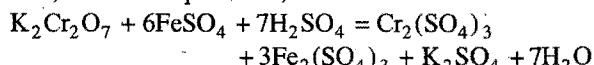
Hence, eq. (ii) should be multiplied by 6,



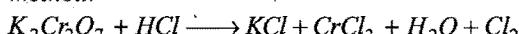
To balance sulphate ions and potassium ions, 7 molecules of H_2SO_4 are needed.



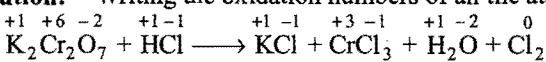
To balance hydrogen and oxygen, $7H_2O$ should be added on RHS. Hence, balanced equation is,



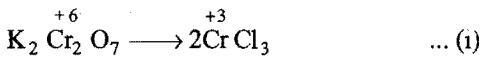
Example 17. Balance the following equation by oxidation number method:



Solution: Writing the oxidation numbers of all the atoms.



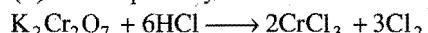
The Ox.no. of Cr has decreased while that of chlorine has increased.



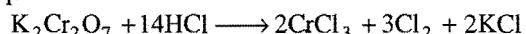
Decrease in Ox.no. of Cr = 6 units per molecule $K_2Cr_2O_7$

Increase in Ox. no. of Cl = 1 unit per molecule HCl

Eq. (ii) is multiplied by 6.



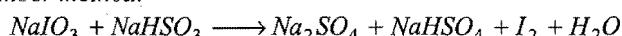
To balance chlorine and potassium, 14 molecules of HCl are required.



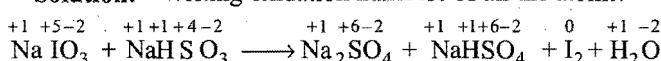
To balance hydrogen and oxygen, 7H₂O are added to RHS. Hence, the balanced equation is,



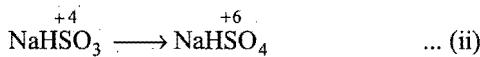
Example 18. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all the atoms.



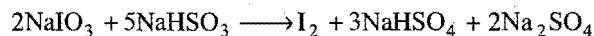
The oxidation no. of I has decreased while that of S has increased.



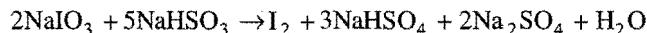
Decrease in Ox.no. of I = 5 units per molecule NaIO₃

Increase in Ox.no. of S = 2 units per molecule NaHSO₃

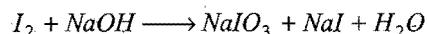
Eq. (i) is multiplied by 2 and eq. (ii) is multiplied by 5 as to make decrease and increase equal.



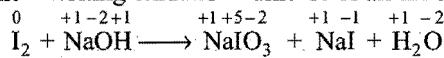
To balance hydrogen and oxygen, one H₂O molecule should be added on RHS. Hence, the balanced equation is



Example 19. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all the atoms,



The Ox.no. of iodine has increased as well as decreased.



Increase in Ox.no. of I = 5 units per I atom

Decrease in Ox.no. of I = 1 unit per I atom

Eq. (ii) should be multiplied by 5 as to make increase and decrease equal.



To balance Na, 6 molecules of NaOH should be added on LHS.



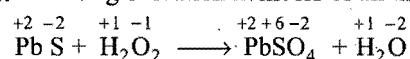
To balance hydrogen and oxygen, 3H₂O should be added on RHS. Hence, the balanced equation is



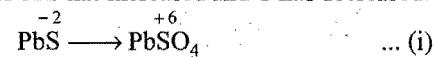
Example 20. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all the atoms,



The oxidation number of S has increased and O has decreased.



Increase in Ox.no. of S = 8 units per PbS molecule

Decrease in Ox.no. of O = 1 unit per $\frac{1}{2}$ H₂O₂ molecule

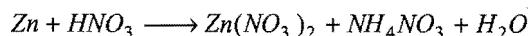
= 2 units per H₂O₂ molecule

Multiplying eq. (ii) by 4 as to make increase and decrease equal.

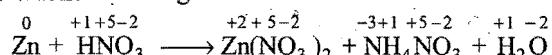


This is the balanced equation.

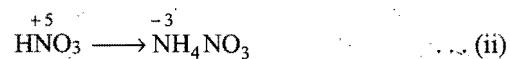
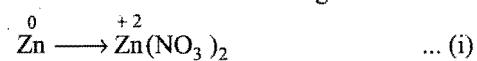
Example 21. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all the atoms,



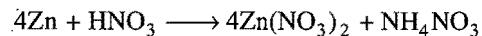
The oxidation numbers of Zn and N have changed.



Increase in Ox.no. of Zn = 2 units per Zn atom

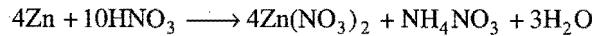
Decrease in Ox.no. of N = 8 units per HNO₃ molecule

Eq. (i) should be multiplied by 4

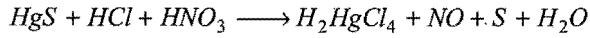


To balance nitrogen, 9 molecules of HNO₃ should be added on LHS.

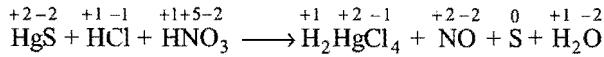
To balance hydrogen and oxygen, 3H₂O molecules should be added on RHS. Hence, the balanced equation is



Example 22. Balance the following equation by oxidation number method:



Solution: Writing the oxidation numbers of the atoms.



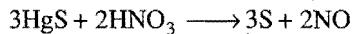
The oxidation numbers of S and N have changed.



Increase in Ox.no. of S = 2 units per HgS molecule

Decrease in Ox.no. of N = 3 units per HNO₃ molecule

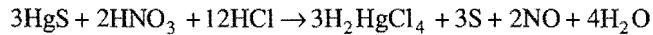
Multiplying eq. (i) by 3 and eq. (ii) by 2 as to make increase and decrease equal



Balancing Hg and chlorine,



To balance hydrogen and oxygen, 4H₂O molecules are added on RHS. Hence, the balanced equation is



Example 23. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all atoms,

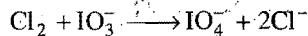


Oxidation numbers of Cl and I have changed.



Decrease in Ox.no. of Cl = 2 units per Cl₂ molecule

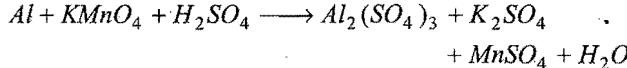
Increase in Ox.no. of I = 2 units per IO₃⁻ molecule



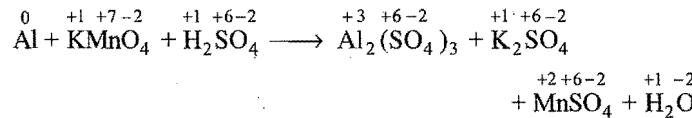
To balance oxygen 2OH⁻ ions be added on LHS and one H₂O molecule on RHS. Hence, the balanced equation is



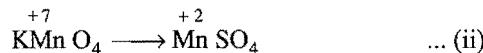
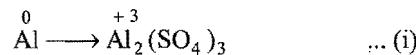
Example 24. Balance the following equation by oxidation number method:



Solution: Writing oxidation numbers of all atoms,



The oxidation numbers of Al and Mn have changed

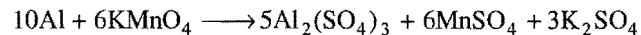


Increase in Ox.no. of Al = 3 units per Al atom

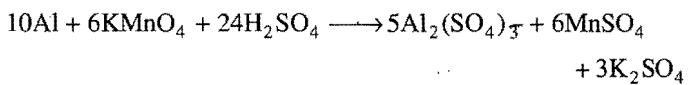
= 6 units per Al₂(SO₄)₃ molecule

Decrease in Ox.no. of Mn = 5 units per KMnO₄ molecule

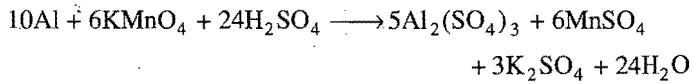
Multiply eq. (i) by 10 and eq. (ii) by 6 as to make increase and decrease equal



To balance SO₄²⁻ ions, 24H₂SO₄ molecules be added on LHS.



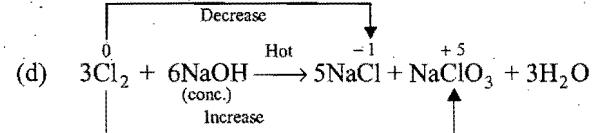
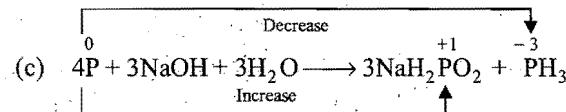
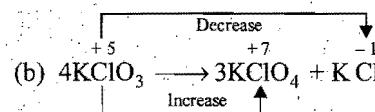
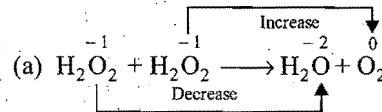
To balance hydrogen and oxygen, 24 H₂O molecules be added on RHS. Hence, the balanced equation is



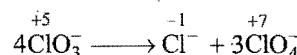
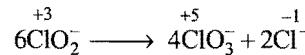
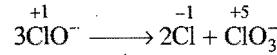
11.10 DISPROPORTIONATION AND OXIDATION-REDUCTION

One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised to a higher state and rest of it is reduced to lower state of oxidation. Such a reaction, in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to **disproportionate**.

The following are some of the examples of disproportionation:



(e) Oxidation state of chlorine lies between -1 to +7; thus out of ClO⁻, ClO₂⁻, ClO₃⁻, ClO₄⁻; ClO₄⁻ does not undergo disproportionation because in this oxidation state of chlorine is highest, i.e., +7. Disproportionation of the other oxoanions are:



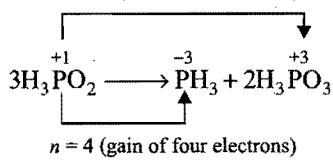
Equivalent mass of substance undergoing disproportionation can be calculated by *n*-factor method:

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{n\text{-factor}}$$

$$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2}$$

Example :

$n = 2$ (loss of two electron)



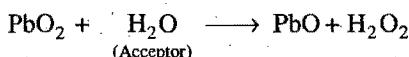
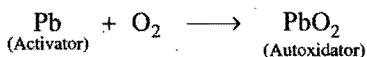
$$n\text{-factor} = \frac{4 \times 2}{4 + 2} = \frac{4}{3}$$

$$\text{Equivalent mass of H}_3\text{PO}_2 = \frac{\text{Molecular mass}}{n\text{-factor}}$$

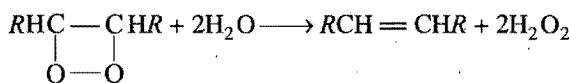
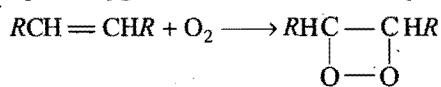
$$= \frac{m}{4/3} = \frac{3m}{4}$$

11.11 AUTOXIDATION

Turpentine and numerous other unsaturated compounds, phosphorus and certain metals like Zn and Pb can absorb oxygen from the air in presence of water. The water is oxidised to hydrogen peroxide. This phenomenon of formation of H_2O_2 by the oxidation of H_2O is known as **autoxidation**. The substance such as turpentine or phosphorus or lead which can activate the oxygen is called **activator**. The activator is supposed to first combine with oxygen to form an addition compound, which acts as an **autoxidator** and reacts with water or some other acceptor so as to oxidise the latter. For example:



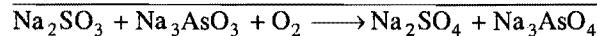
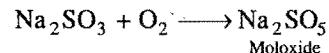
The turpentine or other unsaturated compounds which act as activators are supposed to take-up oxygen molecule at the double bond position to form unstable peroxide called moloxide, which then gives up the oxygen to water molecule or any other acceptor.



The evolution of iodine from KI solution in presence of turpentine can be confirmed with starch solution which turns blue.

With this concept, the phenomenon of induced oxidation can also be explained. Na_2SO_3 solution is oxidised by air but Na_3AsO_3 solution is not oxidised by air. If mixture of both is

taken, it is observed that both are oxidised. This is induced oxidation.



11.12 FORMAL CHARGE

In polyatomic molecule or ion the net charge is possessed by the ion or molecule as a whole and not by particular atom. For certain purpose formal charge (F.C.) is assigned to each atom.

Formal charge (F.C.) on an atom in a Lewis structure	Total number of valence electrons in the free atom	Total number of non-bonding (lone pair) electrons (N)	Total number of bonding (shared electrons) (B)

The formal charge of atom in a polyatomic ion/molecule is defined as:

$$\text{F.C.} = V - N - \frac{1}{2} B$$

The formal charge is the difference between the number of valence electrons in an isolated (i.e., free) atom and the number of electrons assigned to that atom, in its dot structure.

Let us calculate formal charge on each atom of ozone:

Formal charge at oxygen number 1

$$V = 6, N = 4, B = 4$$

$$\text{F.C.} = V - N - \frac{1}{2} B$$

$$= 6 - 4 - \frac{1}{2} \times 4 = 0$$

Formal charge at oxygen number 2

$$V = 6, N = 2, B = 6$$

$$\text{F.C.} = V - N - \frac{1}{2} B$$

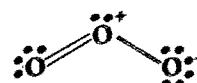
$$= 6 - 2 - \frac{1}{2} \times 6 = 1$$

Formal charge at oxygen number 3

$$V = 6, N = 6, B = 2$$

$$\text{F.C.} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

On the basis of formal charge, the structure of ozone may be drawn as,



we must note that formal charges do not indicate real charge separation within the molecule.

Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a compound. The lowest energy structure means the structure with the smallest formal charges on each atom of the compound. Formal charge is based on the concept that electron pairs are shared equally by neighbouring atoms.

Note: (1) A Lewis dot structure for a molecule is preferable when all formal charges are zero.

(2) In a dot structure adjacent formal charges should be zero or of opposite sign.

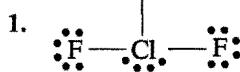
(3) Among the several Lewis dot structure for same species, the structure with negative formal charges on more electronegative atom is preferred.

Let us consider thiocyanate:

	Formal charges			Total
	N	C	S	
Structure I ($\ddot{\text{N}} = \text{C} = \ddot{\text{S}}$) ⁻	-1	0	0	-1
Structure II ($\ddot{\text{C}} = \text{N} = \ddot{\text{S}}$) ⁻	+1	-2	0	-1
Structure III ($\ddot{\text{C}} = \text{S} = \ddot{\text{N}}$) ⁻	-1	-2	+2	-1

Structure III will be correct structure because each atom has non-zero formal charge in the lowest energy state.

Some illustrations of formal charge calculation:



Formal charge at chlorine:

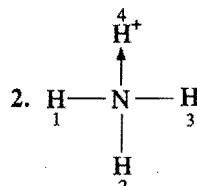
$$V = 7, N = 4, B = 6$$

$$\text{F.C.} = 7 - 4 - \frac{1}{2} \times 6 = 0$$

Formal charge at fluorine:

$$V = 7, N = 6, B = 2$$

$$\text{F.C.} = 7 - 6 - \frac{1}{2} \times 2 = 0$$



Formal charge at nitrogen:

$$V = 5, N = 0, B = 8$$

$$\text{F.C.} = 5 - 0 - \frac{1}{2} \times 8 = +1$$

Formal charge at hydrogens 1,2,3:

$$V = 1, N = 0, B = 2$$

$$\text{F.C.} = V - N - \frac{1}{2} \times B$$

$$= 1 - 0 - \frac{1}{2} \times 2 = 0$$

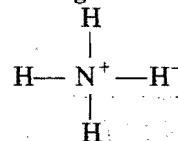
Formal charge at hydrogen number 4:

$$V = 0, N = 0, B = 2$$

$$\text{F.C.} = V - N - \frac{1}{2} \times B$$

$$= 0 - 0 - \frac{1}{2} \times 2 = -1$$

The, structure according to formal charge:



11.13 STOCK NOTATION

In the compounds of metals, the oxidation number is represented by the Roman numeral, placed in parenthesis, after the symbol of the metal in the molecular formula. For example:

(i) Cu₂O (Cuprous oxide, oxidation state of copper = +1); its stock notation will be Cu₂(I)O.

(ii) CuO (Cupric oxide, oxidation state of copper = +2); its stock notation will be Cu(II)O.

The stock notation is not used in case of compounds formed by non-metals.

Stock Notation of Some Compounds

Formula of compound	Chemical name of compound	Oxidation state of metal	Stock notation
HAuCl ₄	Chloroauric acid	Au (+3)	HAu (III) Cl ₄
Tl ₂ O	Thallous oxide	Tl (+1)	Tl ₂ (I) O
FeO	Ferrous oxide	Fe (+2)	Fe (II) O
Fe ₂ O ₃	Ferric oxide	Fe (+3)	Fe ₂ (III) O ₃
Cr ₂ O ₃	Chromic oxide	Cr (+3)	Cr ₂ (III) O ₃
CuI	Cuprous iodide	Cu (+1)	Cu (I) I
MnO	Manganese oxide	Mn (+2)	Mn (II) O
MnO ₂	Manganese dioxide	Mn (+4)	Mn (IV) O ₂
K ₂ Cr ₂ O ₇	Potassium dichromate	Cr (+6)	Kr Cr ₂ (VI) O ₇
KMnO ₄	Potassium permanganate	Mn (+7)	K Mn (VII) O ₄
V ₂ O ₅	Vanadium pentoxide	V (+5)	V ₂ (V) O ₅
FeSO ₄	Ferrous sulphate	Fe (+2)	Fe ₂ (II) SO ₄
Fe ₂ (SO ₄) ₃	Ferric sulphate	Fe (+3)	Fe ₂ (III) (SO ₄) ₃
CuCl ₂	Cupric chloride	Cu (+2)	Cu (II) Cl ₂

11.14 STOICHIOMETRY OF REDOX REACTIONS IN SOLUTIONS

Calculations based on chemical equations are known as stoichiometry. A chemical equation is the symbolic representation of a chemical change. It gives the following informations used in solving the numerical problems based on a chemical equation:

(i) It gives the number of moles of the reactants and the products involved in the reaction.

(ii) It gives relative masses of the reactants and products.

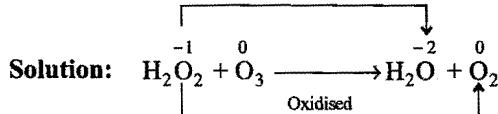
(iii) It gives volume of the gaseous reactants and products.

Problems based on chemical equations have also been dealt in Chapter-1. In this section, we will deal with redox reactions only. In the stoichiometry of redox reactions, the chemical equations must be balanced.

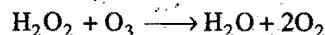
Example 25. Balance the following chemical equation:



Indicating the changes in oxidation numbers of oxygen, find the equivalent weight of H_2O_2 for this reaction. (West Bengal 2005)



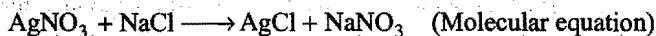
Balanced equation will be:



$$\text{Equivalent mass of } \text{H}_2\text{O}_2 = \frac{34}{2} = 17$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Molecular and ionic equations: When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation. The chemical changes when represented in terms of ions which actually undergo reaction are called ionic equations. The ions which do not undergo any change and equal in number in both reactants and products are termed spectator ions and are not included in the final balanced equations.



[NO_3^- and Na^+ ions are spectator ions.]

2. Oxidation and reduction: Oxidation is a process which involves either of the following:

- (i) addition of oxygen,
- (ii) removal of hydrogen,
- (iii) addition of an electronegative element or group,
- (iv) removal of an electropositive element or group,
- (v) increase in the valency of an electropositive element,
- (vi) loss of one or more electrons by an atom or an ion or a molecule.

Reduction is just reverse of oxidation. It is a process which involves either of the following:

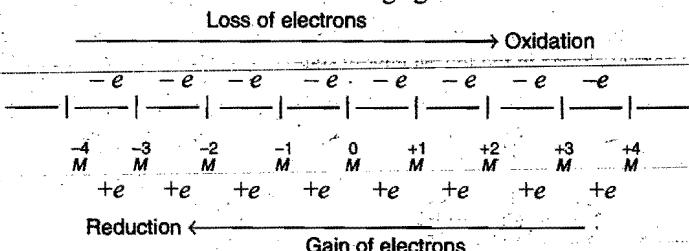
- (i) removal of oxygen,
- (ii) addition of hydrogen,
- (iii) removal of an electronegative element or group,
- (iv) addition of an electropositive element or group,
- (v) decrease in the valency of electropositive element,
- (vi) gain of one or more electrons by an atom or an ion or a molecule.

A substance which undergoes oxidation or gets oxidised acts as a **reducing agent** while a substance which undergoes reduction or gets reduced acts as an **oxidising agent**.

All oxidation-reduction reactions are complimentary of one another and occur simultaneously. Oxidation-reduction reaction is termed **redox reaction**. The word "redox" includes **red + ox**; **red** means reduction and **ox** means oxidation. In redox reaction one substance undergoes oxidation and the other substance undergoes reduction, i.e., the reaction between a

reducing agent and an oxidising agent is termed as redox reaction.

Any material which is capable of accepting electron or electrons acts as an oxidising agent and the material which loses electron or electrons acts as reducing agents.



3. Ion electron method for balancing redox reaction: The following steps are followed:

- (i) Ionic equation of redox reaction is first written.
- (ii) The ionic reaction is split into two half reactions, one for oxidation and the other for reduction.
- (iii) Each half reaction is balanced for the number of atoms of each element. For this purpose: (a) First of all atoms other than H and O for each half reaction are balanced using simple multiples. (b) In acidic and neutral mediums, H ions are added to the side deficient in hydrogen and water molecules to the side deficient in oxygen. (c) In alkaline medium, for each excess of oxygen atom, one water molecule is added to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, one OH^- ion is added for each excess of hydrogen on the same side and one water molecule to the other side.
- (iv) Electrons are added to the side deficient in electrons as to equalise the charges on both sides of the half reactions.
- (v) Electrons are made equal in both the half reactions by multiplying one or both the half reactions by a suitable number.
- (vi) Both the balanced half reactions are added and any term common to both sides is cancelled.

4. Oxidation number or oxidation state: It is defined as the charge (real or imaginary) which an atom appears to have

when it is in combination. In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion. The following rules are followed in ascertaining the oxidation number in any type of compounds:

- (i) The oxidation number of an atom in free elements is zero no matter how complicated the molecule is.
- (ii) The oxidation number of fluorine is always -1.
- (iii) The oxidation number of oxygen is -2 in all compounds except in peroxides, super oxides and oxygen fluorides.
- (iv) The oxidation number of hydrogen is +1 in all of its compounds except in metallic hydrides. In metallic hydrides, oxidation number of hydrogen is -1.
- (v) The oxidation number of an ion is equal to the electrical charge present on it.
- (vi) The oxidation number of alkali metals is +1 and that of alkaline earth metals is +2.
- (vii) For complex ions, the algebraic sum of oxidation no. of all the atoms is equal to the net charge on the ion.
- (viii) In the case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecules is zero.

Oxidation numbers are quite arbitrary. The values may be positive, negative, zero and even fractional. Many elements show different oxidation numbers in different compounds. In the case of representative elements, the highest oxidation number of an element is the same as its group number while highest negative oxidation number is equal to (8-group number) with negative sign with a few exceptions.

I A elements	+1	V A elements	-3 to +5
II A elements	+2	VIA elements	-2 to +6
III A elements	+3, +1	VIIA elements	-1 to +7
IV A elements	-4 to +4		

The valency and oxidation number concepts are different. In some cases (electrovalent compounds), valency and oxidation number are the same but in other cases they have different values. Valency of an element is usually fixed while oxidation number may have different values.

5. Oxidation and reduction in terms of change in oxidation numbers: Oxidation and reduction are defined on the basis of change in oxidation number.

Oxidation is a process in which an atom undergoes algebraic increase in oxidation number and reduction is a process in which an atom undergoes algebraic decrease in oxidation number. In an oxidising agent, there is always decrease in oxidation number and in reducing agent, there is always increase in oxidation number.

6. Balancing oxidation-reduction reactions by oxidation number method:

- (i) The skeleton equation of the chemical change is written.
- (ii) Oxidation numbers are assigned to atoms in the equation. The atoms in which change in oxidation number has taken place are selected and two half reactions involving oxidation and reduction are selected.
- (iii) Change in oxidation numbers in both the equations is made equal by multiplying with suitable integers and then both the equations are added.
- (iv) First of all, those substances are balanced which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally hydrogen and oxygen are balanced.

In ionic equations, the net charges on both sides are made equal. H^+ ions in acidic reactions and OH^- ions in basic reactions are used to balance the charge and number of hydrogen and oxygen atoms.

7. Autoxidation: Certain materials such as turpentine, olefinic compounds, phosphorus, metals like zinc and lead, etc., can absorb oxygen from the air in presence of water and the water is converted to hydrogen peroxide. This phenomenon of formation of H_2O_2 by oxidation of H_2O is known as autoxidation. The material which absorbs oxygen and activates it, is called the activator. The addition compound of activator and oxygen is termed autoxidator. This reacts with water or some other acceptor so as to oxidise the latter.

8. Disproportionation: One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised and rest of it is reduced. This nature of the change is termed disproportionation.

Questions

1. Matrix-Match Type Questions

[A] Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state)
(a) CrO_5	(p) +6
(b) H_2SO_4	(q) +1
(c) CaOCl_2	(r) -1
(d) $(\text{CH}_3)_2\text{SO}$	(s) 0

[B] Match the Column-I with Column-II:

Column-I (Redox process)	Column-II (n-factor for underlined species)
(a) $\underline{\text{As}}_2\text{S}_3 \rightarrow \text{AsO}_3^- + \text{SO}_4^{2-}$	(p) 28
(b) $\underline{\text{I}}_2 \rightarrow \text{I}^- + \text{IO}_3^-$	(q) 4/3
(c) $\underline{\text{H}_3\text{PO}_2} \rightarrow \text{PH}_3 + 2\text{H}_3\text{PO}_3$	(r) 1
(d) $\text{H}_3\text{PO}_2 + \text{NaOH} \rightarrow$ $\text{NaH}_2\text{PO}_2 + \text{H}_2\text{O}$	(s) 5/3

[C] Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state of nitrogen)
(a) Mg_3N_2	(p) -1
(b) NO	(q) +2
(c) $(\text{N}_2\text{H}_5)_2\text{SO}_4$	(r) -2
(d) NH_2OH	(s) -3

[D] Match the Column-I with Column-II:

Column-I (Compound)	Column-II (Oxidation state of)
(a) CrO_5	(p) Oxygen is -2
(b) $\text{Na}_2\text{S}_2\text{O}_3$	(q) Oxygen is -1
(c) H_2SO_5	(r) Sulphur is +6
(d) $\text{H}_2\text{S}_2\text{O}_7$	(s) Sulphur is +2

[E] Match the Column-I with Column-II:

Column-I	Column-II
(a) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow$ $\text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$	(p) Intermolecular redox reaction
(b) $\text{PbO}_2 + \text{H}_2\text{O} \rightarrow \text{PbO} + \text{H}_2\text{O}_2$	(q) Disproportionation
(c) $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$	(r) Intramolecular redox reaction
(d) $\text{Cl}_2 + 2\text{OH}^- \rightarrow$ $\text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$	(s) Metal displacement

2. Indicate which of the substance/ion in the following reactions is an oxidising agent and which is a reducing agent?

- (i) $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2 + \text{SnCl}_4$
- (ii) $2\text{Mg} + \text{SO}_2 \rightarrow 2\text{MgO} + \text{S}$

- (iii) $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$
- (iv) $\text{Ca} + \text{Cl}_2 \rightarrow \text{CaCl}_2$
- (v) $\text{Sn}^{2+} + 2\text{Hg}^{2+} \rightarrow \text{Hg}_2^{2+} + \text{Sn}^{4+}$
- (vi) $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$
- (vii) $2\text{I}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^- + \text{I}_2$
- (viii) $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$
- (ix) $\text{SO}_2 + 2\text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + 2\text{NO}_2$
- (x) $\text{SO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{H}_2\text{SO}_4$

3. Which substance/ion is oxidised and which substance/ion is reduced in the following reactions?

- (i) $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
- (ii) $\text{H}_2\text{S} + 2\text{FeCl}_3 \rightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$
- (iii) $\text{MnO}_4^- + 4\text{HCl} \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$
- (iv) $\text{SnCl}_2 + 2\text{FeCl}_3 \rightarrow \text{SnCl}_4 + 2\text{FeCl}_2$
- (v) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
- (vi) $3\text{N}_2\text{H}_4 + 2\text{BrO}_3^- \rightarrow 3\text{N}_2 + 2\text{Br}^- + 6\text{H}_2\text{O}$
- (vii) $\text{Cl}_2 + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{Cl}^- + \text{SO}_4^{2-} + 2\text{H}^+$
- (viii) $2\text{I}^- + \text{Cl}_2 \rightarrow 2\text{Cl}^- + \text{I}_2$

4. Arrange the following in the order of:

- (a) increasing oxidation number of iodine:
 $\text{I}_2, \text{HI}, \text{HIO}_4, \text{ICl}$
- (b) increasing oxidation number of chlorine:
 $\text{Cl}_2\text{O}_7, \text{Cl}_2\text{O}, \text{HCl}, \text{ClF}_3, \text{Cl}_2$
- (c) increasing oxidation number of nitrogen:
 $\text{NH}_3, \text{N}_3\text{H}, \text{N}_2\text{O}, \text{NO}, \text{N}_2\text{O}_5$

5. Find the oxidation number of :

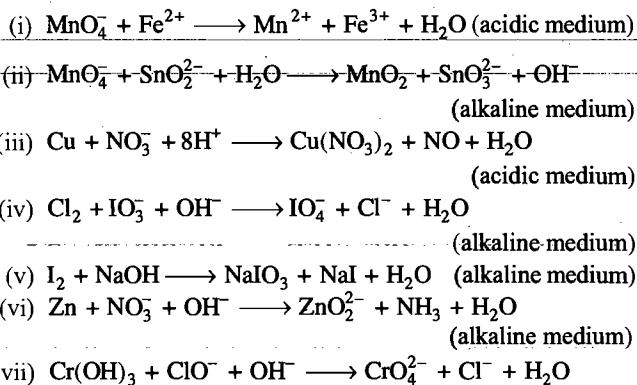
- (i) I in KIO_3
- (ii) P in NaH_2PO_4
- (iii) P in $\text{P}_2\text{O}_7^{4-}$
- (iv) Fe in $[\text{Fe}(\text{CN})_6]^{4-}$
- (v) Ni in $[\text{Ni}(\text{CN})_6]^{4-}$
- (vi) S in $\text{H}_2\text{S}_2\text{O}_8$
- (vii) N in NO_3^-
- (viii) S in S_2Cl_2
- (ix) P in $\text{Mg}_2\text{P}_2\text{O}_7$
- (x) Cr in $\text{K}_2\text{Cr}_2\text{O}_7$
- (xi) Mn in MnO_4^-
- (xii) Pt in $[\text{PtCl}_6]^{2-}$
- (xiii) P in PH_4^+
- (xiv) C in $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- (xv) Fe in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
- (xvi) Cr in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- (xvii) V in $\text{Rb}_4\text{Na}[\text{HV}_{10}\text{O}_{28}]$
- (xviii) Xe in BaXeO_6
- (xix) Cl in $\text{Ca}(\text{ClO}_2)_2$
- (xx) Ni in $\text{Ni}(\text{CO})_4$

(Ranchi 1996)

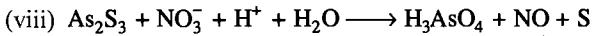
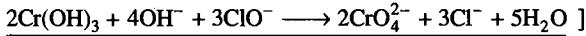
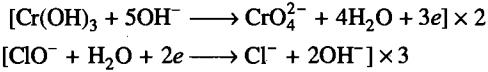
6. (a) Which compound among the following has the lowest oxidation number of Mn?
 KMnO_4 , K_2MnO_4 , MnO_2 and Mn_2O_3
- (b) Which compound among the following has the highest oxidation number of P?
 PH_3 , H_3PO_2 , PCl_3 , H_3PO_4
- (c) Which compound among the following has the zero oxidation state of carbon?
 CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4
- (d) Which compound among the following has the lowest oxidation number of chlorine?
 HClO_4 , HOCl , ClF_3 , HClO_3 , HCl

Short Answer Type

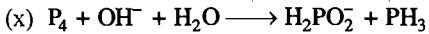
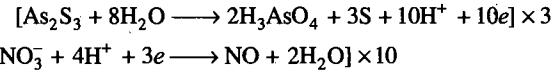
7. Balance the following equations by ion electron method:



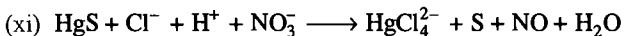
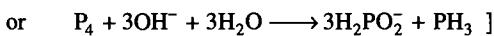
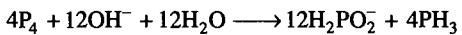
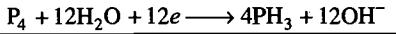
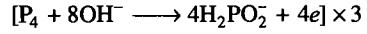
[Hint: Half reactions



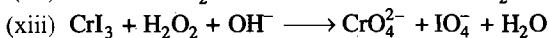
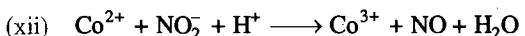
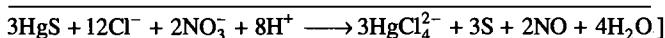
[Hint: Half reactions



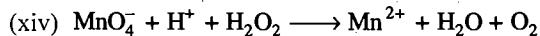
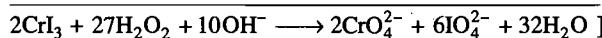
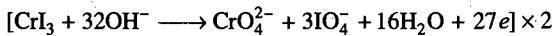
[Hint: Half reactions



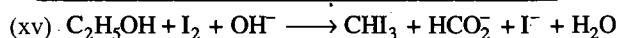
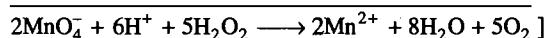
[Hint: Half reactions



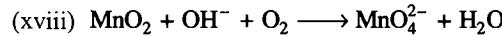
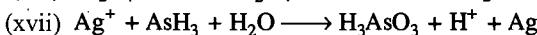
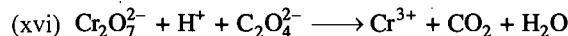
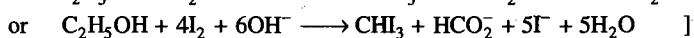
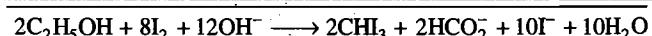
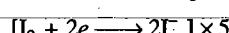
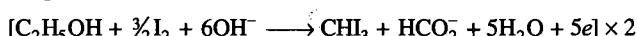
[Hint: Half reactions



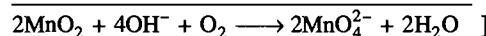
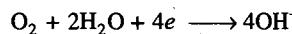
[Hint: Half reactions



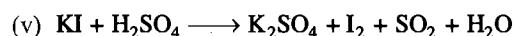
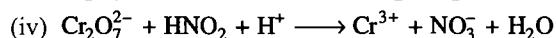
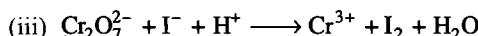
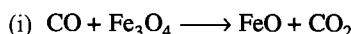
[Hint: Half reactions



[Hint: Half reactions



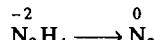
8. Balance the following equations by oxidation number method.



[Hint: Two half reactions

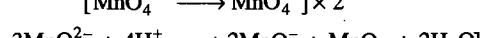
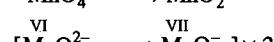
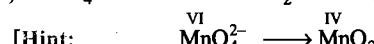
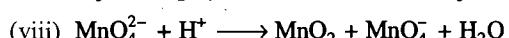
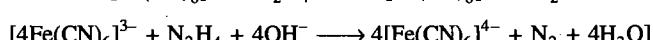
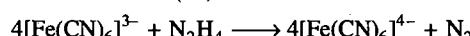


(change in Ox. no. per Fe atom = -1)

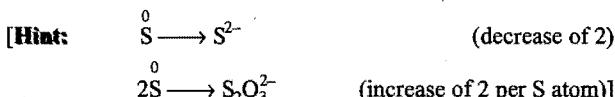


(change in Ox. no. per N atom = +2)

Total increase = $2 \times (+2) = +4$



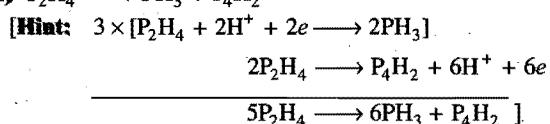
- (ix) $\text{HNO}_3 + \text{Cu}_2\text{O} \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
 (x) $\text{AuCl}_4^- + \text{Sn}^{2+} + \text{H}^+ \rightarrow \text{Sn}^{4+} + \text{AuCl} + \text{HCl}$
 (xi) $\text{S} + \text{OH}^- \rightarrow \text{S}^{2-} + \text{S}_2\text{O}_3^{2-}$



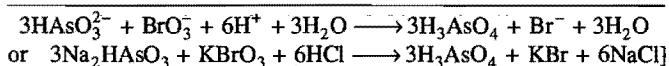
- (xii) $\text{NaClO}_3 + \text{KI} + \text{HCl} \rightarrow \text{NaCl} + \text{KCl} + \text{I}_2 + \text{H}_2\text{O}$
 (xiii) $\text{PbCrO}_4 + \text{H}_2\text{SO}_4 + \text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{PbSO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
 (xiv) $\text{As} + \text{HNO}_3 \rightarrow \text{H}_3\text{AsO}_4 + \text{NO}_2 + \text{H}_2\text{O}$
 (xv) $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4$
 (xvi) $\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O}$

9. Balance the following equations:

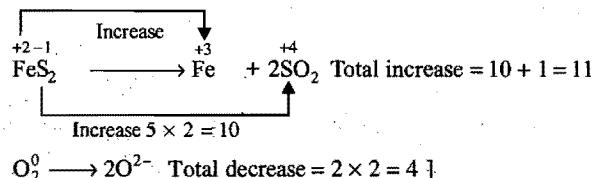
- (i) $\text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 + \text{C} \rightarrow \text{CaSiO}_3 + \text{P}_4 + \text{CO}$
 (ii) $\text{P}_2\text{H}_4 \rightarrow \text{PH}_3 + \text{P}_4\text{H}_2$



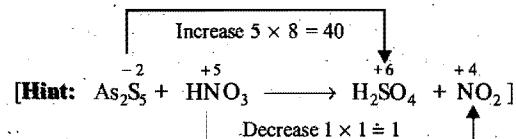
- (iii) $\text{Na}_2\text{HAsO}_3 + \text{KBrO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{KBr} + \text{H}_3\text{AsO}_4$
 [Hint: $[\text{HAsO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + 2e] \times 3$
 $\text{BrO}_3^- + 6\text{H}^+ + 6e \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$]



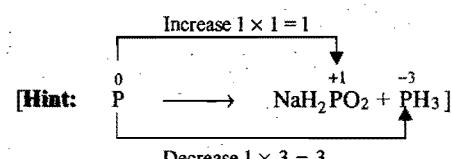
- (iv) $\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$
 [Hint: Both iron and sulphur in FeS_2 undergo a change in oxidation state.



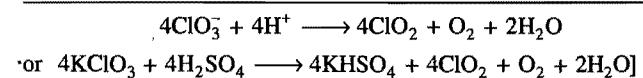
- (v) $\text{As}_2\text{S}_3 + \text{HNO}_3 \rightarrow \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O}$



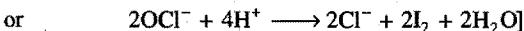
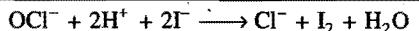
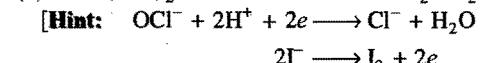
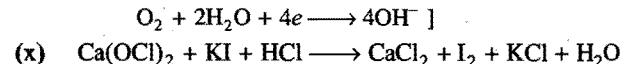
- (vi) $\text{MnO} + \text{PbO}_2 + \text{HNO}_3 \rightarrow \text{HMnO}_4 + \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$
 (vii) $\text{P} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaH}_2\text{PO}_2 + \text{PH}_3$



- (viii) $\text{KClO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{O}_2 + \text{ClO}_2 + \text{H}_2\text{O}$
 [Hint: $[\text{ClO}_3^- + 2\text{H}^+ + e \rightarrow \text{ClO}_2 + \text{H}_2\text{O}] \times 2$
 $2\text{ClO}_3^- \rightarrow 2\text{ClO}_2 + \text{O}_2 + 2e$]



- (ix) $\text{Ag} + \text{KCN} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{KAg(CN)}_2 + \text{KOH}$
 [Hint: $[\text{Ag} + 2\text{CN}^- \rightarrow [\text{Ag}(\text{CN})_2]^- + e] \times 4$



10. Calculate the oxidation state of underlined:

- (a) $\underline{\text{Ba}}_2 \text{XeO}_2$ (b) $\underline{\text{Ba}}\text{Cl}_2$ (c) $\underline{\text{C}}_{12}\text{H}_{22}\text{O}_{11}$ (d) $\underline{\text{IF}}_7$
 (e) $\text{Na}_2[\underline{\text{Fe}}(\text{CN})_5\text{NO}]$ (f) $\underline{\text{RuO}}_4$ (g) $\text{K}_2\underline{\text{TaF}}_7$ (h) $\text{Na}_2\underline{\text{MoO}}_4$
 (i) $\underline{\text{U}}_2\text{O}_7^4$ (j) C in diamond.

11. Give the oxidation state of underlined:

- (a) $\underline{\text{Fe}}_3\text{O}_4$ (b) $\text{Ca}\underline{\text{OCl}}_2$ (c) $\underline{\text{NH}}_4\text{NO}_3$
 (d) $\underline{\text{NH}}_4\text{NO}_2$ (e) KO_2 (f) $\text{H}_2\underline{\text{SO}}_5$
 (g) $(\text{CH}_3)_2\underline{\text{SO}}$ (h) $\text{H}_2\underline{\text{S}}_2\text{O}_8$ (i) $\text{Na}_2\underline{\text{S}}_2\text{O}_3$
 (j) $\text{Na}_2\underline{\text{S}}_4\text{O}_6$ (k) $\underline{\text{CrO}}_5$ (l) $\underline{\text{CoSeO}}_4$

12. Balance the following equations by ion electron method:

- (a) $\text{Zn} + \text{BrO}_4^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow [\text{Zn}(\text{OH})_4]^{2-} + \text{Br}^-$
 (b) $\text{MnO}_4^- + \text{H}_2\text{O} \rightarrow \text{MnO}_4^- + \text{OH}^- + \text{MnO}_2$
 (c) $\text{Fe}(\text{CN})_6^{4-} + \text{H}^+ + \text{MnO}_4^- \rightarrow \text{Fe}^{3+} + \text{CO}_2 + \text{NO}_3^- + \text{Mn}^{2+}$
 (d) $\text{Cu}_3\text{P} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4 + \text{Cr}^{3+}$ (acid medium)
 (e) $\text{Hg}_2(\text{CN})_2 + \text{Ce}^{4+} \rightarrow \text{CO}_3^{2-} + \text{NO}_3^- + \text{Hg}(\text{OH})_2 + \text{Ce}^{3+}$ (basic medium)

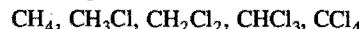
- (f) $\text{K}_3\text{Fe}(\text{CN})_6 + \text{Cr}_2\text{O}_3 + \text{KOH} \rightarrow \text{K}_4\text{Fe}(\text{CN})_6 + \text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$ (basic medium)
 (g) $\text{Na}_2\text{HAsO}_3 + \text{KBrO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{KBr} + \text{H}_3\text{AsO}_4$

13. Calculate the oxidation state of vanadium in the following complex compound: $\text{Rb}_4\text{Na}[\text{HV}_{10}\text{O}_{28}]$

14. (a) Arrange the following compounds in increasing order of oxidation number of manganese:

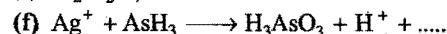
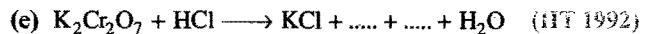
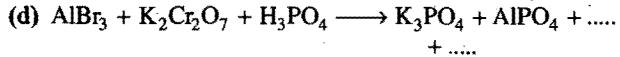
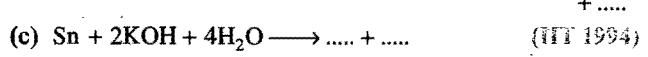
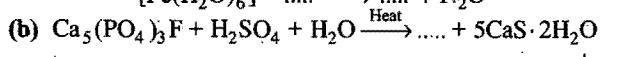
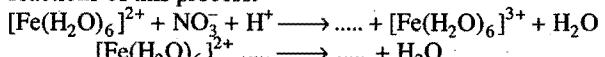


(b) Indicate valency and oxidation states of carbon in the following compounds:



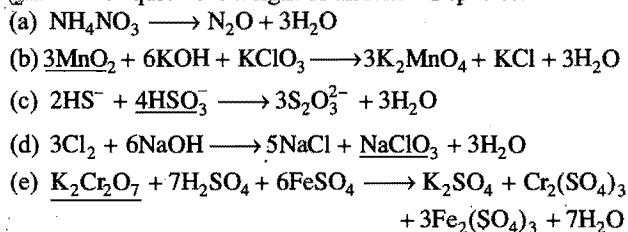
15. Complete and balance the following compounds:

(a) Acidic solution of Fe^{2+} ion gives a brown ring when it comes in contact with NO_3^- ion. Complete the following reactions of this process:

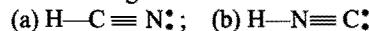


16. Arrange following ions in increasing order of oxidation number of sulphur: $\text{S}_4\text{O}_6^{2-}, \text{HS}^-, \text{HSO}_4^-, \text{S}_2\text{O}_8^{2-}, \text{S}_2\text{O}_3^{2-}, \text{SO}_3^{2-}$

17. Determine equivalent weight of underlined species:



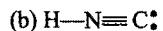
18. Which of the following structures is accurate on the basis of formal charge?



[Hint: (a) H—C≡N:]

$$\begin{aligned}
 \text{F.C.} &= V - N - \frac{1}{2}B \\
 \text{F.C. at 'H'} &= 1 - 0 - \frac{1}{2} \times 2 = 0 \\
 \text{F.C. at 'C'} &= 4 - 0 - \frac{1}{2} \times 8 = 0
 \end{aligned}$$

$$\text{F.C. at 'N'} = 5 - 2 - \frac{1}{2} \times 6 = 0$$



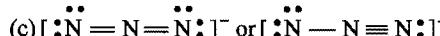
$$\text{F.C. at 'H'} = 1 - 0 - \frac{1}{2} \times 2 = 0$$

$$\text{F.C. at 'N'} = 5 - 0 - \frac{1}{2} \times 8 = +1$$

$$\text{F.C. at 'C'} = 4 - 2 - \frac{1}{2} \times 6 = -1$$

Structure (a) having zero formal charges at each atom will be accurate.]

19. On the basis of formal charge select the most plausible structure:



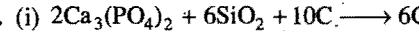
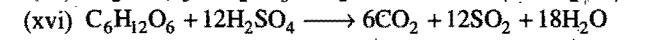
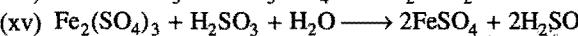
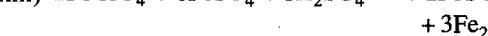
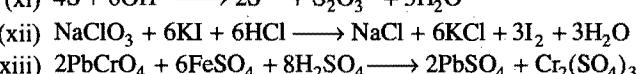
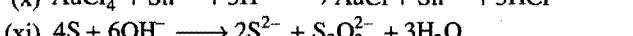
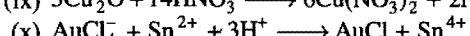
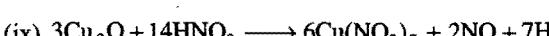
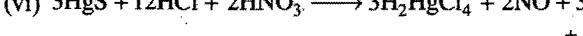
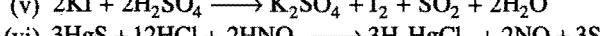
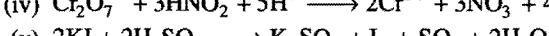
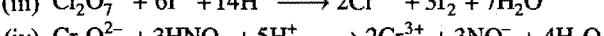
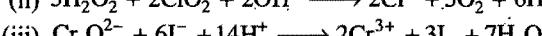
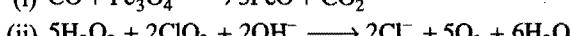
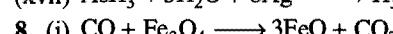
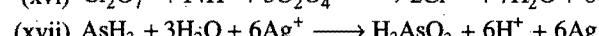
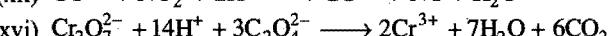
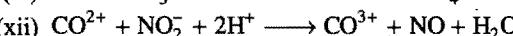
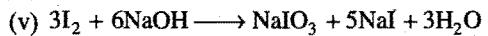
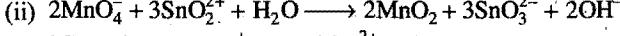
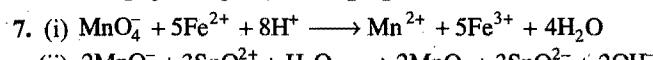
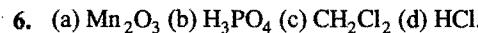
1. [A] (a — p); (b — p); (c — q, r); (d — s)
 [B] (a — p); (b — s); (c — q); (d — r)
 [C] (a — s); (b — q); (c — s); (d — p)
 [D] (a — p, q); (b — p, s); (c — p, q, r); (d — p, r).
 [E] (a — r); (b — p); (c — p, s); (d — q)

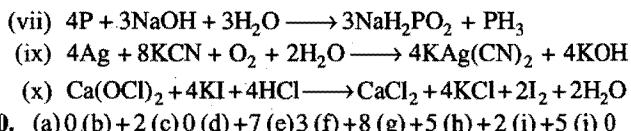
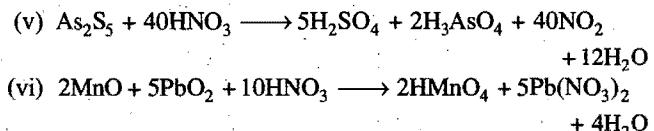
2.	Oxidising agent	Reducing agent
(i)	FeCl ₃	SnCl ₂
(ii)	SO ₂	Mg
(iii)	O ₂	SO ₂
(iv)	Cl ₂	Ca
(v)	Hg ²⁺	Sn ²⁺
(vi)	Cu ²⁺	I ⁻
(vii)	H ₂ O ₂	I ⁻
(viii)	SO ₂	H ₂ S
(ix)	HNO ₃	SO ₂
(x)	Cl ₂	SO ₂

3.	Oxidised	Reduced
(i)	PbS	H ₂ O ₂
(ii)	H ₂ S	FeCl ₃
(iii)	HCl	MnO ₂
(iv)	SnCl ₂	FeCl ₃
(v)	C ₂ O ₄ ²⁻	MnO ₄ ⁻
(vi)	N ₂ H ₄	BrO ₃ ⁻
(vii)	SO ₃ ²⁻	Cl ₂
(viii)	I ⁻	Cl ₂

4. (a) HI(-1), I₂(0), ICl(+1), HIO₄(+7)
 (b) HCl(-1), Cl₂(0), Cl₂O(+1), ClF₃(+3), Cl₂O₇(+7)
 (c) NH₃(-3), N₃H(-1/3), N₂O(+1), NO(+2), N₂O₅(+5).
 5. (i) + 5 (ii) + 5 (iii) + 5 (iv) + 2 (v) + 2 (vi) + 6
 (one peroxy linkage is present) (vii) + 5 (viii) + 1

$$\begin{aligned}
 & \text{(ix)} + 5 \quad \text{(x)} + 6 \quad \text{(xi)} + 7 \quad \text{(xii)} + 4 \quad \text{(xiii)} - 3 \quad \text{(xiv)} \\
 & 0 \text{ (zero)} \quad \text{(xv)} + 3 \quad \text{(xvi)} + 6 \quad \text{(xvii)} + 5 \quad \text{(xviii)} + 8 \quad \text{(xix)} + 3 \quad \text{(xx)} \\
 & 0 \text{ (zero)}
 \end{aligned}$$





OBJECTIVE QUESTIONS

Set-1 : Questions with single correct answer

- Oxidation is defined as:
 - loss of electrons
 - gain of electrons
 - gain of protons
 - loss of protons
 - A reducing agent is a substance which can:
 - accept electrons
 - donate electrons
 - accept protons
 - donate protons
 - A redox reaction is:
 - proton transfer reaction
 - ion combination reaction
 - a reaction in solution
 - electron transfer reaction
 - Which of the following is not a redox reaction?
 - Burning of candle
 - Rusting of iron
 - Dissolving a salt in water
 - Dissolving Zn in dil. H_2SO_4
 - The reaction, $\text{H}_2\text{S} + \text{H}_2\text{O}_2 = \text{S} + 2\text{H}_2\text{O}$ manifests:
 - oxidising action of H_2O_2
 - reducing nature of H_2O_2
 - acidic nature of H_2O_2
 - alkaline nature of H_2O_2
 - The oxidation number of Fe in $\text{K}_4\text{Fe}(\text{CN})_6$ is:

(CBSE 1993; KCET 2008)

 - + 6
 - + 4
 - + 3
 - + 2
 - In $\text{Ni}(\text{CO})_4$, the oxidation state of Ni is:
 - .4
 - zero
 - 2
 - 8
 - Pick the group which does not contain a neutral oxide :

(ISAT 2010)

 - NO_2 , P_4O_{10} , Al_2O_3 , NO
 - MgO , N_2O_5 , SO_3 , N_2O
 - CO_2 , SO_3 , CaO , XeO_3
 - CO, SiO_2 , SnO_2 , Na_2O_3
 - Magnesium reacts with acids producing hydrogen and corresponding magnesium salts. In such reactions Mg undergoes:
 - reduction
 - oxidation
 - neither oxidation nor reduction
 - simple dissolution
 - When P reacts with caustic soda, the products are PH_3 and NaH_2PO_2 . The reaction is an example of:
 - oxidation
 - reduction
 - both oxidation and reduction
 - neutralisation
 - Which of the following reactions is not a redox reaction ?

[PET (Raj.) 2008]

 - $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}$
 - $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq.}) \longrightarrow \text{Zn}^{2+}(\text{aq.}) + \text{Cu}(\text{s})$
 - $2\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{MgO}$
 - $\text{FeO} + \text{C} \longrightarrow \text{Fe} + \text{CO}$
- Which of the following is not a redox change?
 - $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$
 - $2\text{BaO} + \text{O}_2 = 2\text{BaO}_2$
 - $\text{BaO}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + \text{H}_2\text{O}_2$
 - $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$
 - The conversion of $\text{K}_2\text{Cr}_2\text{O}_7$ into $\text{Cr}_2(\text{SO}_4)_3$ is a process of:
 - oxidation
 - reduction
 - decomposition
 - substitution
 - In the reaction, $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$, I_2 acts as:
 - reducing agent
 - oxidising agent
 - oxidising as well as reducing agent
 - none of the above
 - The most common oxidation state of oxygen is -2. This is best explained as due to:
 - 2 electrons in the outermost shell
 - 4 electrons in the outermost shell
 - 6 electrons in the outermost shell
 - 8 electrons in the outermost shell
 - Select the compound in which chlorine shows oxidation state + 7:
 - HClO_4
 - HClO_3
 - HClO_2
 - HClO
 - Which one of the following is a reducing agent?
 - Ozone
 - Chlorine
 - FeCl_3
 - Na_2SO_3
 - The oxidation number of nitrogen in NH_2OH is:
 - zero
 - +1
 - 1
 - 2
 - HBr and HI reduce sulphuric acid. HCl can reduce KMnO_4 and HF can reduce:
 - H_2SO_4
 - KMnO_4
 - $\text{K}_2\text{Cr}_2\text{O}_7$
 - none of these
 - One mole of N_2H_4 loses 10 moles of electrons to form a new compound Y. Assuming that all nitrogen appear in the new compound, what is the oxidation state of nitrogen? (There is no change in the oxidation state of hydrogen.)
 - 1
 - 3
 - +3
 - +5
 - The brown ring complex compound is formulated as $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$. The oxidation state of iron is:

(CET Karnataka 2009)

 - +1
 - +2
 - +3
 - zero
 - A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of :
 - sodium atoms
 - sodium hydroxide
 - sodium amide
 - solvated electrons
 - In which of the following compounds, iron has an oxidation state of +3?

(DPMT 2009)

- (a) $\text{Fe}(\text{NO}_3)_2$
 (b) FeC_2O_4
 (c) $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$
 (d) $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
24. When KMnO_4 is reduced with oxalic acid in acidic solution, the oxidation number of Mn changes from:
 (a) 7 to 2 (b) 7 to 4 (c) 7 to 6 (d) 6 to 2
25. In which of the following reactions the underlined substance is oxidised?
 (a) $3\text{Mg} + \underline{\text{N}_2} + \text{Mg}_3\text{N}_2$ (b) $2\text{KI} + \underline{\text{Br}_2} = 2\text{KBr} + \text{I}_2$
 (c) $\underline{\text{CuO}} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$ (d) $\underline{\text{CO}} + \text{Cl}_2 = \text{COCl}_2$
26. Of the following elements, which one has the same oxidation state in all of its compounds?
 (a) Hydrogen (b) Fluorine (c) Carbon (d) Oxygen
27. When tin(IV) chloride is treated with excess of conc. hydrochloric acid, the complex ion $(\text{SnCl}_6)^{2-}$ is formed. The oxidation state of tin in this complex ion is:
 (a) +4 (b) zero (c) -2 (d) -4
28. In the following reaction,

$$3\text{Br}_2 + 6\text{CO}_3^{2-} + 3\text{H}_2\text{O} = 5\text{Br}^- + \text{BrO}_3^- + 6\text{HCO}_3^-$$
 [PMT (MP) 1997]
 (a) bromine is oxidised, carbonate is reduced
 (b) bromine is reduced, carbonate is oxidised
 (c) bromine is neither reduced nor oxidised
 (d) bromine is reduced as well as oxidised
29. If an element is in its lowest oxidation state, under proper conditions, it can act as:
 (a) a reducing agent
 (b) an oxidising agent
 (c) oxidising as well as reducing agent
 (d) neither oxidising nor reducing agent
30. The oxidation state of phosphorus varies from:
 (a) -1 to +1 (b) -3 to +3
 (c) -3 to +5 (d) -5 to +1
31. In which of the following reactions no change in valency occurs?
 (a) $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + 2\text{H}_2\text{O}$
 (b) $2\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}_2$
 (c) $\text{Cl}_2 + 2\text{NaOH} \longrightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O}$
 (d) $\text{AgNO}_3 + \text{KCl} \longrightarrow \text{AgCl} + \text{KNO}_3$
32. When SO_2 is passed through an acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$, then chromium sulphate is formed. Change in oxidation state of Cr is from:
 (KCET 2008)
 (a) +4 to +2 (b) +6 to +3
 (c) +7 to +2 (d) +5 to +3
33. In a reaction,

$$2\text{Ag} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Ag}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2$$
, H_2SO_4 acts as:
 (a) reducing agent (b) oxidising agent
 (c) dehydrate (d) none of these
34. Oxidation number of iodine varies from:
 (a) -1 to +1 (b) -1 to +7 (c) +3 to +5 (d) -1 to +5
35. Oxidation number of fluorine in F_2O is:
 (a) +1 (b) +2 (c) -1 (d) -2
36. In the compounds KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, the highest oxidation state is of the element:
 (a) potassium (b) chromium (c) oxygen (d) manganese
37. In a reaction, the oxidation number of an element becomes zero from -1. It is a case of:
 (a) oxidation
 (b) reduction
 (c) neither oxidation nor reduction
 (d) both oxidation and reduction
38. $\text{Cl}_2 + \text{H}_2\text{S} \longrightarrow 2\text{HCl} + \text{S}$,
 In the above reaction, oxidation state of chlorine changes from :
 [PET (Raj.) 2008]
 (a) zero to -1 (b) 1 to zero
 (c) zero to 1 (d) remains unchanged
39. During electrolysis the reaction at anode is:
 (a) oxidation (b) reduction
 (c) decomposition (d) none of these
40. Which of the following is a mild oxidising agent?
 (a) Ag_2O (b) KMnO_4 (c) $\text{K}_2\text{Cr}_2\text{O}_7$ (d) Cl_2
41. The common oxidation state of alkali metals in the combined state is:
 (a) +1 (b) +2 (c) -1 (d) -2
42. Carbon is in highest oxidation state in:
 (a) CH_3Cl (b) CCl_4 (c) CHCl_3 (d) CH_2Cl_2
43. The oxidation number and covalency of sulphur in S_8 is:
 (a) +2, 0 (b) 0, 2 (c) 0, 8 (d) 6, 2
44. Addition of iron or zinc to copper sulphate causes precipitation of copper owing to the:
 (a) reduction of Cu^{2+} (b) oxidation of Cu^{2+}
 (c) hydrolysis of CuSO_4 (d) ionisation of CuSO_4
45. In a reaction,

$$\text{H}_2\text{O} (\text{steam}) + \text{C} (\text{glowing}) = \text{CO} + \text{H}_2$$

 (a) H_2O is the reducing agent
 (b) H_2O is the oxidising agent
 (c) carbon is the oxidising agent
 (d) oxidation-reduction does not occur
46. The oxidation numbers of C in CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 are respectively:
 (a) +4, +2, 0, -2, -4 (b) +2, +4, 0, -4, -2
 (c) -4, -2, 0, +2, +4 (d) -2, -4, 0, +4, +2
47. Which of the following statements is correct?
 (a) Oxidation of a substance is followed by reduction of another
 (b) Reduction of a substance is followed by oxidation of another
 (c) Oxidation and reduction are complementary reactions
 (d) It is not necessary that both oxidation and reduction should take place in the same reaction
48. Reduction never involves:
 (a) gain of electrons
 (b) decrease in oxidation number
 (c) loss of electrons
 (d) decrease in valency of electropositive component
49. In which of the following reactions has the underlined substance been reduced?
 (a) $\underline{\text{Carbon monoxide}} + \text{copper oxide} \longrightarrow \text{carbon dioxide} + \text{copper}$
 (b) $\underline{\text{Copper oxide}} + \text{hydrochloric acid} \longrightarrow \text{copper chloride} + \text{water}$

- (c) Hydrogen + iron oxide \longrightarrow iron + water
 (d) Steam + iron \longrightarrow iron oxide + hydrogen
50. In which of the following reactions, the underlined element has decreased its oxidation number during the reaction?
 (a) $\underline{\text{Fe}} + \text{CuSO}_4 \longrightarrow \text{Cu} + \text{FeSO}_4$
 (b) $\underline{\text{H}_2} + \text{Cl}_2 \longrightarrow 2\text{HCl}$
 (c) $\underline{\text{C}} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$
 (d) $\underline{\text{MnO}_2} + 4\text{HCl} \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
51. If three electrons are lost by a metal ion, M^{3+} , its final oxidation number would be:
 (a) zero (b) + 6
 (c) + 2 (d) + 4
52. Select the compound in which chlorine is assigned the oxidation number +5:
 (a) HClO_4 (b) HClO_2 (c) HClO_3 (d) HCl
53. In the alumino-thermic process, aluminium acts as:
 (a) an oxidising agent (b) a flux
 (c) a reducing agent (d) a solder
54. The strongest reducing agent is:
 (a) K (b) Ca (c) Al (d) Zn
55. In the reaction; $\text{Zn} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2$, Zn undergoes:
 (a) oxidation (b) reduction
 (c) simple dissolution (d) double decomposition
56. Phosphorus has the oxidation state of +3 in:
 (a) ortho phosphoric acid (b) phosphorus acid
 (c) meta phosphoric acid (d) pyrophosphoric acid
57. Oxidation number of P in PO_4^{3-} , of S in SO_4^{2-} and that of Cr in $\text{Cr}_2\text{O}_7^{2-}$ are respectively: [CBSE (PMT) 2009]
 (a) -3, +6 and +6 (b) +5, +6 and +6
 (c) +3, +6 and +5 (d) +5, +3 and +6
58. The conversion of PbO into $\text{Pb}(\text{NO}_3)_2$ involves:
 (a) oxidation
 (b) reduction
 (c) neither oxidation nor reduction
 (d) both oxidation and reduction
59. The highest state of Mn is shown in:
 (a) K_2MnO_4 (b) KMnO_4 (c) MnO_2 (d) Mn_2O_3
60. In which one of the following changes, there is transfer of five electrons?
 (a) $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ (b) $\text{CrO}_4^{2-} \longrightarrow \text{Cr}^{3+}$
 (c) $\text{MnO}_4^- \longrightarrow \text{MnO}_2$ (d) $\text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+}$
61. The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_4)_2$ is:
 (a) + 3 (b) + 2 (c) + 1 (d) -1
62. The oxidation state of the most electronegative element in the products of the reaction between BaO_2 and H_2SO_4 are:
 (a) 0 and -1 (b) -1 and -2
 (c) -2 and 0 (d) -2 and +1
63. In the reaction, $4\text{Fe} + 3\text{O}_2 \longrightarrow 4\text{Fe}^{3+} + 6\text{O}^{2-}$ which of the following statements is incorrect? [MLNR 1991]

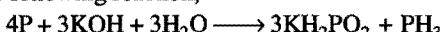
- (a) It is a redox reaction
 (b) Metallic iron is a reducing agent
 (c) Fe^{3+} is an oxidising agent
 (d) Metallic iron is reduced to Fe^{2+}
64. Which of the following halide ions is easiest to oxidise?
 (a) F^- (b) Cl^- (c) Br^- (d) I^-
65. In the reaction of sodium thiosulphate with I_2 in aqueous medium the equivalent weight of sodium thiosulphate is equal to: [JEE (WB) 2010]
 (a) molar mass of sodium thiosulphate
 (b) the average molar masses of $\text{Na}_2\text{S}_2\text{O}_3$ and I_2
 (c) half the molar mass of sodium thiosulphate
 (d) twice of molar mass of sodium thiosulphate
66. The oxidation number of chlorine in HOCl is:
 (a) -1 (b) zero (c) + 1 (d) + 2
67. In the reaction, $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}_4^- + \text{H}_2\text{O}$, chlorine is:
 (a) oxidised
 (b) reduced
 (c) oxidised as well as reduced
 (d) neither oxidised nor reduced
68. The oxidation number of arsenic atom in H_3AsO_4 is:
 (a) -1 (b) -3 (c) + 3 (d) + 5
69. In which of the following reactions, hydrogen is acting as an oxidising agent?
 (a) With iodine to give hydrogen iodide
 (b) With lithium to give lithium hydride
 (c) With nitrogen to give ammonia
 (d) With sulphur to give hydrogen sulphide
70. In acid medium, the reaction, $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ is:
 (a) oxidation by 3 electrons (b) reduction by 3 electrons
 (c) oxidation by 5 electrons (d) reduction by 5 electrons
71. For the redox reaction,

$$\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$$
 the correct coefficients of the reactants for the balanced equation are: (IIT 1992)

MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+
(a) 2	5	16
(b) 16	5	2
(c) 5	16	2
(d) 2	16	5
72. The oxidation number of Pt in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ is:
 (a) + 1 (b) + 2 (c) + 3 (d) + 4
73. Oxidation number of P in $\text{Mg}_2\text{P}_2\text{O}_7$ is:
 (a) + 3 (b) + 2 (c) + 5 (d) -3
74. The oxidation number of phosphorus in PO_4^{3-} , P_4O_{10} and $\text{P}_2\text{O}_7^{4-}$ is: (CPMT 1992)
 (a) + 5 (b) + 3 (c) -3 (d) + 2
75. The oxidation state of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ is:
 (a) + 7 (b) + 6 (c) + 3 (d) + 2
76. Bromine reacts with hot aqueous alkali to give bromide and

- bromate. What is the change that is brought about in oxidation state of bromine to bromate?
- 1 to +5
 - 0 to +5
 - 1 to +7
 - None of these
77. Which one of the following leads to redox reaction?
- $\text{AgNO}_3 + \text{HCl}$
 - $\text{KOH} + \text{HCl}$
 - $\text{KI} + \text{Cl}_2$
 - $\text{NH}_3 + \text{HCl}$
78. Oxidation number of 'S' in $\text{Na}_2\text{S}_4\text{O}_6$ is: [CBSE 1993]
- +0.5
 - 2.5
 - +4
 - +6
79. Which one of the following is not a redox reaction? (AIIMS 1993)
- $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
 - $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
 - $\text{Na} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \frac{1}{2}\text{H}_2$
 - $\text{MnCl}_3 \longrightarrow \text{MnCl}_2 + \frac{1}{2}\text{Cl}_2$
80. The oxidation number of nitrogen in NO_3^- is:
- 1
 - +2
 - +3
 - +5
81. Oxygen has an oxidation state of +2 in:
- H_2O_2
 - OF_2
 - SO_2
 - H_2O
82. When iron is rusted, it is:
- oxidised
 - reduced
 - evaporated
 - decomposed
83. An element, which never has a positive oxidation state in any of its compounds, is:
- boron
 - oxygen
 - chlorine
 - fluorine
84. Starch iodide paper is used to test for the presence of:
- iodine
 - iodide ion
 - oxidising agent
 - reducing agent
85. Which of the acid possesses oxidising, reducing and complex forming properties?
- HNO_3
 - H_2SO_4
 - HCl
 - HNO_2
86. Which substance is serving as a reducing agent in the following reaction?
- $$14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 3\text{Ni} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Ni}^{2+}$$
- (CBSE 1994)
- H_2O
 - Ni
 - H^+
 - $\text{Cr}_2\text{O}_7^{2-}$
87. The oxidation state of iodine in H_4IO_6 is:
- +7
 - 1
 - +5
 - +1
88. Oxidation number of N in NH_4NO_3 is: [PMT (Raj.) 1993]
- 3
 - +5
 - 3 and +5
 - +3 and -5
89. The element, which shows minimum oxidation number in its compounds, is: [PET (Raj.) 1992]
- Fe
 - Mn
 - Ca
 - K
90. In which of the following compounds, the oxidation number of iodine is fractional? [PET (Raj.) 1992]
- IF_7
 - I_3^-
 - IF_5
 - IF_3
91. The missing term in the following equation is:
- $$2\text{Fe}^{3+} + \text{Sn}^{2+} \longrightarrow 2\text{Fe}^{2+} + \dots$$
- Sn^{4+}
 - Sn^{3+}
 - Sn^{2+}
 - Sn^+
92. A compound contains atoms *A*, *B* and *C*. The oxidation number of *A* is +2, of *B* is +5 and of *C* is -2. The possible formula of the compound is:
- ABC_2
 - $\text{B}_2(\text{AC}_3)_2$
 - $\text{A}_3(\text{BC}_4)_2$
 - $\text{A}_3(\text{B}_4\text{C})_2$
93. The correct set of oxidation numbers of nitrogen in ammonium nitrate is: [PET (Raj.) 2007]
- 3, +3
 - 1, +1
 - +1, -1
 - 3, +5
94. In which of the following pairs, the oxidation states of sulphur and chromium are same? [PET (Raj.) 2007]
- $\text{SO}_3^{2-}, \text{CrO}_4^{2-}$
 - $\text{SO}_3, \text{CrO}_4^{2-}$
 - $\text{SO}_2, \text{CrO}_4^{2-}$
 - $\text{SO}_2, \text{Cr}_2\text{O}_7^{2-}$
95. For the redox reaction, $\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} + \text{SnCl}_4$, the correct coefficients of reactants for the balanced equation are:
- 1, 1
 - 1, 2
 - 2, 2
 - 2, 1
96. The value of *n* in the following equation is:
- $$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + n\text{Fe}^{2+} \longrightarrow 2\text{Cr}^{3+} + n\text{Fe}^{3+} + 7\text{H}_2\text{O}$$
- [PET (MP) 2008]
- 2
 - 3
 - 7
 - 6
97. In the reaction, $8\text{Al} + 3\text{Fe}_3\text{O}_4 \longrightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$, the number of electrons transferred from reductant to oxidant is:
- 8
 - 4
 - 16
 - 24
- [Hint: $8\text{Al} \longrightarrow 8\text{Al}^{3+} + 24e^-$
 $9\text{Fe}^{8/3+} + 24e^- \longrightarrow 9\text{Fe}$]
98. Which of the following examples does not represent disproportionation?
- $\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
 - $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 - $3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$
99. Why is the following reaction not possible?
- $$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{3+} + \text{H}^+ \longrightarrow \dots + \dots + \dots$$
- Both $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{3+} are reducing agents
 - Both $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{3+} are oxidising agents
 - $\text{Cr}_2\text{O}_7^{2-}$ is a strong oxidising agent while Fe^{3+} is a weak oxidising agent
 - The solution is acidic in nature
100. Which one of the following statements is not correct?
- Oxidation number of S in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is +6
 - Oxidation number of Os in OsO_4 is +8
 - Oxidation number of S in H_2SO_5 is +8
 - Oxidation number of O in KO_2 is $-\frac{1}{2}$
101. The oxide which cannot act as a reducing agent, is: (CBSE 1995)
- SO_2
 - NO_2
 - CO_2
 - ClO_2
102. Coordination number and oxidation number of Cr in $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$ are respectively: (CBSE 1995)
- 4 and +2
 - 6 and +3
 - 3 and -3
 - 3 and 0

103. In the following reaction,



- (a) P is oxidised only
- (b) P is reduced only
- (c) P is oxidised as well as reduced
- (d) none of the above

104. Which reaction does not involve either oxidation nor reduction?

- (a) $VO^{2+} \longrightarrow V_2O_3$
- (b) $Na \longrightarrow Na^+$
- (c) $CrO_4^{2-} \longrightarrow Cr_2O_7^{2-}$
- (d) $Zn^{2+} \longrightarrow Zn$

105. In which of the following processes is nitrogen oxidised?

- (a) $NH_4^+ \longrightarrow N_2$
- (b) $NO_3^- \longrightarrow NO$
- (c) $NO_2 \longrightarrow NO_2^-$
- (d) $NO_3^- \longrightarrow NH_4^+$

106. It is found that V forms a double salt isomorphous with Mohr's salt. The oxidation number of V in this compound is:

- (a) + 3
- (b) + 2
- (c) + 4
- (d) - 4

107. How many moles of electrons are involved in the reduction of one mole of MnO_4^- ion in alkaline medium to MnO_4^- ?

- (a) 2
- (b) 1
- (c) 3
- (d) 4

108. One mole of N_2H_4 loses 10 moles of electrons to form a new compound Y. Assuming that all nitrogen appears in the new compound, what is the oxidation number of nitrogen in Y (there is no change in the oxidation state of hydrogen)?

- (a) -3
- (b) + 3
- (c) + 5
- (d) + 1

109. Oxidation number of C in HNC is:

- (a) + 2
- (b) -3
- (c) + 3
- (d) zero

110. Oxidation number of Fe in $Fe_{0.94}O$ is:

- (a) 200
- (b) 200 / 94
- (c) 94 / 200
- (d) none of these

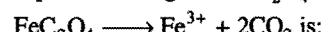
111. Oxidation number of Fe in $Na_2[Fe(CN)_5NO]$ is:

- (a) + 2
- (b) + 1
- (c) + 3
- (d) -2

112. Oxidation number of Cl in $CaOCl_2$ is:

- (a) -1 and + 1
- (b) + 2
- (c) -2
- (d) none of these

113. Equivalent weight of FeC_2O_4 in the change,



- (a) $M/3$
- (b) $M/6$
- (c) $M/2$
- (d) $M/1$

114. Oxidation state of Fe in Fe_3O_8 is: (CBSE 1999)

- (a) 3/2
- (b) 4/5
- (c) 5/4
- (d) 8/3

115. In which of the following compounds transition metal has zero oxidation state? (CBSE 1999)

- (a) CrO_5
- (b) Fe_3O_4
- (c) $FeSO_4$
- (d) $Fe(CO)_5$

116. The oxidation number of sulphur in S_8 , S_2F_2 and H_2S respectively are: (IIT 1999)

- (a) 0, +1 and -2
- (b) +2, +1 and -2
- (c) 0, +1 and +2
- (d) -2, +1 and -2

117. The reaction, $3ClO^- (aq) \rightarrow ClO_3^- (aq) + 2Cl^- (aq)$ is an example of: (IIT (S) 2000)

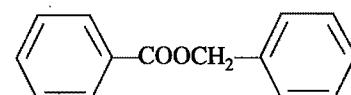
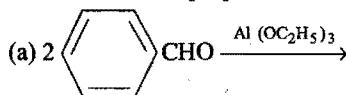
- (a) oxidation reaction
- (b) reduction reaction
- (c) disproportionation reaction
- (d) decomposition reaction

118. The oxidation state of 'S' in $H_2S_2O_8$ is:

[PET (MP) 2002; RPMT 2007]

- (a) +2
- (b) +4
- (c) +6
- (d) +7

119. Which is not a disproportionation reaction?



(d) All of the above

120. Which of the following is a disproportionation reaction?

- (a) $\text{Cu}_2\text{O} + 2\text{H}^+ \longrightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O}$
- (b) $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$
- (c) $\text{CaCO}_3 + 2\text{H}^+ \longrightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$
- (d) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$

121. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^- , MnO_2 , Mn_2O_3 and Mn^{2+} , then the number of electrons transferred in each case respectively is: (AIEEE 2002)

- (a) 4, 3, 1, 5
- (b) 1, 5, 3, 7
- (c) 1, 3, 4, 5
- (d) 3, 5, 7, 1

122. Which of the following is a redox reaction: (AIEEE 2002)

- (a) $\text{NaCl} + \text{KNO}_3 \longrightarrow \text{NaNO}_3 + \text{KCl}$
- (b) $\text{CaC}_2\text{O}_4 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4$
- (c) $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} \longrightarrow \text{MgCl}_2 + 2\text{NH}_4\text{OH}$
- (d) $\text{Zn} + 2\text{AgCN} \longrightarrow 2\text{Ag} + \text{Zn}(\text{CN})_2$

123. For the decolourisation of 1 mole of $KMnO_4$, the no. of moles of H_2O_2 required is: (AIIMS 2004)

- (a) $\frac{1}{2}$
- (b) $\frac{3}{2}$
- (c) $\frac{5}{2}$
- (d) $\frac{7}{2}$

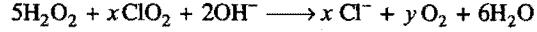
124. In H_2O_2 , the oxidation state of oxygen is: (CPMT 2000)

- (a) -2
- (b) -1
- (c) 0
- (d) -4

125. The reaction of $KMnO_4$ and HCl results in:

- (a) oxidation of Mn in $KMnO_4$ and production of Cl_2
- (b) reduction of Mn in $KMnO_4$ and production of H_2
- (c) oxidation of Mn in $KMnO_4$ and production of H_2
- (d) reduction of Mn in $KMnO_4$ and production of Cl_2

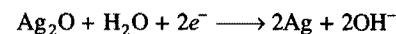
126. Consider the following reaction,



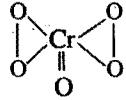
The reaction is balanced if:

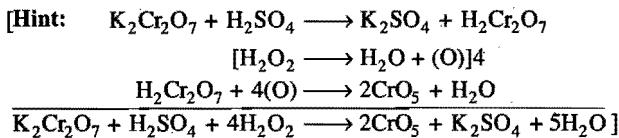
- (a) $x = 5, y = 2$
- (b) $x = 2, y = 5$
- (c) $x = 4, y = 10$
- (d) $x = 5, y = 5$

127. In the chemical reaction,



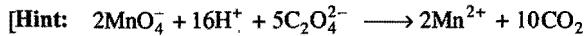
- (a) water is oxidised
- (b) electrons are reduced
- (c) silver is oxidised
- (d) silver is reduced
- (e) hydrogen is reduced

128. The reaction, $2\text{H}_2\text{O}(l) \rightarrow 4\text{H}^+(aq.) + \text{O}_2(g) + 4e^-$ is:
 (a) a redox reaction (b) a hydrolysis reaction
 (c) a solvolysis reaction (d) an oscillatory reaction
 (e) an acid catalyst reaction
129. Which of the following molecules can act as an oxidising agent as well as a reducing agent?
 (a) H_2S (b) SO_3 (c) H_2O_2 (d) F_2
 (e) H_2SO_4
130. Which of the following is not a reducing agent?
 (a) SO_2 (b) H_2O_2 (c) CO_2 (d) NO_2
131. Equivalent mass of oxidising agent in the reaction,
 $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$ is:
 (a) 32 (b) 64 (c) 16 (d) 8
132. A, B and C are three elements forming part of a compound in oxidation states of +2, +5 and -2 respectively. What could be the compound?
 (a) $A_2(BC)_2$ (b) $A_2(BC_4)_3$ (c) $A_3(BC_4)_2$ (d) ABC
133. Among the following, identify the species with an atom in +6 oxidation state:
 (a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2
134. On reduction of KMnO_4 by oxalic acid in acidic medium, the oxidation number of Mn changes. What is the magnitude of this change?
 (a) 7 to 2 (b) 6 to 2 (c) 5 to 2 (d) 7 to 4
135. The oxidation number of iron in Fe_3O_4 is:
 (a) +2 (b) +3 (c) 8/3 (d) 2/3
136. Number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ reduced by one mole of Sn^{2+} ions is:
 (a) 1/3 (b) 3 (c) 1/6 (d) 6
137. In standardization of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is:
 (a) molecular weight /2 (b) molecular weight /6
 (c) molecular weight /3 (d) same as molecular weight
138. In the balanced chemical reaction,
 $\text{IO}_3^- + a\text{I}^- + b\text{H}^+ \rightarrow c\text{H}_2\text{O} + d\text{I}_2$
 a, b, c and d respectively correspond to: (AIIMS 2005;
 AMU 2009)
 (a) 5, 6, 3, 3 (b) 5, 3, 6, 3 (c) 3, 5, 3, 6 (d) 5, 6, 5, 5
 [Hint: The balanced equation will be:
 $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$]
139. In alkaline medium ClO_2 oxidises to H_2O_2 and O_2 and itself gets reduced to Cl^- . How many moles of H_2O_2 are oxidised by 1 mole of ClO_2 ? (PET 2005)
 (a) 1 (b) 1.5 (c) 2.5 (d) 3.5
 (e) 5
 [Hint: The balanced chemical equation is:
 $2\text{ClO}_2 + 5\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{Cl}^- + 5\text{O}_2 + 6\text{H}_2\text{O}$
 $2 \text{ mol ClO}_2 \equiv 5 \text{ mol H}_2\text{O}_2$
 $1 \text{ mol ClO}_2 \equiv 2.5 \text{ mol H}_2\text{O}_2$]
140. Oxidation number of xenon in XeOF_2 is: [CET (J&K) 2005]
 (a) zero (b) 2 (c) 4 (d) 3
141. The oxidation number of cobalt in $\text{K}[\text{Co}(\text{CO})_4]$ is:
 (a) +1 (b) +3 (c) -1 (d) -3
142. The oxidation state of iodine in IPO_4 is: [JEE (Orissa) 2005]
 (a) +1 (b) +3 (c) +5 (d) +7
 [Hint: Let oxidation state of iodine be x
 $x - 3 = 0, x = +3$,
 $\therefore \text{PO}_4^{3-}$ has combined oxidation number -3.]
143. The oxidation state of Cr in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is:
 (a) +3 (b) +2 (c) +1 (d) 0
144. Nitrogen forms a variety of compounds in all oxidation states ranging from: [PMT (Himachal) 2006]
 (a) -3 to +5 (b) -3 to +3
 (c) -3 to +4 (d) -3 to +6
145. In alkaline medium, H_2O_2 reacts with Fe^{3+} and Mn^{2+} separately to give: [JEE (Orissa) 2006]
 (a) Fe^{4+} and Mn^{4+} (b) Fe^{2+} and Mn^{2+}
 (c) Fe^{2+} and Mn^{4+} (d) Fe^{4+} and Mn^{2+}
 [Hint: $2\text{K}_3^{3+}[\text{Fe}(\text{CN})_6] + 2\text{KOH} + 2\text{H}_2\text{O}_2 \rightarrow 2\text{K}_4^{2+}[\text{Fe}(\text{CN})_6] + 2\text{H}_2\text{O} + \text{O}_2$
 $\text{Mn}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{4+} + \text{H}_2\text{O}_4$]
146. CrO_5 has structure as shown,
- 
- The oxidation number of chromium in the above compound is: [PMT (Kerala) 2006; JEE (Orissa) 2008]
 (a) +4 (b) +5 (c) +6 (d) +10 (e) 0
147. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4 ? (AIEEE 2006)
 (a) $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
 (b) $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
 (c) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$
 (d) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
148. The oxidation numbers of the sulphur atoms in peroxy-monosulphuric acid (H_2SO_5) and peroxydisulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) are respectively: [JEE (J & K) 2009]
 (a) +8 and +7 (b) +3 and +3
 (c) +6 and +6 (d) +4 and +6
149. When phosphorus reacts with caustic soda, the products are PH_3 and NaH_2PO_2 . This reaction is an example of: [BHU (Mains) 2007]
 (a) oxidation (b) reduction
 (c) disproportionation (d) none of these
150. When hydrogen peroxide is added to acidified potassium dichromate, a blue colour is produced due to formation of: [PET (Kerala) 2007]
 (a) CrO_3 (b) Cr_2O_3 (c) CrO_5 (d) CrO_4^{2-}
 (e) $\text{Cr}_2\text{O}_7^{2-}$



151. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acid medium will be :
(a) 7.5 moles (b) 0.2 moles (c) 0.6 moles (d) 0.4 moles

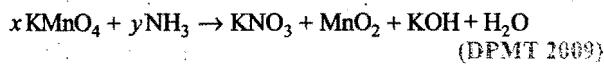
[CBSE-PMT (Pre) 2008]



Number of moles of MnO_4^- required to oxidise one mole of oxalate $= \frac{2}{5} = 0.4$]

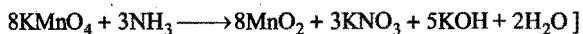
152. Oxidation number of iodine in IO_3^- , IO_4^- , KI and I_2 respectively are : [PMT (Kerala) 2008]
(a) -1, -1, 0, +1 (b) +3, +5, +7, 0
(c) +5, +7, -1, 0 (d) -1, -5, -1, 0
(e) -2, -5, -1, 0

153. In the redox reaction :



- (a) $x = 4, y = 6$ (b) $x = 3, y = 8$
(c) $x = 8, y = 6$ (d) $x = 8, y = 3$

[Hint : Balanced equation is :



Assertion-Reason TYPE QUESTIONS

Set-1

The questions given below consist of an 'Assertion' (A) and 'Reason' (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
 - (b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
 - (c) If (A) is correct, but (R) is incorrect.
 - (d) If (A) is incorrect, but (R) is correct.
1. (A) In aqueous solution, SO_2 reacts with H_2S liberating sulphur.
(R) SO_2 is an effective reducing agent.
 2. (A) Fluorine acts as a stronger reducing agent than oxygen.
(R) Fluorine is more electronegative.
 3. (A) $PbCl_2$ is more stable than $PbCl_4$.
(R) $PbCl_4$ is a powerful oxidising agent.
 4. (A) Among halogens fluorine is the.
(R) Fluorine is the most electronegative element.
 5. (A) In the reaction between potassium permanganate and potassium iodide, potassium permanganate act as oxidising agent.
(R) Oxidation state of manganese changes from +2 to +7 during the reaction.

Set-2

The questions given below consist of two statements each as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four:

- (a) If both (A) and (R) are true, and (R) is the correct explanation of (A).
 - (b) If both (A) and (R) are true, but (R) is not the correct explanation of (A).
 - (c) If (A) is true, but (R) is false.
 - (d) If (A) and (R) are both false.
1. (A) Identification of cathode and anode is done with the help of thermometer.
(R) Higher is the value of reduction potential, greater would be its reducing power. (AIIMS 1999)
 2. (A) Zinc reacts with H_2SO_4 to give H_2 gas but copper does not.
(R) Zinc has higher reduction potential than copper.
 3. (A) Absolute electrode potential can be easily measured by using vacuum tube voltmeter.
(R) Oxidation or reduction cannot take place alone.
 4. (A) Sulphur dioxide and chlorine are both bleaching agents.
(R) Both are reducing agents. (AIIMS 1994)
 5. (A) Hydrogen peroxide acts only as oxidising agent.
 $(H_2O_2 \rightarrow H_2O + O)$
(R) All peroxides behave as the oxidising agent only.

6. (A) HClO_4 is stronger acid than HClO_3 .
(R) Oxidation state of Cl in HClO_4 is +VII and in HClO_3 ; it is +V.
7. (A) Oxidation number of Ni in $\text{Ni}(\text{CO})_4$ is taken zero.
(R) The oxidation number of CO has been taken to be zero.
8. (A) Oxidation state of 'H' is +1 in CuH_2 and is -1 in CaH_2 .
(R) Ca is stronger electropositive than hydrogen.
9. (A) Iodine shows oxidation state of +1 and +3 in the compounds ICl and ICl_3 respectively.
(R) Iodine coming below the halogens F, Cl and Br in the halogen group of elements in the periodic table shows a higher degree of electropositive nature. (SCRA 2007)

Answers OBJECTIVE QUESTIONS

1. (a)	2. (b)	3. (d)	4. (c)	5. (a)	6. (d)	7. (b)	8. (c)
9. (b)	10. (c)	11. (a)	12. (c)	13. (b)	14. (b)	15. (c)	16. (a)
17. (d)	18. (c)	19. (d)	20. (c)	21. (b)	22. (d)	23. (c)	24. (a)
25. (d)	26. (b)	27. (a)	28. (d)	29. (a)	30. (c)	31. (d)	32. (b)
33. (b)	34. (b)	35. (c)	36. (d)	37. (a)	38. (a)	39. (a)	40. (a)
41. (a)	42. (b)	43. (b)	44. (a)	45. (b)	46. (c)	47. (c)	48. (c)
49. (d)	50. (d)	51. (b)	52. (c)	53. (c)	54. (a)	55. (a)	56. (b)
57. (b)	58. (c)	59. (b)	60. (a)	61. (c)	62. (b)	63. (d)	64. (d)
65. (a)	66. (c)	67. (c)	68. (d)	69. (b)	70. (d)	71. (a)	72. (b)
73. (c)	74. (a)	75. (b)	76. (b)	77. (c)	78. (b)	79. (a)	80. (d)
81. (b)	82. (a)	83. (d)	84. (c)	85. (d)	86. (b)	87. (a)	88. (c)
89. (d)	90. (b)	91. (a)	92. (c)	93. (d)	94. (b)	95. (c)	96. (d)
97. (d)	98. (a)	99. (b)	100. (c)	101. (c)	102. (b)	103. (c)	104. (c)
105. (a)	106. (b)	107. (a)	108. (b)	109. (a)	110. (b)	111. (a)	112. (a)
113. (d)	114. (d)	115. (d)	116. (a)	117. (c)	118. (c)	119. (c)	120. (a)
121. (c)	122. (c)	123. (c)	124. (b)	125. (d)	126. (b)	127. (d)	128. (a)
129. (c)	130. (c)	131. (c)	132. (c)	133. (d)	134. (a)	135. (c)	136. (a)
137. (b)	138. (a)	139. (c)	140. (c)	141. (c)	142. (b)	143. (a)	144. (a)
145. (c)	146. (c)	147. (a)	148. (c)	149. (c)	150. (c)	151. (d)	152. (c)
153. (d)	154. (c)	155. (d)	156. (c)	157. (d)			

Answers ASSERTION-REASON TYPE QUESTIONS

• Set-1

1. (b) 2. (b) 3. (b) 4. (b) 5. (c)

• Set-2

1. (d) 2. (c) 3. (d) 4. (c) 5. (d) 6. (b) 7. (a) 8. (a)
9. (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. Oxidation states of carbon atoms in diamond and graphite are:
(a) +2, +4 (b) +4, +2 (c) -4, 4 (d) zero, zero
2. Oxidation state(s) of chlorine in CaOCl_2 (bleaching powder) is/are:
(a) +1 and -1 (b) +1 only
(c) -1 only (d) none of these
3. Oxidation number of sulphur in S_8 , S_2F_2 and H_2S are:
(a) +2, 0, +2 (b) 0, +1, -2 (c) -2, 0, +2 (d) 0, +1, +2
4. The reaction, $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{S}$, shows:
(a) acidic nature of H_2O_2 (b) reducing nature of H_2O_2
(c) oxidising action of H_2O_2 (d) alkaline nature of H_2O_2
5. For the redox reaction,



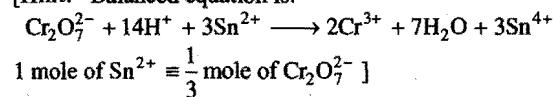
the correct coefficients of the reactants for the balanced reaction are:

	MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+
(a)	2	5	16
(b)	16	3	12
(c)	15	16	12
(d)	2	16	5

6. Number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ that can be reduced by 1 mole of Sn^{2+} ions is:

(a) $\frac{1}{3}$	(b) $\frac{3}{2}$	(c) $\frac{5}{6}$	(d) $\frac{6}{5}$
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[Hint: Balanced equation is:

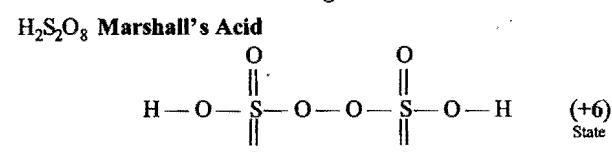
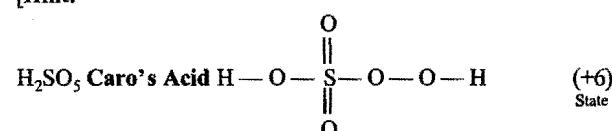


7. The reaction, $3\text{ClO}^- (\text{aq.}) \rightarrow \text{ClO}_3^- (\text{aq.}) + 2\text{Cl}^- (\text{aq.})$, is an example of:
(a) reduction reaction
(b) oxidation reaction
(c) disproportionation reaction
(d) spallation reaction

8. The oxidation states of sulphur in Caro's and Marshall's acid are:

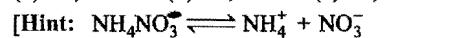
(a) +6, +6	(b) +4, +6	(c) +6, -6	(d) +6, +4
------------	------------	------------	------------

[Hint:



Both these acids have peroxy link.]

9. Which among the following compounds have +6 state with the metal atoms?
(a) $[\text{Fe}(\text{CN})_6]^{4-}$ (b) $[\text{Fe}(\text{CN})_6]^{3-}$
(c) $[\text{Cr}(\text{CN})_6]^{3-}$ (d) CrO_2Cl_2
10. The oxidation number of nitrogen atoms in NH_4NO_3 are:
(a) +3, +3 (b) +3, -3 (c) -3, +5 (d) -5, +3



$$\text{NH}_4^+ \ x + 4 = +1$$

$$x = -3$$

$$\text{NO}_3^- \ x - 6 = -1$$

$$x = +5]$$

11. In the chemical reaction,
 $\text{K}_2\text{Cr}_2\text{O}_7 + x\text{H}_2\text{SO}_4 + y\text{SO}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + z\text{H}_2\text{O}$
the values of x , y and z respectively are:
(a) $x = 1$, $y = 3$, $z = 1$ (b) $x = 4$, $y = 1$, $z = 4$
(c) $x = 3$, $y = 2$, $z = 1$ (d) $x = 2$, $y = 2$, $z = 2$
12. In which of the following pairs both members contain peroxy linkage?
(a) $\text{H}_2\text{S}_2\text{O}_8$, $\text{H}_4\text{P}_2\text{O}_6$ (b) H_2SO_5 , $\text{H}_4\text{P}_2\text{O}_7$
(c) H_2TiO_4 , $\text{H}_4\text{P}_2\text{O}_8$ (d) S_3O_9 , P_4O_7
13. Which of the following agents is the most oxidising?
(a) O_3 (b) KMnO_4 (c) H_2O_2 (d) $\text{K}_2\text{Cr}_2\text{O}_7$
14. When methane is burnt in oxygen to produce CO_2 and H_2O , the oxidation number changes by:
(a) -8 (b) zero (c) +8 (d) +4



Oxidation number change = +4 - (-4) = +8]

15. Which of the following has been arranged in order of increasing oxidation number of nitrogen?
(a) $\text{NH}_3 < \text{N}_2\text{O}_5 < \text{NO} < \text{N}_2$
(b) $\text{NO}_2^+ < \text{NO}_3^- < \text{NO}_2^- < \text{N}_3^-$
(c) $\text{NH}_4^+ < \text{N}_2\text{H}_4 < \text{NH}_2\text{OH} < \text{N}_2\text{O}$
(d) $\text{NO}_2 < \text{NaN}_3 < \text{NH}_4^+ < \text{N}_2\text{O}$
16. In the ethylene molecule the two carbon atoms have the oxidation numbers:
(a) -1, -1 (b) -2, -2 (c) -1, -2 (d) +2, -2
17. In which of the following coordination compounds do the transition metals have an oxidation number of +6?
(a) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (b) $[\text{Fe}(\text{CO})_5]$
(c) $[(\text{H}_2\text{O})_5\text{Cr} - \text{O} - \text{Cr}(\text{H}_2\text{O})_5]^{4+}$
(d) $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$
18. In the redox reaction:
 $x\text{MnO} + y\text{PbO}_2 + z\text{HNO}_3 \rightarrow \text{HMnO}_4 + \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$
(a) $x = 2$, $y = 5$, $z = 10$ (b) $x = 2$, $y = 7$, $z = 8$
(c) $x = 2$, $y = 5$, $z = 8$ (d) $x = 2$, $y = 5$, $z = 5$

19. In the redox reaction:



- (a) $x = 4, y = 6$ (b) $x = 8, y = 3$
 (c) $x = 8, y = 6$ (d) $x = 3, y = 8$

20. In the ionic equation:



- (a) $x = 1, y = 4, z = 6$ (b) $x = 1, y = 6, z = 4$
 (c) $x = 1, y = 8, z = 12$ (d) $x = 1, y = 8, z = 8$

21. The oxidation number of Cr is +6 in:

- (a) FeCr_2O_4 (b) KCrO_3Cl (c) CrO_5 (d) $[\text{Cr}(\text{OH})_4]^-$

22. The oxidation number of carbon is zero in:

- (a) HCHO (b) CH_2Cl_2 (c) $\text{C}_6\text{H}_{12}\text{O}_6$ (d) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

23. Which of the following have been arranged in order of decreasing oxidation number of sulphur?

- (a) $\text{H}_2\text{S}_2\text{O}_7 > \text{Na}_2\text{S}_4\text{O}_6 > \text{Na}_2\text{S}_2\text{O}_3 > \text{S}_8$
 (b) $\text{SO}^{2+} > \text{SO}_4^{2-} > \text{SO}_3^{2-} > \text{HSO}_4^-$

- (c) $\text{H}_2\text{SO}_5 > \text{H}_2\text{SO}_3 > \text{SCl}_2 > \text{H}_2\text{S}$
 (d) $\text{H}_2\text{SO}_4 > \text{SO}_2 > \text{H}_2\text{S} > \text{H}_2\text{S}_2\text{O}_8$

24. Oxidation number of carboxylic carbon atom in CH_3COOH is:

- (a) +2 (b) +4 (c) +1 (d) +3

25. Which among the following are autoredox reactions?

- (a) $\text{P}_4 + \text{OH}^- \longrightarrow \text{H}_2\text{PO}_4^- + \text{PH}_3$
 (b) $\text{S}_2\text{O}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{S}$
 (c) $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
 (d) $\text{AgCl} + \text{NH}_3 \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$

26. Oxidation state of nitrogen is incorrectly given for: [PMT (Pb.) 2006]

Compound	Oxidation state
(a) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	-3
(b) NH_2OH	-1
(c) $(\text{N}_2\text{H}_5)_2\text{SO}_4$	+2
(d) Mg_3N_2	-3

27. Oxidation number of C in HNC is:

- (a) +2 (b) -3
 (c) +3 (d) zero

Hint: HNC
 $+1 - 3 + x = 0$
 $x = +2$

28. Which of the following groups of molecules act both as oxidising agent as well as reducing agent?

- (a) $\text{KMnO}_4, \text{O}_3, \text{SO}_3$ (b) $\text{HClO}_4, \text{HNO}_2, \text{H}_2\text{O}_2$
 (c) $\text{HNO}_2, \text{SO}_2, \text{H}_2\text{O}_2$ (d) $\text{HNO}_3, \text{SO}_2, \text{H}_2\text{SO}_4$

29. Match the List-I with List-II and select the correct answer from the given Codes:

List-I (Compound)	List-II (Oxidation state of nitrogen)			
A. N_2O_5	(i) -2			
B. NaN_3		(ii) +5		
C. NO			(iii) -1/3	
D. N_2H_4				(iv) +2

Codes:	A	B	C	D
(a)	(ii)	(iii)	(iv)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(i)	(ii)	(iii)
(d)	(iii)	(i)	(iv)	(ii)

30. The oxidation state of molybdenum in its oxo complex species $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O}_2)]^{2-}$ is:
 (a) 2 (b) 3 (c) 4 (d) 5
31. KMnO_4 is a strong oxidising agent in acid medium. To provide acid-medium, H_2SO_4 is used instead of HCl. This is because: [PMT (Kerala) 2007]

- (a) H_2SO_4 is a stronger acid than HCl
 (b) HCl is oxidised by KMnO_4 to Cl_2
 (c) H_2SO_4 is a dibasic acid
 (d) rate is faster in the presence of H_2SO_4
 (e) only H_2SO_4 is completely ionized

32. Which of the following oxides cannot work as a reducing agent? [PET (Raj.) 2006]

- (a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2

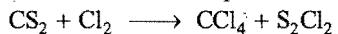
33. The coordination number and oxidation state of Cr in $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ are respectively: [PET (Raj.) 2006]

- (a) 3 and +3 (b) 2 and 0
 (c) 6 and +3 (d) 4 and +2

34. The reaction, $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_4 + \text{PH}_3$ is an example of: [JEE (Orissa) 2008]

- (a) disproportionation reaction
 (b) neutralisation reaction
 (c) double decomposition reaction
 (d) pyrolytic reaction

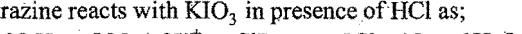
35. Balance the following equation and choose the correct value of sum of coefficients of the products :



- (a) 5 (b) 3 (c) 6 (d) 2

36. 6×10^{-3} mole $\text{K}_2\text{Cr}_2\text{O}_7$ reacts completely with 9×10^{-3} mole X^{n+} to give XO_4^- and Cr^{3+} . The value of 'n' is :
 (a) 1 (b) 2 (c) 3 (d) 5

37. Hydrazine reacts with KIO_3 in presence of HCl as:



The equivalent masses of N_2H_4 and KIO_3 respectively are :

- (a) 8, 87 (b) 8, 35.6 (c) 16, 53.5 (d) 8, 53.5

Answers

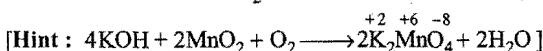
- | | | | | | | | |
|---------------|---------|---------|---------|------------|------------------|------------|---------|
| 1. (d) | 2. (a) | 3. (b) | 4. (c) | 5. (a) | 6. (a) | 7. (c) | 8. (a) |
| 9. (d) | 10. (c) | 11. (a) | 12. (c) | 13. (a) | 14. (c) | 15. (c) | 16. (b) |
| 17. (d) | 18. (a) | 19. (b) | 20. (a) | 21. (b, c) | 22. (a, b, c, d) | 23. (a, c) | 24. (d) |
| 25. (a, b, c) | 26. (c) | 27. (a) | 28. (c) | 29. (a) | 30. (b) | 31. (b) | 32. (a) |
| 33. (c) | 34. (a) | 35. (d) | 36. (a) | 37. (d) | | | |

Integer Answer TYPE QUESTIONS

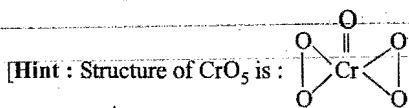
This section contains 9 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

X	Y	Z	W
①	②	③	④
①	②	③	④
②	③	④	⑤
③	④	⑤	⑥
④	⑤	⑥	⑦
⑤	⑥	⑦	⑧
⑥	⑦	⑧	⑨
⑦	⑧	⑨	①
⑧	⑨	①	②
⑨	①	②	③

1. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is: (IIT 2009)

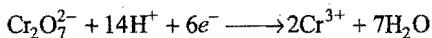


2. How many peroxy links are there in CrO_5 ?



There are two peroxy links in this molecule.]

3. How many moles of electrons are involved in the conversion of 1 mol $\text{Cr}_2\text{O}_7^{2-}$ into Cr^{3+} ion?



4. In the following reaction, hydrazine is oxidised to N_2



The equivalent mass of N_2H_4 (hydrazine) is:

5. Nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) can be reduced to aniline ($\text{C}_6\text{H}_5\text{NH}_2$) by electrolytic reduction; the equivalent mass of nitrobenzene will be equal to $\left(\frac{\text{molecular mass}}{n}\right)$. The value of n is:

[Hint : $\text{C}_6\text{H}_5\text{NO}_2 + 6[\text{H}] \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$]

6. How many sulphur atoms in $\text{Na}_2\text{S}_4\text{O}_6$ have zero oxidation state?

7. 6×10^{-3} mole $\text{K}_2\text{Cr}_2\text{O}_7$ reacts completely with 9×10^{-3} mole x^{n+} to give XO_3^- and Cr^{3+} . The value of n is:

8. The sum of oxidation number of nitrogen in NH_4NO_3 is :

9. The value of n in the molecular formula $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ is: (IIT 2010)

[Hint : $\text{Si}_6\text{O}_{18}^{12-}$ is a cyclic silicate. The value of n will be '3' to balance the charge $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$

$$2n + 6 - 12 = 0$$

$$n = 3$$

Answers

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1. (6) | 2. (2) | 3. (6) | 4. (8) | 5. (6) | 6. (2) | 7. (1) | 8. (2) |
| 9. (3) | | | | | | | |

LINKED COMPREHENSION TYPE QUESTIONS

● Passage 1

Valecy and oxidation number are different for an element. Valecy of carbon is generally 4, however, the oxidation state may be -4, -2, 0, +2, -1, etc. In the compounds containing carbon, hydrogen and oxygen, the oxidation number of carbon can be calculated as:

$$\text{Oxidation number of carbon} = \frac{2n_O - n_H}{n_C}$$

where, n_H , n_O and n_C are number of respective atoms.

Answer the following questions:

1. Which of the following compounds have zero oxidation state at carbon?
(a) $\text{C}_6\text{H}_{12}\text{O}_6$ (b) HCOOH (c) HCHO (d) CH_4
2. Which of the following oxides of carbon has fractional oxidation state?
(a) Carbon monoxide (b) Carbon dioxide
(c) Carbon suboxide (d) All of these
3. Which of the following compounds of carbon has highest oxidation state?
(a) CH_4 (b) CH_3OH (c) CH_2O (d) HCOOH
4. Oxidation state of carbon in diamond is:
(a) zero (b) +1 (c) -1 (d) +2
5. In which of the following compounds, the valency of carbon is two?
(a) Carbenes (b) Allenes (c) Alkenes (d) Ketenes

● Passage 2

Oxidation and reduction process involves the transaction of electrons. Loss of electrons is oxidation and the gain of electrons is reduction. It is thus obvious that in a redox reaction, the oxidant is reduced by accepting the electrons and the reductant is oxidised by losing electrons. The reactions in which a species disproportionates into two oxidation states (lower and higher) are called disproportionation reactions. In electrochemical cells, redox reaction is involved, i.e., oxidation takes place at anode and reduction at cathode.

Answer the following questions:

1. The reaction,
$$\text{Cl}_2 \longrightarrow \text{Cl}^- + \text{ClO}_3^-$$

is:
(a) oxidation
(b) reduction
(c) disproportionation
(d) neither oxidation nor reduction
2. Select the correct statement:
(a) oxidation takes place at anode in electrochemical cell
(b) reduction takes place at cathode in electrolytic cell
(c) oxidation takes place at cathode in electrolytic cell
(d) all are correct
3. In the reaction:
$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

- (a) I_2 is a reducing agent (b) I_2 is an oxidising agent
(c) $\text{S}_2\text{O}_3^{2-}$ is a reducing agent (d) $\text{S}_2\text{O}_3^{2-}$ is an oxidising agent
4. Determine the change in oxidation number of sulphur in H_2S and SO_2 respectively in the following reaction:
$$2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$$

(a) 0, +2 (b) +2, -4 (c) -2, +2 (d) +4, 0
5. Which of the following reactions is/are correctly indicated?

Oxidant	Reducant
(a) HNO_3 + Cu	$\longrightarrow \text{Cu}^{2+} + \text{NO}_2$
(b) 2Zn + O ₂	$\longrightarrow \text{ZnO}$
(c) Cl ₂ + 2Br ⁻	$\longrightarrow 2\text{Cl}^- + \text{Br}_2$
(d) 4Cl ₂ + CH ₄	$\longrightarrow \text{CCl}_4 + 4\text{HCl}$

● Passage 3

Redox reactions are of three types:

- (i) *Intermolecular redox reactions,*
- (ii) *Intramolecular redox reactions,*
- (iii) *Auto redox reactions*

OR

Disproportionation reactions.

Redox reactions are divided into two main types:

- (i) *Chemical redox reactions,*
- (ii) *Electrochemical redox reactions which either produce or consume electricity.*

Oxidation and reduction process takes place in a reaction simultaneously.

Answer the following questions:

1. Which of the following is a redox reaction?
(a) $\text{NaCl} + \text{KNO}_3 \longrightarrow \text{NaNO}_3 + \text{KCl}$
(b) $\text{CaC}_2\text{O}_4 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4$
(c) $\text{Mg(OH)}_2 + 2\text{NH}_4\text{Cl} \longrightarrow \text{MgCl}_2 + 2\text{NH}_4\text{OH}$
(d) $\text{Zn} + 2\text{AgCN} \longrightarrow 2\text{Ag} + \text{Zn}(\text{CN})_2$
2. Select the intramolecular redox reaction(s) among the following:
(a) $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
(b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
(c) $\text{Cl}_2 \longrightarrow \text{Cl}^- + \text{ClO}_3^-$
(d) $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
3. In which of the following reactions, H_2O_2 acts as reducing agent?
(a) $\text{Cl}_2 + \text{H}_2\text{O}_2 \longrightarrow 2\text{HCl} + \text{O}_2$
(b) $\text{H}_2\text{O}_2 + \text{O}_3 \longrightarrow \text{H}_2\text{O} + 2\text{O}_2$
(c) $\text{HCHO} + \text{H}_2\text{O}_2 \longrightarrow \text{HCOOH} + \text{H}_2\text{O}$
(d) $\text{PbO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{PbO} + \text{H}_2\text{O} + \text{O}_2$
4. Which among the following acts as oxidising as well as reducing agent?
(a) HNO_2 (b) HNO_3 (c) H_2SO_4 (d) KMnO_4
5. The value of x in the following reaction,
$$\text{MnO}_4^- + 8\text{H}^+ + xe \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
 is:
(a) 5 (b) 10 (c) 2 (d) 3

- Passage 1.** 1. (a, c) 2. (c) 3. (d) 4. (a) 5. (a)
Passage 2. 1. (c) 2. (a, b) 3. (b, c) 4. (b) 5. (a, c, d)
Passage 3. 1. (d) 2. (a, b, d) 3. (a, b, d) 4. (a) 5. (a)

SELF ASSESSMENT

ASSIGNMENT NO. 11

SECTION-I

Straight Objective Type Questions

This section contains 8 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. In the reaction:

$$\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \longrightarrow 2\text{SO}_4^{2-} + \text{I}_2$$
 [PET (MP) 2007]
 - (a) oxidation of iodide into iodine takes place
 - (b) reduction of iodine into iodide takes place
 - (c) both oxidation and reduction of iodine takes place
 - (d) none of the above
2. The oxidation state of chromium in chromium trioxide is:
[ICET (J&K) 2007]
 - (a) +3 (b) +4 (c) +5 (d) +6
3. For the reaction between KMnO_4 and H_2O_2 , the number of electrons transferred per mol of H_2O_2 is:
 - (a) one (b) two
 - (c) three (d) four
4. In the ionic equation,

$$\text{BiO}_3^- + 6\text{H}^+ + xe^- \longrightarrow \text{Bi}^{3+} + 3\text{H}_2\text{O}$$
 the value of x is:
 - (a) 6 (b) 2
 - (c) 4 (d) 3
5. In $[\text{Cr}(\text{O}_2)(\text{NH}_3)_4\text{H}_2\text{O}]\text{Cl}_2$, oxidation number of Cr is +3, then oxygen will be in the form:
 - (a) dioxo (b) peroxy
 - (c) superoxo (d) oxo
6. In the reaction, $\text{CrO}_5 + \text{SnCl}_2 \longrightarrow \text{CrO}_4^{2-} + \text{SnCl}_4$, the element undergoing oxidation and reduction respectively are:
 - (a) Cr, Sn (b) Sn, Cr
 - (c) Sn, O (d) Cl, C
7. Equivalent mass of KMnO_4 in acidic, basic and neutral are in the ratio of:
 - (a) 3 : 5 : 15 (b) 5 : 3 : 1
 - (c) 5 : 1 : 3 (d) 3 : 15 : 5
8. A compound of Xe and F is found to have 53.5% Xe. What is the oxidation number of Xe in this compound?
 - (a) -4 (b) 0
 - (c) +4 (d) +6

SECTION-II

Multiple Answers Type Objective Questions

9. Peroxide ions are present in:
 - (a) H_2O_2
 - (b) BaO_2
 - (c) OF_2
 - (d) $\text{H}_2\text{S}_2\text{O}_8$
10. The metals undergoing disproportionation are:
 - (a) Sn
 - (b) Na
 - (c) Cu
 - (d) Ca
11. The non-metals undergoing disproportionation are:
 - (a) P_4
 - (b) Cl_2
 - (c) I_2
 - (d) F
12. Which of the following can act as oxidising as well as reducing agent?
 - (a) O_3
 - (b) HNO_3
 - (c) SO_2
 - (d) H_2O_2
13. When Cl_2 reacts with aqueous NaOH in cold condition then oxidation number of chlorine changes from 0 to:
 - (a) -1
 - (b) +1
 - (c) -2
 - (d) +2
14. Select those species that can function both as oxidising and also as reducing agent:
[BUH (Mains) 2010]
 - (a) KI
 - (b) KI_3
 - (c) I_2
 - (d) H_2O_2
15. The species that contain peroxide ions are:
[BUH (Mains) 2010]
 - (a) PbO_2
 - (b) H_2O_2
 - (c) SrO_2
 - (d) BaO_2

SECTION-III

Assertion-Reason Type Questions

This section contains 4 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 - (b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
 - (c) Statement-1 is true; statement-2 is false.
 - (d) Statement-1 is false; statement-2 is true.
16. **Statement-1:** Spectator ions are the species that are present in the solution but do not take part in the reaction.

Because

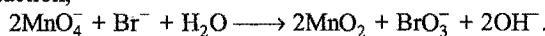
Statement-2: The phenomena of formation of H_2O_2 by the oxidation of H_2O is known as auto-oxidation.
[Hint: $\text{Zn} + 2\text{H}^+ + 2\text{Cl}^- \longrightarrow \text{Zn}^{2+} + 2\text{Cl}^- + \text{H}_2$. Here, Cl^- ion is spectator ion.]

17. Statement-1: Oxidation number of carbon in HCN is + 2.

Because

Statement-2: Carbon always shows an oxidation state of + 4.

18. Statement-1: Bromide ion acts as a reducing agent in the reaction,



Because

Statement-2: Oxidation number of bromine increases from -1 to +5.

19. Statement-1: Oxidation number of carbon in HCHO is zero.

Because

Statement-2: HCHO is a covalent organic compound.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

	p	q	r	s
a	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
b	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
c	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4×4 matrix should be as follows:

20. Match the Column-I with Column-II:

Column-I (Chemical species)	Column-II (Oxidation number of sulphur)
(a) S	(p) + 6
(b) H_2S	(q) + 1
(c) S_2Cl_2	(r) 0
(d) $\text{H}_2\text{S}_2\text{O}_8$	(s) - 2

21. Match the Column-I with Column-II:

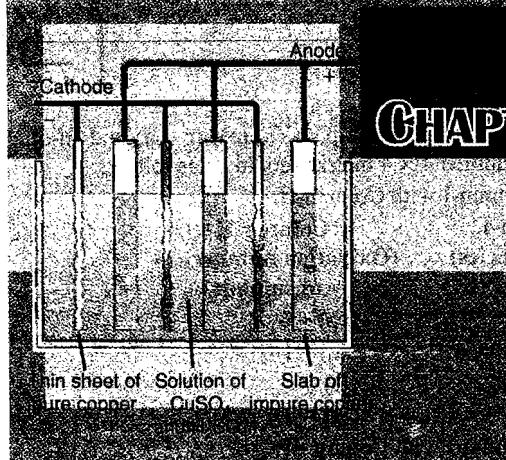
Column-I (Compound)	Column-II (Oxidation state of sulphur)
(a) Sulphuric acid (H_2SO_3)	(p) + 5
(b) Peroxy mono sulphuric acid (H_2SO_5)	(q) + 3
(c) Dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$)	(r) + 6
(d) Dithionous acid ($\text{H}_2\text{S}_2\text{O}_4$)	(s) + 4

22. Match the Column-I with Column-II:

Column-I	Column-II
(a) $\text{O}_2^- \longrightarrow \text{O}_2 + \text{O}_2^{2-}$	(p) Redox reaction
(b) $\text{CrO}_4^{2-} + \text{H}^+ \longrightarrow$	(q) One of the products has trigonal planar structure
(c) $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \longrightarrow$	(r) dimeric bridged tetrahedral metal ion
(d) $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow$	(s) disproportionation

Answers

- | | | | | | | | |
|---------------------------------|------------|---------------|-----------------------------|------------|-----------------------------|---------------|---------|
| 1. (a) | 2. (d) | 3. (c) | 4. (b) | 5. (c) | 6. (c) | 7. (d) | 8. (d) |
| 9. (a, b, d) | 10. (a, c) | 11. (a, b, c) | 12. (c, d) | 13. (a, b) | 14. (b, c, d) | 15. (b, c, d) | 16. (b) |
| 17. (c) | 18. (a) | 19. (b) | 20. (a-r) (b-s) (c-q) (d-p) | | 21. (a-s) (b-r) (c-p) (d-q) | | |
| 22. (a-p,s) (b-r) (c-p,q) (d-p) | | | | | | | |



CHAPTER 12

ELECTROCHEMISTRY

SECTION I : ELECTROLYTES AND ELECTROLYSIS

12.1 INTRODUCTION

Electrochemistry deals with the interactions of electrical energy with chemical species. It is broadly divided into two categories, namely (i) production of chemical change by electrical energy (phenomenon of electrolysis) and (ii) conversion of chemical energy into electrical energy, *i.e.*, generation of electricity by spontaneous redox reactions. In this chapter both of these aspects will be described. All electrochemical reactions involve transfer of electrons and are, therefore, oxidation-reduction (redox) reactions.

Substances which allow the passage of electric current through them are called **electrical conductors** or simply conductors. Those which do not allow the flow of electric current through them are termed **insulators**. Electrical conductors are of two types:

(i) Metallic or electronic conductors: Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as **metallic or electronic conductors**. Metals such as copper, silver, aluminium, etc., non-metals like carbon (graphite—an allotropic form of carbon) and various alloys belong to this class. These materials contain electrons which are relatively free to move. The passage of current through these materials has no observable effect other than a rise in their temperature.

(ii) Electrolytic conductors: Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as **electrolytic conductors**. The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed **electrolytes**.

The substances whose aqueous solutions do not conduct electric current are called **non-electrolytes**. Solutions of cane sugar, glycerine, alcohol, etc., are examples of non-electrolytes.

In order to pass the current through an electrolytic conductor

(aqueous solution or fused electrolyte), two rods or plates (metallic conductors) are always needed which are connected with the terminals of a battery. These rods or plates are known as **electrodes**. The electrode through which the current enters the electrolytic solution is called the **anode** (positive electrode) while the electrode through which the current leaves the electrolytic solution is known as **cathode** (negative electrode). The electrolytic solution conducts electricity not by virtue of flow of electrons as in metallic conductors but as a result of movement of charged particles called **ions** towards the respective oppositely charged electrodes. The ions which carry positive charge and move towards cathode are termed **cations** while ions carrying negative charge which move towards anode are called **anions**. When these ions reach the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from the ions. Removal of electrons is termed **oxidation** (de-electronation) which occurs at anode while addition of electrons is called **reduction** (electronation) that takes place at cathode. Hence, flow of electrons through the outer circuit from anode to cathode across the boundary is accompanied by oxidation and reduction.

Distinction between metallic and electrolytic conduction

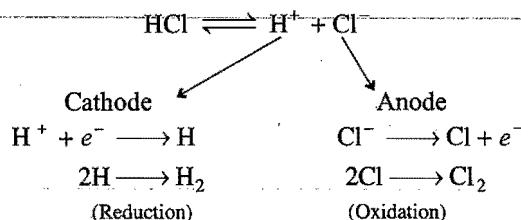
Metallic conduction	Electrolytic conduction
1. Electric current flows by movement of electrons.	Electric current flows by movement of ions.
2. No chemical change occurs.	Ions are oxidised or reduced at the electrodes.
3. It does not involve the transfer of any matter.	It involves transfer of matter in the form of ions.
4. Ohm's law is followed.	Ohm's law is followed.
5. Resistance increases with increase of temperature.	Resistance decreases with increase of temperature.
6. Faraday's law is not followed.	Faraday's law is followed.

The process of chemical decomposition of an electrolyte by passage of electric current through its solution is called electrolysis.

Or

Chemical change (oxidation and reduction) occurring at electrodes when electric current is passed through electrolytic solution is called electrolysis.

Molecules of an electrolyte when dissolved in water split up into ions, i.e., into cations and anions. On passing current, these ions move towards oppositely charged electrodes. On reaching the electrodes the ions lose their charge either by accepting electrons or losing electrons and thereby deposited at the respective electrodes or undergo a secondary change. For example, when electric current is passed through a solution of hydrochloric acid, the H^+ ions move towards cathode and Cl^- ions move towards anode.



The decomposition of HCl into H_2 and Cl_2 as a result of passage of current is termed electrolysis of HCl. It is, thus, a process in which electric current brings the chemical change.

The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical change is done is known as **electrolytic cell**. An electrolytic cell consists of a vessel for the electrolytic solution or fused electrolyte and two metallic electrodes immersed in the reaction material which are connected to a source of electric current. The metallic electrodes which do not react with ions or final products are called **inert electrodes**. Inert electrodes are usually used in an electrolytic cell.

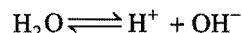
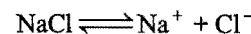
12.2 PREFERENTIAL DISCHARGE THEORY

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged at the electrodes simultaneously but certain ions are liberated at the electrodes in preference to others. This is explained by **preferential discharge theory**. It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H^+ ions is lower than Na^+ ions when platinum or most of the other metals* are used as cathodes. Similarly, discharge potential of Cl^- ions is

lower than that of OH^- ions. This can be explained by some examples given below:

(i) Electrolysis of sodium chloride solution

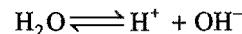
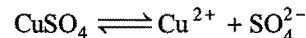
The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- ions due to ionisation of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.



At cathode	At anode
$H^+ + e^- \rightarrow H$	$Cl^- \rightarrow Cl + e^-$
$2H \rightarrow H_2$	$2Cl \rightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

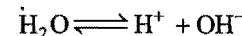
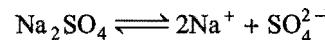
(ii) Electrolysis of copper sulphate solution using platinum electrodes



At cathode	At anode
$Cu^{2+} + 2e^- \rightarrow Cu$	$2OH^- \rightarrow H_2O + O + 2e^-$
$O + O \rightarrow O_2$	

Copper is discharged at cathode as Cu^{2+} ions have lower discharge potential than H^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, copper is deposited at cathode and oxygen gas is evolved at anode.

(iii) Electrolysis of sodium sulphate solution using inert electrodes



At cathode	At anode
$H^+ + e^- \rightarrow H$	$2OH^- \rightarrow H_2O + O + 2e^-$
$2H \rightarrow H_2$	$O + O \rightarrow O_2$

Hydrogen is discharged at cathode as H^+ ions have lower discharge potential than Na^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, hydrogen is evolved at cathode and oxygen is evolved at anode, i.e., the net reaction describes the electrolysis of water. The ions of Na_2SO_4 conduct the current through the solution and take no part in the overall chemical reaction.

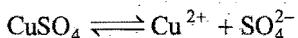
*When Hg is used as a cathode, Na^+ ions have lower discharge potential than H^+ ions.

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below:

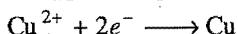
For cations: K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , H^+ , Cu^{2+} , Hg^{2+} , Ag^+

For anions: SO_4^{2-} , NO_3^- , OH^- , Cl^- , Br^- , I^-

(iv) Electrolysis of copper sulphate solution using copper electrodes



At cathode, copper is deposited.

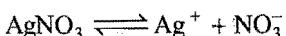


At anode, the copper of the electrode is oxidised to Cu^{2+} ions or SO_4^{2-} ions dissolve equivalent amount of copper of the anode.

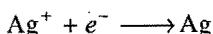


Thus, during electrolysis, copper is transferred from anode to cathode.

(v) Electrolysis of silver nitrate solution using silver electrodes



At cathode, silver is deposited.



At anode, the silver of the electrode is oxidised to Ag^+ ions which go into the solution or NO_3^- ions dissolve equivalent amount of silver of the electrode.

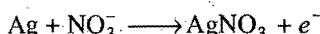
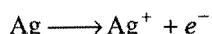


Table 12.1 Some More Examples of Electrolysis

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified $CuCl_2$ solution	Pt	$Cu^{2+} + 2e^- \longrightarrow Cu$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Molten $PbBr_2$	Pt	$Pb^{2+} + 2e^- \longrightarrow Pb$	$2Br^- \longrightarrow Br_2 + 2e^-$
Sodium chloride solution	Hg	$2Na^+ + 2e^- \longrightarrow 2Na$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Silver nitrate solution	Pt	$Ag^+ + e^- \longrightarrow Ag$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
Sodium nitrate solution	Pt	$2H^+ + 2e^- \longrightarrow H_2$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

12.3 FARADAY'S LAWS OF ELECTROLYSIS

The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented by Faraday in 1834, in the form of laws of electrolysis.

(i) Faraday's first law

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$

$$= I \times t$$

So,

$$W \propto I \times t$$

or

$$W = Z \times I \times t$$

where, Z is a constant, known as **electrochemical equivalent**, and is characteristic of the substance deposited.

When a current of one ampere is passed for one second, i.e., one coulomb ($Q = 1$), then

$$W = Z$$

Thus, **electrochemical equivalent** can be defined as the **mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second**. For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. This is the value of electrochemical equivalent of silver.

(ii) Faraday's second law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

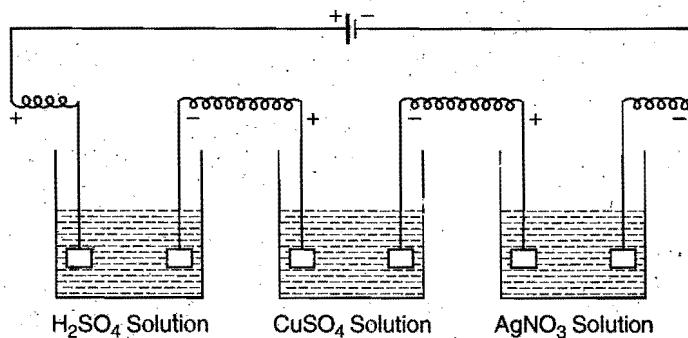


Fig. 12.1 Voltameters arranged in series

The law can be illustrated by passing same quantity of electric current through three voltameters containing solutions of H_2SO_4 , CuSO_4 and AgNO_3 respectively as shown in Fig. 12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

$$\begin{aligned} \frac{\text{Mass of hydrogen}}{\text{Mass of copper}} &= \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}} \\ \text{or } \frac{\text{Mass of copper}}{\text{Mass of silver}} &= \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}} \\ \text{or } \frac{\text{Mass of silver}}{\text{Mass of hydrogen}} &= \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of hydrogen}} \end{aligned}$$

It is observed that by passing one coulomb of electric charge,

$$\text{Hydrogen evolved} = 0.00001036 \text{ g},$$

$$\text{Copper deposited} = 0.0003292 \text{ g},$$

$$\text{and } \text{Silver deposited} = 0.001118 \text{ g}$$

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

$$\text{For hydrogen} = \frac{1}{0.00001036} \approx 96500 \text{ coulomb}$$

$$\text{For copper} = \frac{31.78}{0.0003292} \approx 96500 \text{ coulomb}$$

$$\text{For silver} = \frac{107.88}{0.001118} \approx 96500 \text{ coulomb}$$

This follows that 96500 coulomb of electric charge will deposit one g-equivalent of any substance. 96500 coulomb is termed as one **Faraday** and is denoted by F .

Again according to first law,

$$W = Z \times Q$$

When, $Q = 96500$ coulomb, W becomes gram equivalent mass (E).

Thus,

$$E = Z \times 96500$$

or

$$Z = \frac{E}{96500}$$

$$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

***Coulomb:** It is the unit of electric charge. It is the amount of charge that moves past any given point in a circuit when a current of 1 ampere is supplied for one second.

$$1 \text{ coulomb} = 1 \text{ ampere-second}$$

It is also defined as the amount of charge which is required to deposit by electrolysis 0.001118 g of silver from a solution of silver nitrate.

An electron has 1.6×10^{-19} coulomb of negative charge. Hence, one coulomb of charge is carried by 6.24×10^{18} electrons. 1 mole of electrons carry a charge of 96500 coulomb. This quantity of charge is called **Faraday**.

Charge carried by 1 mole of electrons

$$= (6.023 \times 10^{23}) (1.6 \times 10^{-19})$$

$$= 96368 \text{ coulomb}$$

$$\approx 96500 \text{ coulomb}$$

Fundamental unit of charge: As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is ' n ', then one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.02×10^{23} ions. Then,

$$\text{The charge carried by an ion} = \frac{nF}{6.02 \times 10^{23}} \text{ coulomb}$$

$$\text{For } n = 1,$$

$$\text{The fundamental unit of charge} = \frac{F}{6.02 \times 10^{23}}$$

$$\text{i.e., } \frac{96500}{6.02 \times 10^{23}} \approx 1.6 \times 10^{-19} \text{ coulomb}$$

$$\text{or } 1 \text{ coulomb} * = 6.24 \times 10^{18} \text{ electrons}$$

The rate of flowing of electric charge through a conductor is called the electric current.

$$\text{Electric current} = \frac{\text{Electric charge}}{\text{Time}}$$

$$1 \text{ ampere} = \frac{1 \text{ coulomb}}{1 \text{ second}}$$

Volt is a unit of electrical potential difference. It is defined as potential energy per unit charge.

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}} = \frac{1 \text{ newton} \times 1 \text{ metre}}{1 \text{ ampere} \times 1 \text{ second}}$$

Electrical energy = Potential difference \times Quantity of charge

$$\begin{aligned} &= V \times Q \\ &= V \times I \times t \quad (I = \text{ampere}; t = \text{second}) \\ &= \text{watt-second} \end{aligned}$$

Faraday's Law for Gaseous Electrolytic Product

We know that,

$$W = ZQ$$

$$= ZIt$$

$$W = \frac{ItE}{96500} \quad \dots (i)$$

where,

$$Z = E / 96500$$

Equation (i) is used to calculate the mass of solid substance dissolved or deposited at an electrode.

For the gases, we use

$$V = \frac{ItV_e}{96500} \quad \dots (ii)$$

where, V = Volume of gas evolved at STP at an electrode

V_e = Equivalent volume

= Volume of gas evolved at an electrode at STP by 1 faraday charge

Illustration

O_2 : $M = 32$, $E = 8$

$$\begin{aligned} 32 \text{ g } O_2 &\equiv 22.4 \text{ L at STP} & [M = \text{Molecular mass}] \\ 8 \text{ g } O_2 &\equiv 5.6 \text{ L at STP} & [E = \text{Equivalent mass}] \end{aligned}$$

Thus, V_e of $O_2 = 5.6 \text{ L}$

H_2 : $M = 2$, $E = 1$

$$\begin{aligned} 2 \text{ g } H_2 &\equiv 22.4 \text{ L at STP} \\ 1 \text{ g } H_2 &\equiv 11.2 \text{ L at STP} \end{aligned}$$

Thus, V_e of $H_2 = 11.2 \text{ L}$

Cl_2 : $M = 71$, $E = 35.5$

$$71 \text{ g } Cl_2 \equiv 22.4 \text{ L at STP}$$

$$35.5 \text{ g } Cl_2 \equiv 11.2 \text{ L at STP}$$

Thus, V_e of $Cl_2 = 11.2 \text{ L}$

12.4 APPLICATIONS OF ELECTROLYSIS

The phenomenon of electrolysis has wide applications. The important ones are:

(1) Determination of equivalent masses of elements: According to second law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$\frac{W_A}{W_B} = \frac{\text{Equivalent mass of } A}{\text{Equivalent mass of } B}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated from the above relationship. The equivalent masses of those non-metals which are evolved at anodes can also be determined by this method.

(2) Electrometallurgy: The metals like sodium, potassium, magnesium, calcium, aluminium, etc., are obtained by electrolysis of fused electrolytes.

Fused electrolyte

$NaCl + CaCl_2 + KF$

$CaCl_2 + CaF_2$

$Al_2O_3 + cryolite$

$MgCl_2 (35\%) + NaCl (50\%) + CaCl_2 (15\%)$

$NaOH$

$KCl + CaCl_2$

Metal isolated

Na

Ca

Al

Mg

Na

K

(3) Manufacture of non-metals: Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(4) Electro-refining of metals: The metals like copper, silver, gold, aluminium, tin, etc., are refined by electrolysis.

(5) Manufacture of compounds: Compounds like $NaOH$, KOH , Na_2CO_3 , $KClO_3$, white lead, $KMnO_4$, etc., are manufactured by electrolysis.

(6) Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating.

The aims of electroplating are:

- (i) To prevent the inferior metal from corrosion.
- (ii) To make it more attractive in appearance.

The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode-article in the form of a thin film. The following are the requirements for fine coating:

- (i) The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.
- (ii) The surface of the article should be rough so that the metal deposited sticks permanently.
- (iii) The concentration of the electrolyte should be so adjusted as to get smooth coating.
- (iv) Current density must be the same throughout.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4 + \text{dilute } H_2SO_4$
With silver	Ag	Object	$KAg(CN)_2$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$KAu(CN)_2$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Thickness of Coated Layer

Let the dimensions of metal sheet to be coated be ($a \text{ cm} \times b \text{ cm}$).

Thickness of coated layer = $c \text{ cm}$

Volume of coated layer = $(a \times b \times c) \text{ cm}^3$

$$\begin{aligned} \text{Mass of the deposited substance} &= \text{volume} \times \text{density} \\ &= (a \times b \times c) \times d \text{ g} \end{aligned}$$

$$\therefore (a \times b \times c) \times d = \frac{I \times t \times E}{96500}$$

Using above relation we may calculate the thickness of coated layer.

Note: Sometimes radius of atom of deposited metal is given instead of density, e.g.,

$$\text{Radius of silver atom} = 10^{-8} \text{ cm}$$

$$\text{Atomic mass of Ag} = 108$$

$$\text{Mass of single silver atom} = \frac{108}{6.023 \times 10^{23}} \text{ g}$$

$$\text{Volume of single atom} = \frac{4}{3} \times \pi R^3$$

$$= \frac{4}{3} \times 3.14 \times (10^{-8})^3 \text{ cm}^3$$

$$\text{Density of Ag} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}}$$

$$= \frac{108 / 6.023 \times 10^{23}}{\frac{4}{3} \times 3.14 \times (10^{-8})^3} = 42.82 \text{ g/cm}^3$$

Current Efficiency

Sometimes the ammeter shows false current due to mechanical fault. In this case,

$$\% \text{ current efficiency} = \frac{\text{Actual current}}{\text{Ammeter current}} \times 100$$

[Note : The conditions for the operating electrolytic cell are:
 $\Delta G > 0$ and $E < 0$]

SOME SOLVED EXAMPLES

Example 1. Find the charge in coulomb on 1 g-ion of N^{3-} .

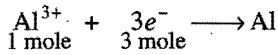
$$\text{Solution: Charge on one ion of } N^{3-} \\ = 3 \times 1.6 \times 10^{-19} \text{ coulomb}$$

$$\text{one g-ion} = 6.02 \times 10^{23} \text{ ions}$$

$$\text{Thus, charge on one g-ion of } N^{3-} \\ = 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \\ = 2.89 \times 10^5 \text{ coulomb}$$

Example 2. How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b) 1 mole of MnO_4^- to Mn^{2+} ?

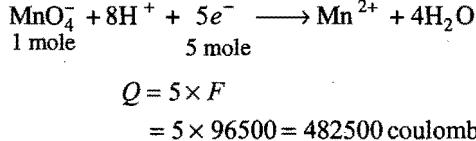
Solution: (a) The reduction reaction is:



Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+} .

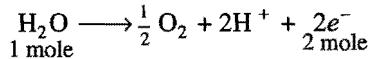
$$Q = 3 \times F \\ = 3 \times 96500 = 289500 \text{ coulomb}$$

(b) The reduction reaction is:



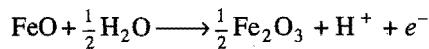
Example 3. How much electric charge is required to oxidise (a) 1 mole of H_2O to O_2 and (b) 1 mole of FeO to Fe_2O_3 ?

Solution: (a) The oxidation reaction is:



$$Q = 2 \times F \\ = 2 \times 96500 = 193000 \text{ coulomb}$$

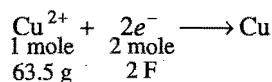
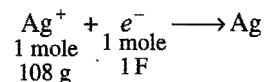
(b) The oxidation reaction is:



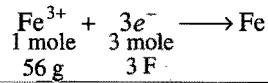
$$Q = F = 96500 \text{ coulomb}$$

Example 4. Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing $AgNO_3$, second $CuSO_4$ and third $FeCl_3$ solution. How many grams of each metal will be deposited assuming only cathodic reaction in each cell?

Solution: The cathodic reactions in the cells are respectively,



and



$$\text{Hence, } Ag \text{ deposited} = 108 \times 0.4 = 43.2 \text{ g}$$

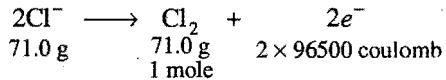
$$Cu \text{ deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

and

$$Fe \text{ deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$$

Example 5. An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

Solution: The reaction taking place at anode is:



$$71.0 \text{ g} \quad 71.0 \text{ g} \quad 2 \times 96500 \text{ coulomb}$$

$$Q = I \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60$ coulomb of electric charge

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

$$\text{Volume of } Cl_2 \text{ liberated at NTP} = 9.3264 \times 22.4 = 208.91 \text{ L}$$

Example 6. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours?

Solution: We know that,

$$\text{Watt} = \text{ampere} \times \text{volt}$$

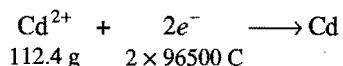
$$100 = \text{ampere} \times 110$$

$$\text{Ampere} = \frac{100}{110}$$

$$\text{Quantity of charge} = \text{ampere} \times \text{second}$$

$$= \frac{100}{110} \times 10 \times 60 \times 60 \text{ coulomb}$$

The cathodic reaction is:



$$112.4 \text{ g} \quad 2 \times 96500 \text{ C}$$

Mass of cadmium deposited by passing $\frac{100}{110} \times 10 \times 60 \times 60$ coulomb charge

$$= \frac{112.4}{2 \times 96500} \times \frac{100}{110} \times 10 \times 60 \times 60 = 19.0598 \text{ g}$$

Example 7. In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold salt and the second cell contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere.

Solution: We know that,

$$\frac{\text{Mass of Au deposited}}{\text{Eq. mass of Au}} = \frac{\text{Eq. mass of Cu}}{\text{Mass of Cu deposited}}$$

$$\text{Eq. mass of Au} = \frac{197}{3}; \text{Eq. mass of Cu} = \frac{63.5}{2}$$

Mass of copper deposited

$$= 9.85 \times \frac{63.5}{2} \times \frac{3}{197} \text{ g} = 4.7625 \text{ g}$$

Let Z be the electrochemical equivalent of Cu.

$$E = Z \times 96500$$

$$\text{or } Z = \frac{E}{96500} = \frac{63.5}{2 \times 96500}$$

$$\text{Applying } W = Z \times I \times t$$

$$t = 5 \text{ hour} = 5 \times 3600 \text{ second}$$

$$4.7625 = \frac{63.5}{2 \times 96500} \times I \times 5 \times 3600$$

$$\text{or } I = \frac{4.7625 \times 2 \times 96500}{63.5 \times 5 \times 3600} = 0.804 \text{ ampere}$$

Example 8. How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm^2 with 0.005 mm thick layer? Density of silver is 10.5 g/cm^3 .

Solution: Mass of silver to be deposited

$$= \text{volume} \times \text{density}$$

$$= \text{Area} \times \text{thickness} \times \text{density}$$

$$\text{Given: Area} = 80 \text{ cm}^2, \text{ thickness} = 0.0005 \text{ cm and density} = 10.5 \text{ g/cm}^3$$

$$\text{Mass of silver to be deposited} = 80 \times 0.0005 \times 10.5$$

$$= 0.42 \text{ g}$$

$$\text{Applying to silver } E = Z \times 96500$$

$$Z = \frac{108}{96500} \text{ g}$$

Let the current be passed for t seconds.

We know that, $W = Z \times I \times t$

So,

$$0.42 = \frac{108}{96500} \times 3 \times t$$

or

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ second}$$

Example 9. What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?

Solution: Applying $E = Z \times 96500$ (E for chlorine = 35.5),

$$35.5 = Z \times 96500$$

$$\text{or } Z = \frac{35.5}{96500} \text{ g}$$

Now, applying the formula

$$W = Z \times I \times t$$

$$\text{where, } W = 10 \text{ g}, Z = \frac{35.5}{96500}, t = 60 \times 60 = 3600 \text{ second}$$

$$I = \frac{10 \times 96500}{35.5 \times 3600} = 7.55 \text{ ampere}$$

Example 10. 0.2964 g of copper was deposited on passage of a current of 0.5 ampere for 30 minutes through a solution of copper sulphate. Calculate the atomic mass of copper. (1 faraday = 96500 coulomb)

Solution: Quantity of charge passed

$$= 0.5 \times 30 \times 60 = 900 \text{ coulomb}$$

$$900 \text{ coulomb deposit copper} = 0.2964 \text{ g}$$

$$96500 \text{ coulomb deposit copper} = \frac{0.2964}{900} \times 96500 = 31.78 \text{ g}$$

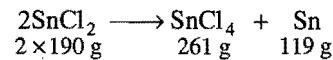
Thus, 31.78 is the equivalent mass of copper.

$$\text{At. mass} = \text{Eq. mass} \times \text{Valency}$$

$$= 31.78 \times 2 = 63.56$$

Example 11. 19 g of molten SnCl_2 is electrolysed for some time using inert electrodes until 0.119 g of Sn is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of the masses of $\text{SnCl}_2 : \text{SnCl}_4$ after electrolysis.

Solution: The chemical reaction occurring during electrolysis is:



119 g of Sn is deposited by the decomposition of 380 g of SnCl_2 .

So, 0.119 g of Sn is deposited by the decomposition of

$$\frac{380}{119} \times 0.119 = 0.380 \text{ g of SnCl}_2$$

$$\text{Remaining amount of SnCl}_2 = (19 - 0.380) = 18.62 \text{ g}$$

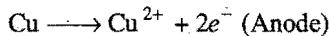
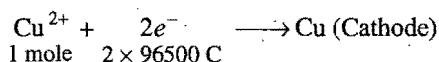
$$380 \text{ g of SnCl}_2 \text{ produce} = 261 \text{ g of SnCl}_4$$

So, 0.380 g of SnCl_2 produce $= \frac{261}{380} \times 0.380 = 0.261$ g of SnCl_4

Thus, the ratio $\text{SnCl}_2 : \text{SnCl}_4 = \frac{18.62}{0.261}$, i.e., 71.34 : 1

Example 12. A current of 2.68 ampere is passed for one hour through an aqueous solution of copper sulphate using copper electrodes. Calculate the change in mass of cathode and that of the anode. (At. mass of copper = 63.5)

Solution: The electrode reactions are:



Thus, cathode increases in mass as copper is deposited on it and the anode decreases in mass as copper from it dissolves.

Charge passed through cell = $2.68 \times 60 \times 60$ coulomb

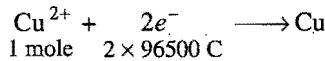
$$\begin{aligned} \text{Copper deposited or dissolved} &= \frac{63.5}{2 \times 96500} \times 2.68 \times 60 \times 60 \\ &= 3.174 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Increase in mass of cathode} &= \text{Decrease in mass of anode} \\ &= 3.174 \text{ g} \end{aligned}$$

Example 13. An ammeter and a copper voltameter are connected in series through which a constant current flows. The ammeter shows 0.52 ampere. If 0.635 g of copper is deposited in one hour, what is the percentage error of the ammeter?

(At. mass of copper = 63.5)

Solution: The electrode reaction is:



$$\begin{aligned} 63.5 \text{ g of copper deposited by passing charge} \\ &= 2 \times 96500 \text{ coulomb} \end{aligned}$$

$$\begin{aligned} 0.635 \text{ g of copper deposited by passing charge} \\ &= \frac{2 \times 96500}{63.5} \times 0.635 \text{ coulomb} \\ &= 2 \times 965 \text{ coulomb} \\ &= 1930 \text{ coulomb} \end{aligned}$$

We know that,

$$Q = I \times t$$

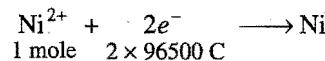
$$1930 = I \times 60 \times 60$$

$$I = \frac{1930}{3600} = 0.536 \text{ ampere}$$

$$\therefore \text{Percentage error} = \frac{(0.536 - 0.52)}{0.536} \times 100 = 2.985$$

Example 14. A current of 3.7 ampere is passed for 6 hours between platinum electrodes in 0.5 litre of a 2 M solution of $\text{Ni}(\text{NO}_3)_2$. What will be the molarity of the solution at the end of electrolysis? What will be the molarity of the solution if nickel electrodes are used? ($1F = 96500$ coulomb; $\text{Ni} = 58.7$)

Solution: The electrode reaction is:



Quantity of electric charge passed

$$= 3.7 \times 6 \times 60 \times 60 \text{ coulomb} = 79920 \text{ coulomb}$$

$$\begin{aligned} \text{Number of moles of } \text{Ni}(\text{NO}_3)_2 \text{ decomposed or nickel deposited} \\ &= \frac{1}{2 \times 96500} \times 79920 = 0.4140 \end{aligned}$$

$$\begin{aligned} \text{Number of moles of } \text{Ni}(\text{NO}_3)_2 \text{ present before electrolysis} \\ &= 0.5 \times 2 = 1.0 \end{aligned}$$

$$\begin{aligned} \text{Number of moles of } \text{Ni}(\text{NO}_3)_2 \text{ present after electrolysis} \\ &= (1.0 - 0.4140) = 0.586 \end{aligned}$$

Since, 0.586 moles are present in 0.5 litre,

$$\text{Molarity of the solution} = 2 \times 0.586 = 1.72 \text{ M}$$

When nickel electrodes are used, anodic nickel will dissolve and get deposited at the cathode. The molarity of the solution will, thus, remain unaffected.

Example 15. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with volume of solution kept at 100 mL and the current at 1.2 amp. Calculate the gases evolved at NTP during the entire electrolysis.

Solution: 0.4 g of $\text{Cu}^{2+} = \frac{0.4}{31.75} = 0.0126$ g-equivalent

At the same time, the oxygen deposited at anode

$$= 0.0126 \text{ g-equivalent}$$

$$= \frac{8}{32} \times 0.0126 = 0.00315 \text{ g-mole}$$

After the complete deposition of copper, the electrolysis will discharge hydrogen at cathode and oxygen at anode.

The amount of charge passed = $1.2 \times 7 \times 60 = 504$ coulomb

$$\begin{aligned} \text{So, Oxygen liberated} &= \frac{1}{96500} \times 504 = 0.00523 \text{ g-equivalent} \\ &= \frac{8}{32} \times 0.00523 = 0.001307 \text{ g-mole} \end{aligned}$$

Hydrogen liberated = 0.00523 g-equivalent

$$= \frac{1}{2} \times 0.00523 = 0.00261 \text{ g-mole}$$

$$\begin{aligned} \text{Total gases evolved} &= (0.00315 + 0.001307 + 0.00261) \text{ g-mole} \\ &= 0.007067 \text{ g-mole} \end{aligned}$$

Volume of gases evolved at NTP

$$= 22400 \times 0.007067 \text{ mL}$$

$$= 158.3 \text{ mL}$$

Example 16. A current of 1.70 ampere is passed through 300 mL of 0.160 M solution of zinc sulphate for 230 seconds with a current efficiency of 90 per cent. Find out the molarity of Zn^{2+} ions after the deposition of zinc. Assume the volume of the solution to remain constant during electrolysis. (IIT 1991)

Solution: Amount of charge passed = 1.70×230 coulomb

$$\text{Amount of actual charge passed} = \frac{90}{100} \times 1.70 \times 230 \\ = 351.9 \text{ coulomb}$$

No. of moles of Zn deposited by passing 351.9 coulomb of charge

$$= \frac{1}{2 \times 96500} \times 351.9 = 0.000182$$

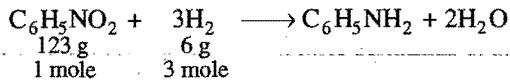
Molarity of Zn^{2+} ions after deposition of zinc

$$= \left[0.160 - \frac{0.000182 \times 1000}{300} \right] M \\ = 0.154 M$$

Example 17. Calculate the electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volt, how much energy will be consumed?

[AIPMT (Mains) 2008]

Solution: The reduction reaction is:



Hydrogen required for reduction of $\frac{12.3}{123}$ or 0.1 mole of nitrobenzene $= 0.1 \times 3 = 0.3$ mole

Amount of charge required for liberation of 0.3 mole of hydrogen $= 2 \times 96500 \times 0.3 = 57900$ coulomb

Actual amount of charge required as efficiency is 50%

$$= 2 \times 57900 = 115800 \text{ coulomb}$$

$$\text{Energy consumed} = 115800 \times 3.0 = 347400 \text{ J} \\ = 347.4 \text{ kJ}$$

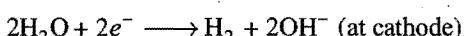
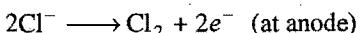
Example 18. An aqueous solution of sodium chloride on electrolysis gives $\text{H}_2(\text{g})$, $\text{Cl}_2(\text{g})$ and NaOH according to the reaction:



A direct current of 25 ampere with a current efficiency 62% is passed through 20 L of NaCl solution (20% by mass). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1 kg of Cl_2 ? What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.

(IIT 1992)

Solution: Reactions at anode and cathode are:



$$1 \text{ kg of Cl}_2 = \frac{1000}{71.0} = 14.08 \text{ mole}$$

Charge to produce one mole of $\text{Cl}_2 = 2 \times 96500$ coulomb

Charge to produce 14.08 mole of $\text{Cl}_2 = 2 \times 96500 \times 14.08$ coulomb

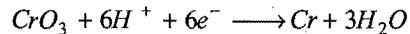
$$\text{Effective current} = \frac{62}{100} \times 25.0 = 15.5 \text{ ampere}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{2 \times 96500 \times 14.08}{15.5} \\ = 175318.7 \text{ second} = 48.699 \text{ hour}$$

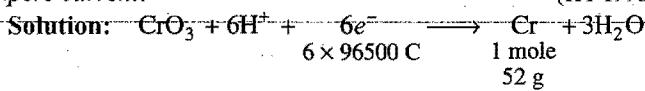
$$\text{OH}^- \text{ ions produced} = 2 \times \text{moles of Cl}_2 \\ = 2 \times 14.08 = 28.16 \text{ mole}$$

$$\text{Molarity} = \frac{\text{Mole}}{\text{Volume}} = \frac{28.16}{20} = 1.408 \text{ M}$$

Example 19. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following reaction:



Calculate the mass of chromium plated out by 24000 coulomb. How long will it take to plate out 1.5 g of chromium using 12.5 ampere current?



Mass of chromium plated out by 24000 coulomb charge

$$= \frac{52}{6 \times 96500} \times 24000 = 2.155 \text{ g}$$

Charge required for plating out 1.5 g of chromium

$$= \frac{6 \times 96500}{52} \times 1.5 = 16701.92 \text{ coulomb}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{16701.92}{12.5} = 1336.15 \text{ second} \\ = 22.27 \text{ minute}$$

Example 20. After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time, 600 mL of the solution was left which was found to be 1 N in NaOH . During the same period 31.75 g of copper was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage theoretical yield of NaOH obtained.

Solution: Equivalent mass of $\text{NaOH} = 40$

$$\text{Amount of NaOH formed} = \frac{40}{1000} \times 600 = 24 \text{ g}$$

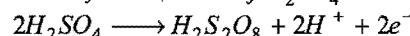
31.75 g of Cu = 1 g-equivalent of Cu.

During the same period, 1 g-equivalent of NaOH should have been formed.

1 g-equivalent of $\text{NaOH} = 40 \text{ g}$

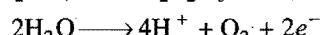
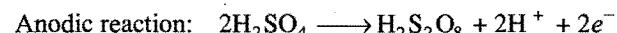
$$\% \text{ yield} = \frac{24}{40} \times 100 = 60$$

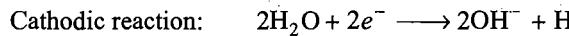
Example 21. Peroxy disulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) can be prepared by electrolytic oxidation of H_2SO_4 as:



Oxygen and hydrogen are by products. In such an electrolysis 9.72 litre of H_2 and 2.35 litre of O_2 were generated at NTP. What is the mass of peroxy disulphuric acid formed?

Solution:





Total equivalent of $\text{H}_2\text{S}_2\text{O}_8$ + equivalent of oxygen
= Equivalent of H_2

$$9.72 \text{ litre H}_2 = \frac{9.72}{11.2} = 0.868 \text{ equivalent}$$

$$2.35 \text{ litre O}_2 = \frac{2.35}{5.6} = 0.42 \text{ equivalent}$$

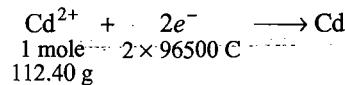
$$\text{Equivalent of } \text{H}_2\text{S}_2\text{O}_8 = (0.868 - 0.420) \\ = 0.448$$

$$\text{Mass of } \text{H}_2\text{S}_2\text{O}_8 = 0.448 \times \frac{194}{2} = 43.456 \text{ g}$$

Example 22. Cadmium amalgam is prepared by electrolysis of a solution of CdCl_2 using a mercury cathode. Find how long a current of 5 ampere should be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2 g mercury. At mass of Cd = 112.40.

Solution: 2 g Hg require Cd to prepare 12% amalgam

$$= \frac{12}{88} \times 2 = 0.273 \text{ g}$$



Charge required to deposit 0.273 g of Cd

$$= \frac{2 \times 96500}{112.40} \times 0.273 \text{ coulomb}$$

Charge = ampere \times second

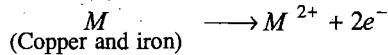
$$\text{Second} = \frac{2 \times 96500 \times 0.273}{112.40 \times 5} = 93.75$$

Example 23. Assume that impure copper contains iron, gold and silver as impurities. After passing a current of 140 ampere for 482.5 second, the mass of anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Estimate the percentage of iron and copper originally present.

Solution: The increase at the cathode is due to copper only. Hence, there is 22.011 g of copper and rest impurities of iron, gold and silver.

$$\text{Mass of impurities} = (22.260 - 22.011) = 0.249 \text{ g}$$

At anode, only copper and iron are oxidised; the gold and silver collect below anode in the form of anodic mud.



$$\text{No. of moles of metal oxidised} = \frac{140 \times 482.5}{2 \times 96500} = 0.35$$

$$\text{No. of moles of copper} = \frac{22.011}{63.5} = 0.3466$$

$$\text{No. of moles of iron} = (0.35 - 0.3466) = 0.0034$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Amount of energy used in the passage of 1 amp current for 100 sec under a potential of 115 V is:

(a) 20 kJ (b) 11.5 kJ (c) 115 kJ (d) 0.115 kJ

[Ans. (b)]

[Hint: $Q = I \times t = 1 \times 100 = 100 \text{ C}$

Energy = charge \times potential

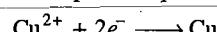
$$= 100 \times 115 = 11500 \text{ J} = 11.5 \text{ kJ}$$

2. One litre of 1 M CuSO_4 solution is electrolysed. After passing $2F$ charge, the molarity of CuSO_4 will be:

(a) $M/2$ (b) $M/4$ (c) M (d) zero

[Ans. (d)]

[Hint: $2F$ charge will deposit 2 equivalent or 1 mole of copper



Thus, all the copper from CuSO_4 solution will be deposited and molarity of remaining CuSO_4 solution will be zero.]

3. The time required to coat a metal surface of 80 cm^2 with $5 \times 10^{-3} \text{ cm}$ thick layer of silver (density 1.05 g/cm^3) by passing a current of 3 amp through silver nitrate solution is:

(a) 115 sec (b) 125 sec (c) 135 sec (d) 145 sec

[Ans. (b)]

[Hint:

Mass of silver in coated layer = volume \times density

$$= (80 \times 5 \times 10^{-3}) \times 1.05 \text{ g}$$

$$= 0.42 \text{ g}$$

$$W = \frac{ItE}{96500}$$

$$\therefore t = \frac{W \times 96500}{I \times E} = \frac{0.42 \times 96500}{3 \times 108} = 125.09 \text{ sec}$$

4. 4.5 g of aluminium (At. mass = 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be:

[CBSE (PMT) 2005]

(a) 44.8 L (b) 22.4 L (c) 11.2 L (d) 5.6 L

[Ans. (d)]

[Hint: Number of equivalents of aluminium deposited

$$= \frac{4.5}{9} = 0.5$$

Number of equivalents of H_2 will also be 0.5.

Volume of H_2 gas at STP = Number of equivalents

\times Equivalent volume

$$= 0.5 \times 11.2 = 5.6 \text{ L}$$

5. Cost of electricity for the production of $x \text{ L H}_2$ at NTP at cathode is Rs x ; then cost of production of $x \text{ L O}_2$ at NTP at anode will be : (assume 1 mole of electrons as one unit of electricity)

(a) $2x$ (b) $4x$ (c) $16x$ (d) $32x$

[Ans. (a)]

[Hint: $\frac{\text{Volume of H}_2}{\text{Volume of O}_2} = \frac{\text{Equivalent volume of H}_2}{\text{Equivalent volume of O}_2}$

$$\frac{x}{\text{Volume of O}_2} = \frac{11.2}{5.6} = 2$$

$$\text{Volume of O}_2 = \frac{x}{2}$$

Thus, $\frac{x}{2}$ L O₂ requires Rs x for its production,

i.e., x L O₂ will require Rs 2x for the production.]

6. What current is to be passed for 0.25 sec for deposition of certain weight of metal which is equal to its electrochemical equivalent? [AMU (Medical) 2006]

(a) 4 A (b) 100 A (c) 200 A (d) 2 A

Ans. (a)]

Hint: $W = ZIt$

$$\frac{W}{Z} = It$$

$$1 = It = I \times 0.25$$

$$I = 4 \text{ amp.}]$$

7. If the aqueous solutions of the following salts are electrolysed for 1 hour with 10 ampere current, which solution will deposit the maximum mass of the metal at cathode? The atomic weights are: Fe = 56, Zn = 65, Ag = 108, Hf = 178 and W = 184. [PMT (Kerala) 2006]

(a) ZnSO₄ (b) FeCl₃ (c) HfCl₄ (d) WCl₆

(e) AgNO₃

Ans. (e)]

Hint: Greater is the equivalent mass of the metal more will be the amount deposited at cathode.

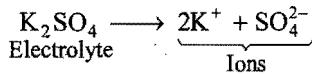
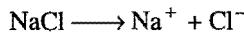
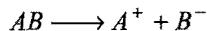
Compound	Equivalent mass of metals
ZnSO ₄	65/2 = 32.5
FeCl ₃	56/3 = 18.66
HfCl ₄	178/4 = 44.5
WCl ₆	184/6 = 30.66
AgNO ₃	108/1 = 108

∴ Maximum amount of silver will be deposited at cathode.]

12.5 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as theory of electrolytic dissociation or ionic theory. The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.



8. When a quantity of electricity is passed through CuSO₄ solution, 0.16 g of copper gets deposited. If the same quantity of electricity is passed through acidulated water, then the volume of H₂ liberated at STP will be: (given atomic weight of Cu = 64) [KCET 2006]

(a) 4 cm³ (b) 56 cm³ (c) 604 cm³ (d) 8 cm³

Ans. (b)]

Hint: Number of equivalents of copper deposited = $\frac{0.16}{32} = 0.005$

Volume of H₂ gas at STP = $11.2 \times 0.005 = 0.056 \text{ litre} = 56 \text{ cm}^3$]

9. Number of faraday's required to generate one gram atom of magnesium from molten MgCl₂ is: [PMT (MP) 2007]

(a) 1 (b) 2 (c) 3 (d) 4

Ans. (b)]

Hint: Mg²⁺ + 2e⁻ → Mg

1 mole of Mg atom requires 2 mole of electrons, i.e., 2 faraday of charge.]

10. A direct current deposits 54 g of silver (Atomic mass = 108) during electrolysis. How much aluminium (Atomic mass = 27) would be deposited from aluminium chloride solution by the same amount of electricity? [PMT (Kerala) 2008]

(a) 4.5 g (b) 5.4 g (c) 54 g (d) 2.7 g

(e) 27 g

Ans. (a)]

Hint: Equivalent mass of silver = 108

Equivalent mass of aluminium in (AlCl₃) = $\frac{27}{3} = 9$

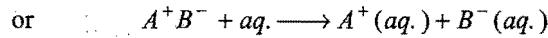
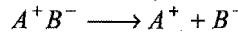
$$\frac{W_{\text{Ag}}}{W_{\text{Al}}} = \frac{E_{\text{Ag}}}{E_{\text{Al}}}$$

$$\frac{54}{W_{\text{Al}}} = \frac{108}{9}$$

$$W_{\text{Al}} = 4.5 \text{ g}$$

SECTION II : CONDUCTANCE AND CONDUCTORS

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.



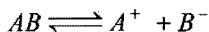
(ii) The process of splitting of the molecules into ions of an electrolyte is called **ionisation**. The fraction of the total number of molecules present in solution as ions is known as **degree of ionisation** or **degree of dissociation**. It is denoted by 'α'

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

It has been observed that all electrolytes do not ionise to the same extent. Some are almost completely ionised while others are

feebly ionised. The degree of ionisation depends on a number of factors (see 12.6).

(iii) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionised and non-ionised molecules, *i.e.*,



Applying the law of mass action to above equilibrium

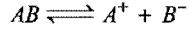
$$\frac{[A^+][B^-]}{[AB]} = K$$

K is known as ionisation constant. The electrolytes having high value of K are termed **strong electrolytes** and those having low value of K as **weak electrolytes**.

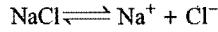
(iv) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, *i.e.*, electrolysis occurs.

The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

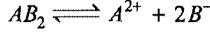
(v) The electrolytic solution is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.



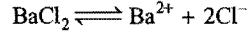
(Both ions are equal)



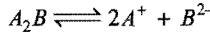
(Both ions are equal)



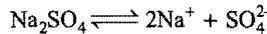
(Anions are double that of cations)



(Anions are double that of cations)



(Cations are double that of anions)



(Cations are double that of anions)

(vi) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.

(vii) The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure.

(viii) The conductivity of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.

Evidences in Favour of Ionic Theory

A large number of experimental observations are available which support Arrhenius theory. A few of them are given below:

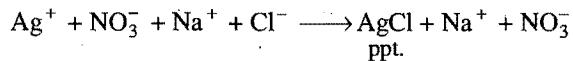
(i) **Ions present in solid electrolytes:** X-ray diffraction studies have shown that electrolytes are composed of ions. For example, a crystal of $NaCl$ does not contain $NaCl$ units but Na^+ and Cl^- ions. Each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion in turn is surrounded by six Na^+ ions. The whole system is composed of equal number of Na^+ and Cl^- ions. The ionic compounds behave as good conductors in fused state. It can only be possible if ions are already present in ionic solids.

(ii) **Ohm's law applicability:** The electrolytic solutions like metallic conductors obey Ohm's law, *i.e.*, the strength of the current flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of the conductor. Mathematically,

$$I = E / R$$

This can only be possible if ions are already present in the solution and no part of the current is used in splitting up the molecules into ions. The current has only directive effect on the ions.

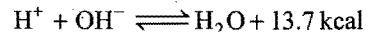
(iii) **Ionic reactions:** Evidence for the existence of ions in aqueous solutions of electrolytes is furnished by well known reactions in inorganic chemistry. A white precipitate of silver chloride is obtained whenever Ag^+ ions come in contact with chloride ions.



But no precipitation occurs when $AgNO_3$ solution is added to CCl_4 , $CHCl_3$ or C_2H_5Cl as these substances being non-electrolytes do not furnish Cl^- ions in solution.

An acid which gives all tests of H^+ ions in aqueous solution, does not give the same tests when dissolved in any organic solvent because no ionisation of the acid occurs in the organic solvent to furnish H^+ ions.

(iv) **Heat of neutralization:** When one gram-equivalent of a strong acid is neutralized by one gram-equivalent of a strong base, the heat evolved is always the same, *i.e.*, 13.7 kcal. This can be explained on the basis of Arrhenius theory that an acid furnished H^+ ions and base OH^- ions when dissolved in water and the process of neutralisation involves the common reaction.



Thus, heat of neutralisation is actually the heat of formation of H_2O from H^+ and OH^- ions.

(v) **Abnormal colligative properties:** The abnormal behaviour towards colligative properties as observed in the case of electrolytes can be explained on the basis of ionic theory. When an electrolyte is dissolved in water, the number of particles in the solution is always more than the number of molecules actually dissolved due to ionisation. The van't Hoff factor,

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

is always more than one, *i.e.*, $i = 1 + (n - 1)\alpha$ where, ' n ' is the number of ions produced by the ionisation of one molecule of the electrolyte and ' α ' is the degree of ionisation.

(vi) **Colour of solutions:** The colour of the electrolytes in solution, if any, is due to their ions. The $CaSO_4$ is blue in solution due to the presence of Ca^{2+} ions. Potassium permanganate ($KMnO_4$) is purple in solution due to the presence of MnO_4^- ions.

(vii) **Explanation of some other phenomena:** Ionic theory provides satisfactory explanations regarding various phenomena such as electrolysis, conductivity, salt hydrolysis, solubility product, etc.

Limitations of Arrhenius Theory

- (i) Ostwald's dilution law which is based on Arrhenius theory is not applicable to strong electrolytes.
- (ii) Strong electrolytes conduct electricity in fused state, i.e., in absence of water. This is in contradiction of Arrhenius theory according to which the presence of solvent is a must for ionisation.
- (iii) Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

12.6 FACTORS PERTAINING TO DEGREE OF IONISATION

The degree of ionisation of an electrolyte in solution depends upon the following factors:

(i) Nature of solute: When the ionisable parts of a molecule of a substance are held more by covalent bonding than by electrovalent bonding, less ions are furnished in solution. Such substances are termed weak electrolytes. H_2S , HCN , NH_4OH , CH_3COOH are examples of this class. NaCl , $\text{Ba}(\text{NO}_3)_2$, KOH , etc., are strong electrolytes, in which the transfer of electrons seems to be more or less complete, furnish ions immediately when dissolved. Strong electrolytes are almost completely ionised in solution.

(ii) Nature of solvent: The main function of the solvent is to weaken the electrostatic forces of attraction between the two ions and separate them. The force of attraction holding the ions together in any medium is expressed as:

$$F = \frac{1}{K} \frac{q_1 q_2}{r^2}$$

where, K is the dielectric constant of medium.

Any solvent which has high value of dielectric constant has the capacity of separating ions. Water is considered to be the best solvent as it has the highest dielectric constant. The dielectric constants of some of the solvents are given below at 25°C.

Water	Methyl alcohol	Ethyl alcohol	Acetone
81	35	27	21

(iii) Dilution: The extent of ionisation of an electrolyte is inversely proportional to the concentration of its solution. Thus, degree of ionisation increases with the increase of dilution of the solution, i.e., decreasing the concentration of the solution.

(iv) Temperature: The degree of ionisation increases with the increase of temperature. This is due to the fact that at higher temperature molecular speed is increased which overcomes the forces of attraction between the ions.

12.7 ELECTROLYTIC CONDUCTANCE

The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance, i.e.,

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{R} \quad \dots (\text{i})$$

It is expressed in the unit called reciprocal ohm (ohm^{-1} or mho) or siemens.

Specific Conductance or Conductivity

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a), i.e.,

$$R \propto \frac{l}{a} \text{ or } R = \rho \frac{l}{a} \quad \dots (\text{ii})$$

where, ρ is called the specific resistance.

If $l = 1 \text{ cm}$ and $a = 1 \text{ cm}^2$, then

$$R = \rho \quad \dots (\text{iii})$$

The specific resistance is, thus, defined as the resistance of one centimetre cube of a conductor.

The reciprocal of specific resistance is termed the **specific conductance** or it is the conductance of one centimetre cube of a conductor.

It is denoted by the symbol κ . Thus,

$$\kappa = \frac{1}{\rho}, \quad \kappa = \text{kappa} \quad \text{The specific conductance} \quad \dots (\text{iv})$$

Specific conductance is also called conductivity.

From eq. (ii), we have

$$\rho = \frac{a}{l} \cdot R \text{ or } \frac{1}{\rho} = \frac{l}{a} \cdot \frac{1}{R}$$

$$\kappa = \frac{l}{a} \times C \quad \left(\frac{l}{a} = \text{cell constant} \right)$$

or Specific conductance = conductance \times cell constant

In the case of electrolytic solutions, the specific conductance is defined as the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimetre apart as shown in Fig. 12.2.

The unit of specific conductance is $\text{ohm}^{-1} \text{ cm}^{-1}$.

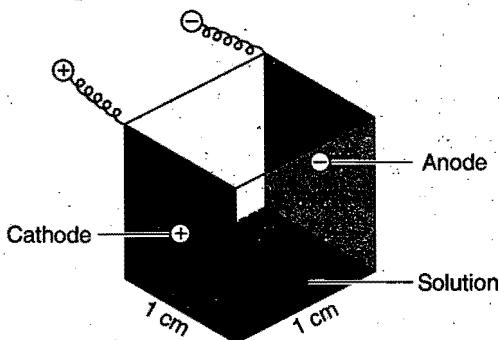


Fig. 12.2 Representation of specific conductance

Equivalent Conductance

One of the factors on which the conductance of an electrolytic solution depends, is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductances.

Equivalent conductance is defined as the conductance of all the ions produced by **one gram-equivalent** of an electrolyte in a given solution. It is denoted by Λ .

To understand the meaning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If 1 cm^3 (1 mL)

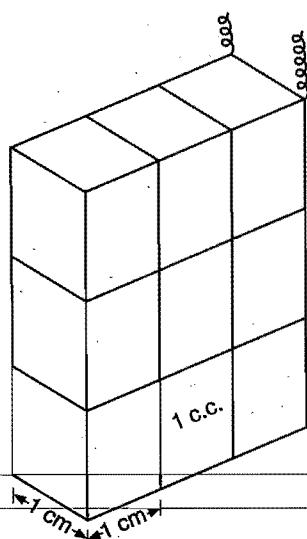


Fig. 12.3

solution containing 1 gram-equivalent of an electrolyte is placed in this container and conductance is measured.

According to definitions,

$$\begin{aligned}\text{Conductance} &= \text{Specific conductance } (\kappa) \\ &= \text{Equivalent conductance } (\Lambda)\end{aligned}$$

If the solution is diluted to say (9 cm³) (9 mL), the conductance of the solution will be the same but specific conductance becomes 1/9 th as it contains nine cubes. The conductance is also equal to the equivalent conductance because the solution still has 1 g-equivalent of the electrolyte. This is shown in Fig. 12.3. Thus,

$$\text{Equivalent conductance } (\Lambda) = 9 \times \kappa$$

In general,

$$\Lambda = \kappa \times V \quad \dots (v)$$

where, V is the volume in mL containing 1 g-equivalent of the electrolyte.

In case, if the concentration of the solution is c g-equivalent per litre, then the volume containing 1 g-equivalent of the electrolyte will be $1000/c$.

So, equivalent conductance,

$$\begin{aligned}\Lambda &= \kappa \times \frac{1000}{c} \quad \dots (vi) \\ \Lambda &= \kappa \times \frac{1000}{N}\end{aligned}$$

where, N = normality

The unit of equivalent conductance is ohm⁻¹ cm² eq⁻¹.

Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionisation of 1 g-mole of an electrolyte when present in V mL of solution. It is denoted by μ .

$$\text{Molar conductance } \mu = \kappa \times V \quad \dots (vii)$$

where, V is the volume in mL containing 1 g-mole of the electrolyte. If c is the concentration of the solution in g-mole per litre, then

$$\mu = \kappa \times \frac{1000}{c}$$

Its unit is ohm⁻¹ cm² mol⁻¹.

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}$$

where,

$$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Measurement of Conductance

It is now known to us that when the solution of an electrolyte is taken between two parallel electrodes of cross-sectional area 'a' and 'l' cm apart, then the specific conductance, κ , should be:

$$\kappa = \frac{l}{a} \cdot \frac{1}{R}$$

Thus, knowing the values of R, l and a , the specific conductance can be measured. The resistance of the solution between two parallel electrodes is determined by using Wheatstone bridge method. The diagram of the apparatus is shown in Fig. 12.4. AB is a uniform wire and X is a sliding contact which moves over it. C is the conductivity cell containing the solution of the electrolyte and S represents the source of alternating current. R is the resistance box and T is a headphone to detect the flow of current. A suitable resistance is taken out from the resistance box and the sliding contact X is moved on the wire to search a point of minimum sound in the headphone. At this point, the bridge is balanced.

$$\frac{\text{Resistance of solution}}{\text{Resistance from resistance box}} = \frac{\text{Resistance } XB}{\text{Resistance } XA} = \frac{\text{Length } XB}{\text{Length } XA}$$

Thus, resistance of solution can be determined. Reciprocal of this resistance gives the conductance of solution.

Direct current (DC) cannot be used because it produces two complications.

- (i) Change in the concentration of the solution occurs due to electrolysis which will change the resistance.
- (ii) Polarisation at the electrodes sets in which also changes the resistance.

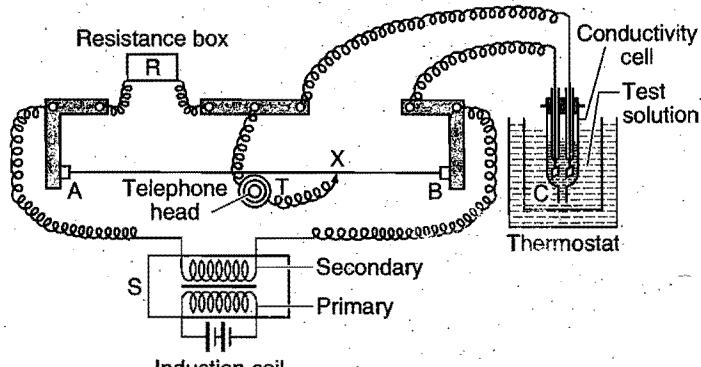


Fig. 12.4 Determination of conductivity

Thus, an alternating current (AC) is used to overcome the above complications.

The solution whose conductance is to be measured is taken in a special type of cell known as conductivity cell. Various types of cells are shown in Fig. 12.5. The electrodes consist of platinum discs coated with finely divided platinum black and welded to platinum wires fused in two glass tubes. The glass tubes contain

mercury and are firmly fixed in the cover of cells. Contact with the platinum is made by dipping the copper wires of the circuit in the mercury contained in the tubes. As the conductivity changes with temperature, the cell is usually placed in a constant temperature bath during the experiment. Cells with long paths are used for concentrated solutions and cells with short paths and large electrodes are used for dilute solutions.

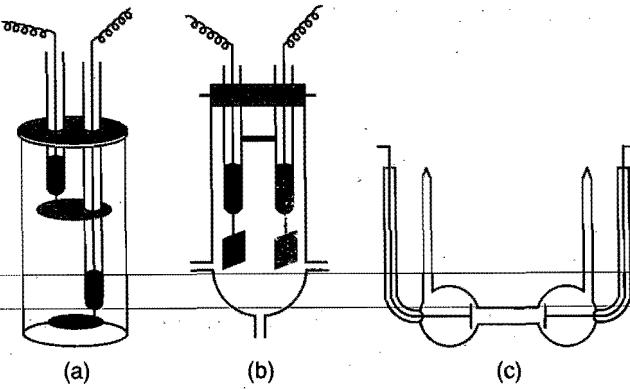


Fig. 12.5 Conductance cells

Cell Constant

Since, the electrodes are not exactly 1 unit apart and may not possess a surface area of 1 square unit, the measured resistance does not give the specific conductance of the solution. Actual measurements of l and a being inconvenient, an indirect method is employed to determine the value of $\frac{l}{a}$ which is a constant quantity for a particular cell and is known as cell constant. We know that,

$$\frac{\text{Specific conductance}}{\text{Conductance}} = \frac{l}{a} = \text{Cell constant}$$

The resistance of cell, i.e., conductance is measured when filled with a standard solution (say $N/10\text{KCl}$ solution) at a given temperature. The standard values of specific conductance of KCl solutions of various concentrations at different temperatures are known. Thus, the cell constant is calculated by using the above equation. The same cell constant applies to a measurement with any other solution.

The determination of specific conductance of an electrolytic solution, thus, consists of two steps:

Step I: Determination of cell constant by using a standard KCl solution of known concentration in the conductivity cell.

Step II: Determination of resistance of the given solution using the same cell. The reciprocal of this gives the value of conductance.

Multiplication of conductance and cell constant gives the value of specific conductance of the solution.

In order to determine equivalent conductance or molar conductance, the concentration of the experimental solution should be known. In conductance measurements, the solutions are always prepared in **conductivity water** which has no conductance due to dissolved impurities. It is prepared by distilling a number of times the distilled water to which a little KMnO_4 and KOH have been added in a hard glass distillation assembly. Such water has very low conductance of the order of

$4.3 \times 10^{-8} \text{ ohm}^{-1}$. For ordinary purposes, double distilled water may be used.

Effect of Dilution on Equivalent Conductance

The value of equivalent conductance increases with dilution. This is due to the fact that degree of ionisation increases with dilution thereby increasing the total number of ions in solution. Solution which contains large number of ions compared to another solution of the same concentration at the same temperature has more conductance and is said to be **strong electrolyte**. The one which has relatively small number of ions is called a **weak electrolyte**. The number of ions from an electrolyte depends on the degree of dissociation. The curve (Fig. 12.6) shows the variation of the equivalent conductance of some electrolytes with dilution. It shows that electrolytes behave in two ways on dilution:

(i) Electrolytes like KCl have high value of conductance even at low concentration and there is no rapid increase in their equivalent conductance on dilution. Such electrolytes are termed **strong electrolytes**. In the case of strong electrolytes, there is a tendency for equivalent conductance to approach a limiting value when the concentration approaches zero. When the whole of the electrolyte has ionised, further addition of the water does not bring any change in the value of equivalent conductance. This stage is called infinite dilution. The equivalent conductance has a limiting value at infinite dilution and is represented by Λ_∞ .

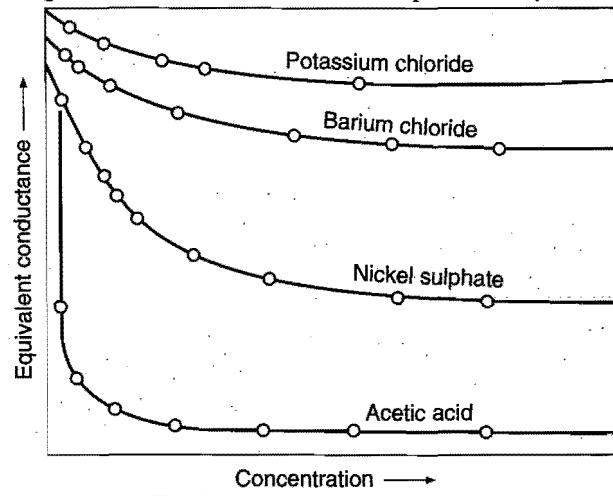


Fig. 12.6 Conductance curve

(ii) Electrolytes like acetic acid have a low value at high concentration and there is a rapid increase in the value of equivalent conductance with dilution. Such electrolytes are termed **weak electrolytes**. There is no indication that a limiting value of equivalent conductance can be attained even when the concentration approaches zero. Thus, graphically, Λ_∞ of weak electrolytes cannot be obtained.

It is thus concluded that equivalent conductance of electrolytes whether strong or weak increases with dilution and reaches to a maximum or limiting value which is termed Λ_∞ (equivalent conductance at infinite dilution). Λ_∞ in the case of strong electrolytes can be obtained by extrapolation of the graph of equivalent conductance to zero concentration but in the case of weak electrolytes it cannot be obtained accurately. An indirect

method for obtaining Λ_∞ for weak electrolytes has been given by Kohlrausch.

12.8 KOHLRAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations. Thus,

$$\Lambda_\infty = \lambda_c + \lambda_a$$

The λ_c and λ_a are called the ionic conductances of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = ku_c$$

and

$$\lambda_a = ku_a$$

where, u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 C, i.e., one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte; it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionised at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

Calculation of absolute ionic mobilities: It has been experimentally found that ionic conductance is directly proportional to ionic mobilities.

$$\lambda_+ \propto u_+$$

$$\lambda_- \propto u_-$$

where, u_+ and u_- are ionic mobilities of cations and anions.

$$\lambda_+ = Fu_+ \text{ where, } F = \text{Faraday}$$

$$\lambda_- = Fu_- = 96500 \text{ coulomb}$$

$$\begin{aligned} \text{Ionic mobility} &= \frac{\text{Ionic velocity}}{\text{Potential gradient}} \\ &= \frac{\text{Ionic velocity (cm/sec)}}{\text{Potential difference (volt)/electrode separation}} \end{aligned}$$

Relation between Equivalent and Molar Conductance at Infinite Dilution

$$\Lambda^\infty = \frac{1}{z^+} \lambda_+^\infty + \frac{1}{z^-} \lambda_-^\infty \quad \dots (i)$$

where, z^+ and z^- are corresponding charges on the ions,

$$\text{e.g.,} \quad \Lambda_{\text{BaCl}_2}^\infty = \frac{1}{2} \lambda_{\text{Ba}^{2+}}^\infty + \frac{1}{1} \lambda_{\text{Cl}^-}^\infty \quad \dots (ii)$$

$$\Lambda_{\text{AlCl}_3}^\infty = \frac{1}{3} \lambda_{\text{Al}^{3+}}^\infty + \frac{1}{1} \lambda_{\text{Cl}^-}^\infty \quad \dots (iii)$$

$$\Lambda_{\text{Al}_2(\text{SO}_4)_3}^\infty = \frac{1}{3} \lambda_{\text{Al}^{3+}}^\infty + \frac{1}{2} \lambda_{\text{SO}_4^{2-}}^\infty \quad \dots (iv)$$

Molar Conductance at Infinite Dilution

$$\begin{aligned} \Lambda_m^\infty \text{ or } \mu^\infty &= \text{Molar conductance at infinite dilution} \\ &= m\lambda_+^\infty + n\lambda_-^\infty \end{aligned}$$

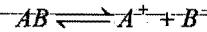
where, m and n are number of ions formed.

$$\mu_{\text{Al}_2(\text{SO}_4)_3}^\infty = 2\lambda_{\text{Al}^{3+}}^\infty + 3\lambda_{\text{SO}_4^{2-}}^\infty = 6\Lambda_{\text{Al}_2(\text{SO}_4)_3}^\infty$$

$$\mu_{\text{BaCl}_2}^\infty = \lambda_{\text{Ba}^{2+}}^\infty + 2\lambda_{\text{Cl}^-}^\infty = 2\Lambda_{\text{BaCl}_2}^\infty$$

12.9 THEORY OF WEAK ELECTROLYTES

(i) Weak electrolytes are not completely ionized when dissolved in a polar medium like water. There exists equilibrium between ions and unionised molecules.



(ii) Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

$$\begin{array}{ccccccc} AB & \rightleftharpoons & A^+ & + & B^- \\ t=0 & & C & & 0 & & 0 \\ t_{\text{eq.}} & & C - C\alpha & & C\alpha & & C\alpha \end{array}$$

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \quad \dots (i)$$

For weak electrolytes, $\alpha \ll 1$

$$(1-\alpha) \approx 1$$

Thus, equation (i) can be written as:

$$\begin{aligned} K &= C\alpha^2 \\ \alpha &= \sqrt{\frac{K}{C}} \end{aligned} \quad \dots (ii)$$

From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionisation ' α ' increases. At high degree of ionisation both equivalent and molar conductance increase.

(iii) Degree of ionisation can be calculated as:

$$\alpha = \frac{\Lambda_e^C}{\Lambda_e^\infty} = \frac{\Lambda_m^C}{\Lambda_m^\infty} \quad \dots (iii)$$

Λ_e^C, Λ_m^C = Equivalent and molar conductance at concentration ' C '

$\Lambda_e^\infty, \Lambda_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Substituting the values of ' α ' from eq. (iii) in eq. (i), we get

$$K = \frac{C \times \left(\frac{\Lambda_e^C}{\Lambda_e^\infty} \right)^2}{1 - \frac{\Lambda_e^C}{\Lambda_e^\infty}} = \frac{C(\Lambda_e^C)^2}{\Lambda_e^\infty (\Lambda_e^\infty - \Lambda_e^C)} \quad \dots (iv)$$

Similarly,

$$K = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty (\Lambda_m^\infty - \Lambda_m^C)} \quad \dots (v)$$

Equations (iv) and (v) are called **Ostwald equations**.

Example 24. 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

Solution: Given, $l = 2.1$ cm, $a = 4.2$ sq cm, $R = 50$ ohm

$$\text{Specific conductance, } \kappa = \frac{l}{a} \cdot \frac{1}{R}$$

$$\text{or } \kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Equivalent conductivity} = \kappa \times V$$

V = the volume containing 1 g-equivalent = 1000 mL

$$\text{So, Equivalent conductivity} = 0.01 \times 1000 \\ = 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Example 25. Specific conductance of a decinormal solution of KCl is $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of a cell containing the solution was found to be 56. What is the cell constant?

Solution: We know that,

$$\text{Sp. conductance} = \text{Cell constant} \times \text{Conductance}$$

$$\text{or Cell constant} = \frac{\text{Sp. conductance}}{\text{Conductance}} \\ = \text{Sp. conductance} \times \text{Resistance} \\ = 0.0112 \times 56 = 0.6272 \text{ cm}^{-1}$$

Example 26. The specific conductivity of 0.02 M KCl solution at $25^\circ C$ is $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of this solution at $25^\circ C$ when measured with a particular cell was 250.2 ohm. The resistance of 0.01 M CuSO₄ solution at $25^\circ C$ measured with the same cell was 8331 ohm. Calculate the molar conductivity of the copper sulphate solution.

$$\text{Solution: Cell constant} = \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}} \\ = \frac{2.768 \times 10^{-3}}{1/250.2} \\ = 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M CuSO₄ solution

$$\text{Sp. conductivity} = \text{Cell constant} \times \text{Conductance} \\ = 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

$$\text{Molar conductance} = \text{Sp. cond.} \times \frac{1000}{C} \\ = \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} = 8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example 27. The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and $91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$, respectively, at $25^\circ C$. Calculate the equivalent conductance of acetic acid at infinite dilution.

Solution: According to Kohlrausch's law,

$$\Lambda_{\infty \text{CH}_3\text{COONa}} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} = 91.0 \quad \dots (i)$$

$$\Lambda_{\infty \text{HCl}} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.16 \quad \dots (ii)$$

$$\Lambda_{\infty \text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.45 \quad \dots (iii)$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} \\ = 91.0 + 426.16 - 126.45$$

$$\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} = \Lambda_{\infty \text{CH}_3\text{COOH}} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Example 28. The equivalent conductivity of $N/10$ solution of acetic acid at $25^\circ C$ is $14.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$.

Calculate the degree of dissociation of CH₃COOH if $\Lambda_{\infty \text{CH}_3\text{COOH}}$ is 390.71.

Solution:

$$\Lambda_{\infty \text{CH}_3\text{COOH}} = 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

$$\Lambda_{\text{CH}_3\text{COOH}} = 14.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{14.3}{390.71}$$

= 0.0366, i.e., 3.66% dissociated

Example 29. A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductances of Na⁺ and Cl⁻ ions at the same temperature are 43.0 and 65.0 ohm⁻¹ respectively, calculate the degree of dissociation of NaCl solution.

Solution: Equivalent conductivity of $N/10$ NaCl solution

$$\Lambda_v = \text{Sp. conductivity} \times \text{dilution} \\ = 0.0092 \times 10,000 = 92 \text{ ohm}^{-1}$$

$$\Lambda_\infty = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} \\ = 43.0 + 65.0 = 108 \text{ ohm}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{92}{108} = 0.85$$

Example 30. At $18^\circ C$, the conductivities at infinite dilution of NH₄Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 mho respectively. If the equivalent conductivity of $N/100$ solution of NH₄OH is 9.93 mho, calculate the degree of dissociation of NH₄OH at this dilution.

$$\text{Solution: } \Lambda_{\infty \text{NH}_4\text{Cl}} = \lambda_{\text{NH}_4^+} + \lambda_{\text{Cl}^-} = 129.8 \quad \dots (i)$$

$$\Lambda_{\infty \text{NaOH}} = \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-} = 217.4 \quad \dots (ii)$$

$$\Lambda_{\infty \text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 108.9 \quad \dots (iii)$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\lambda_{\text{NH}_4^+} + \lambda_{\text{Cl}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} =$$

$$\lambda_{\text{NH}_4^+} + \lambda_{\text{OH}^-} = 129.8 + 217.4 - 108.9$$

$$\Lambda_{\infty \text{NH}_4\text{OH}} = 238.3 \text{ mho}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{9.93}{238.3} = 0.04167$$

or
4.17 % dissociated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

11. If the equivalent conductance of 1 M benzoic acid is $12.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ and if the conductance of benzoate ion and H^+ ions are 42 and $288.42 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ respectively, its degree of dissociation is: (DPMT 2005)

- (a) 39% (b) 3.9%
(c) 0.35% (d) 0.039%

[Ans. (b)]

$$[\text{Hint: } \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{12.8}{(42 + 288.42)} = 0.0387]$$

Percentage dissociation = $0.0387 \times 100 = 3.9\%$]

12. Equivalent conductances of NaCl , HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and $91 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ respectively. The equivalent conductance of CH_3COOH at infinite dilution would be:

- (a) $101.38 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (b) $253.62 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
(c) $390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (d) $678.90 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

[Ans. (c)]

$$[\text{Hint: } \Lambda_{\text{CH}_3\text{COOH}}^\circ = \Lambda_{\text{CH}_3\text{COONa}}^\circ + \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{NaCl}}^\circ \\ = 91 + 426.16 - 126.45 \\ = 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}]$$

13. The specific conductance of saturated solution of AgCl is found to be $1.86 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and that of water is $6 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. The solubility of AgCl is

Given, $\Lambda_{\text{AgCl}}^\circ = 137.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

- (a) $1.7 \times 10^{-3} \text{ M}$ (b) $1.3 \times 10^{-5} \text{ M}$
(c) $1.3 \times 10^{-4} \text{ M}$ (d) $1.3 \times 10^{-6} \text{ M}$

[Ans. (b)]

$$[\text{Hint: } \kappa_{\text{AgCl}} = \kappa_{\text{AgCl}}(\text{solution}) - \kappa_{\text{H}_2\text{O}} \\ = 1.86 \times 10^{-6} - 6 \times 10^{-8} = 1.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\Lambda_{\text{AgCl}}^\circ = \kappa \times \frac{1000}{S}$$

$$\therefore S = \frac{\kappa \times 1000}{\Lambda_{\text{AgCl}}^\circ} = \frac{1.8 \times 10^{-6} \times 1000}{137.2} = 1.31 \times 10^{-5} \text{ M}]$$

14. The specific conductivity of $N/10 \text{ KCl}$ solution at 20°C is $0.0212 \text{ ohm}^{-1} \text{ cm}^{-1}$ and the resistance of the cell containing this solution at 20°C is 55 ohm. The cell constant is:

- (a) 4.616 cm^{-1} (b) 1.166 cm^{-1}
(c) 2.173 cm^{-1} (d) 3.324 cm^{-1}

[Ans. (b)]

$$[\text{Hint: } \kappa = C \times \frac{l}{A}$$

$$\frac{l}{A} = \kappa \times \frac{1}{C} = \kappa \times R = 0.0212 \times 55 = 1.166 \text{ cm}^{-1}]$$

15. The resistance of 1 N solution of CH_3COOH is 250 ohm; when measured in a cell of cell constant 1.15 cm^{-1} . The equivalent conductance will be:

- (a) $4.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (b) $9.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
(c) $18.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (d) $0.023 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

[Ans. (a)]

$$[\text{Hint: } \kappa = C \times \frac{l}{A} = \frac{1}{250} \times 1.15 = 4.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\Lambda_e = \kappa \times \frac{1000}{N} = 4.6 \times 10^{-3} \times \frac{1000}{1} = 4.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}]$$

16. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 ohm. The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell when filled with 0.2 M of the same solution is 520 ohm. The molar conductivity of 0.02 M solution of the electrolyte will be: (AIEEE 2006)

- (a) $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (b) $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(c) $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (d) $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

[Ans. (a)]

$$[\text{Hint: } \kappa = \frac{1}{R} \times \frac{l}{A}$$

$$1.29 = \frac{1}{100} \times \frac{l}{A}$$

$$\frac{l}{A} = 129 \text{ m}^{-1}$$

$$\Lambda_m = \kappa \times \frac{1000}{M}$$

$$= \left(\frac{1}{R} \times \frac{l}{A} \right) \times \frac{1000}{M}$$

$$= \left(\frac{1}{520} \times 129 \right) \times \frac{1000}{0.02} \times 10^{-6} \\ = 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}]$$

17. If the molar conductance values of Ca^{2+} and Cl^- at infinite dilution are respectively $118.88 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}$ and $77.33 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}$ then that of CaCl_2 is:

- (in $\text{m}^2 \text{ mho mol}^{-1}$) (a) 118.88×10^{-4} (b) 154.66×10^{-4}
(c) 273.54×10^{-4} (d) 196.21×10^{-4}

[Ans. (c)]

$$[\text{Hint: } \Lambda_m^\circ \text{ CaCl}_2 = \lambda^\circ \text{ Ca}^{2+} + 2\lambda^\circ \text{ Cl}^-$$

$$= (118.88 \times 10^{-4}) + 2(77.33 \times 10^{-4}) \\ = 273.54 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}]$$

18. The molar conductivities of KCl , NaCl and KNO_3 are 152, 128 and $111 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. What is the molar conductivity of NaNO_3 ? (VITEEE 2008)

- (a) $101 \text{ S cm}^2 \text{ mol}^{-1}$ (b) $87 \text{ S cm}^2 \text{ mol}^{-1}$
(c) $-101 \text{ S cm}^2 \text{ mol}^{-1}$ (d) $-391 \text{ S cm}^2 \text{ mol}^{-1}$

[Ans. (b)]

$$[\text{Hint: } \Lambda_{\text{NaNO}_3}^\circ = \Lambda_{\text{NaCl}}^\circ + \Lambda_{\text{KNO}_3}^\circ - \Lambda_{\text{KCl}}^\circ$$

$$= 128 + 111 - 152 = 87 \text{ S cm}^2 \text{ mol}^{-1}]$$

SECTION III : ELECTROCHEMICAL CELL

12.10 ELECTROCHEMICAL CELL

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

- Electrolytic cell
- Galvanic or voltaic cell

(a) Electrolytic Cell

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

(b) Galvanic or Voltaic Cell

It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called **half-cells**. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

12.11 DANIELL CELL

It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current (Fig. 12.7). It consists of two half-cells. The half-cell on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution. The half-cell on the right consists of copper metal electrode in a solution of $CuSO_4$. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.

When the zinc and copper electrodes are joined by a wire, the following observations are made:

- There is a flow of electric current through the external circuit.
- The zinc rod loses its mass while the copper rod gains in mass.
- The concentration of $ZnSO_4$ solution increases while the concentration of copper sulphate solution decreases.
- The solutions in both the compartments remain electrically neutral.

During the passage of electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidised to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are

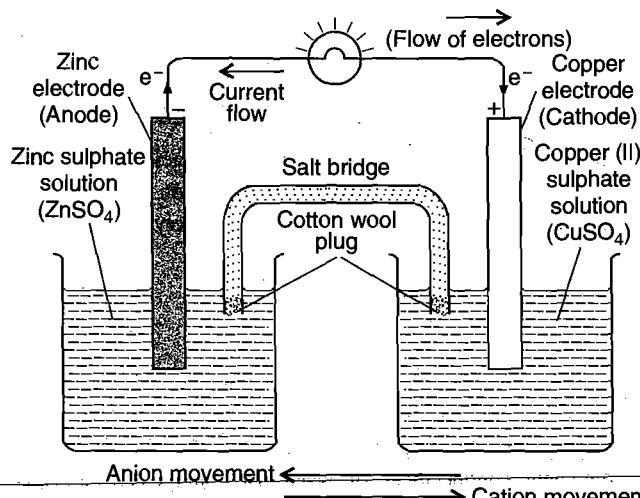


Fig. 12.7 Daniell cell

used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:



Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at copper electrode, reduction takes place; it is the cathode of the cell and is positively charged.

Thus, the above points can be summed up as:

- Voltaic or Galvanic cell consists of two **half-cells**. The reactions occurring in half-cells are called **half-cell reactions**. The half-cell in which oxidation occurs is called **oxidation half-cell** and the reaction taking place in it is called **oxidation half-cell reaction**. Similarly, the half-cell in which reduction occurs is called **reduction half-cell** and the reaction taking place in it is called **reduction half-cell reaction**.
 - The electrode where oxidation occurs is called anode and the electrode where reduction occurs is termed cathode.
 - Electrons flow from anode to cathode in the external circuit.
 - Overall ion movement during the operation of the galvanic cell shows that negative ions (anions) move away from cathode where they are present in excess, towards anode, where they are needed to balance the charge of the positive ions (cations) formed. Similarly, cations move away from the anode where they are in excess, towards the cathode, where they balance the anions left in excess.
- Example : An $Au(NO_3)_3$ solution containing a gold electrode is connected by means of salt bridge to a $PbCl_2$ solution containing lead electrode. The cell can be correctly represented as,

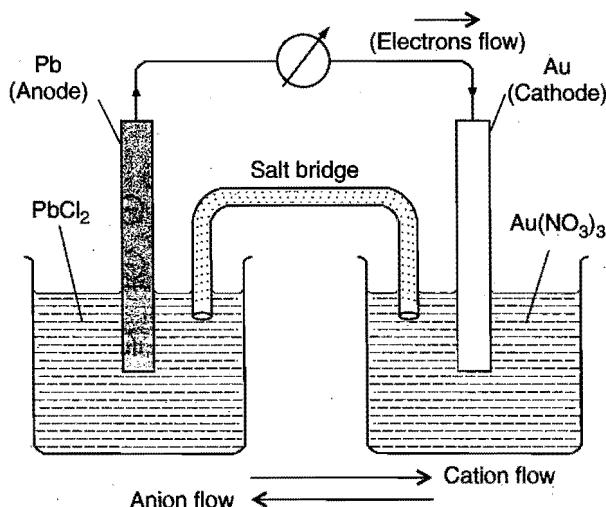
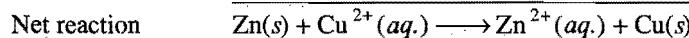
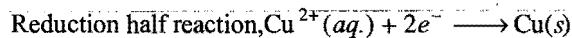


Fig. 12.8

- (v) Chemical energy is converted into electrical energy.
 (vi) The net reaction is the sum of two half-cell reactions. The reactions in Daniell cell can be represented as:



Electrode Signs

The signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells (Fig. 12.9).

ELECTROLYTIC CELL
(emf is applied to cell)

VOLTAIC OR GALVANIC CELL
(emf is generated by cell)

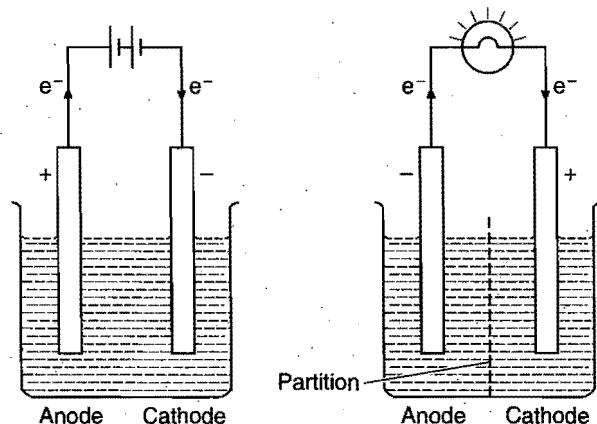


Fig. 12.9

Difference in electrolytic cell and galvanic cell

Electrolytic cell	Galvanic cell
1. Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
2. Anode is positive electrode. Cathode is negative electrode.	Anode is negative electrode. Cathode is positive electrode.
3. Ions are discharged on both the electrodes.	Ions are discharged only on the cathode.
4. If the electrodes are inert, concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
5. Both the electrodes can be fitted in the same compartment.	The electrodes are fitted in different compartments.

12.12 SALT BRIDGE AND ITS SIGNIFICANCE

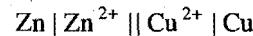
Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, KNO_3 , NH_4NO_3 , etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimise diffusion effects. This is used as a salt bridge.

Significance of salt bridge: The following are the functions of the salt bridge:

- It connects the solutions of two half-cells and completes the cell circuit.
- It prevents transference or diffusion of the solutions from one half-cell to the other.
- It keeps the solutions in two half-cells electrically neutral. In anodic half-cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell, negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralise these negative ions, sufficient number of positive ions are provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

- It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.



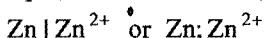
Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

	Electrolytic cell		Voltaic or Galvanic cell	
	Anode	Cathode	Anode	Cathode
Sign	+	-	-	+
Electron flow	out	in	out	in
Half reaction	oxidation	reduction	oxidation	reduction

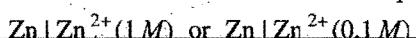
12.13 REPRESENTATION OF AN ELECTRO-CHEMICAL CELL (Galvanic Cell)

The following universally accepted conventions are followed in representing an electrochemical cell:

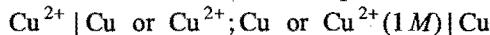
- The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.
- A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,



The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example,



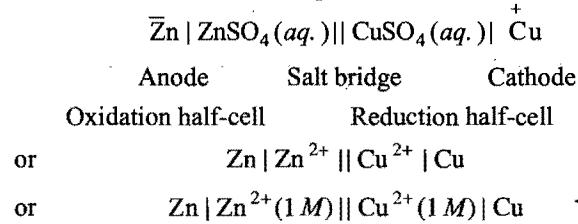
- The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,



- The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

- Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:



12.14 ELECTRODE POTENTIAL

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential**. For example, when a plate of zinc is placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to solution and thus a potential difference is set-up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having Cu^{2+} ions, it becomes positively charged with respect to solution. A potential difference is set-up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution. The development of negative charge (as on zinc plate) or positive charge (as on copper plate) can be explained in the following manner. When a metal rod is dipped in its salt solution, two changes occur:

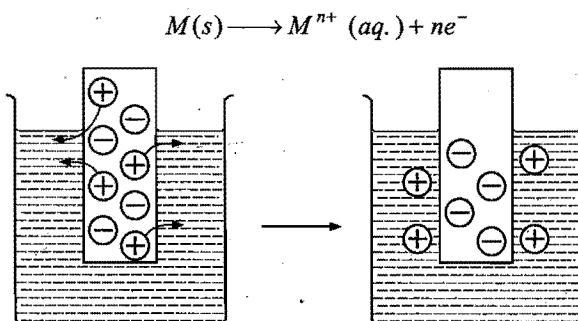


Fig. 12.10 (a)

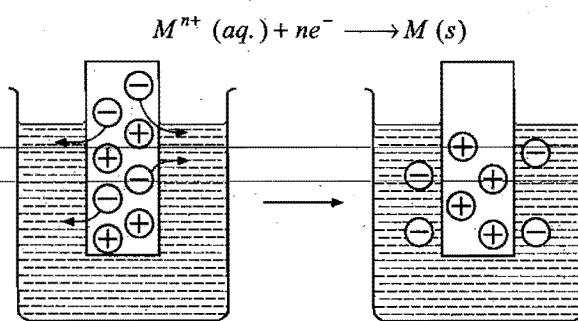


Fig. 12.10 (b)

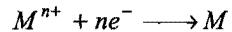
- (a) Oxidation :** Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.
- (b) Reduction :** Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

- The conversion of metal atoms into metal ions by the attractive force of polar water molecules.



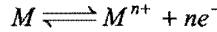
The metal ions go into the solution and the electrons remain on the metal making it negatively charged. The tendency of the metal to change into ions is known as **electrolytic solution pressure**.

- Metal ions start depositing on the metal surface leading to a positive charge on the metal.



This tendency of the ions is termed **osmotic pressure**.

In the beginning, both these changes occur with different speeds but soon an equilibrium is established.



In practice, one effect is greater than the other, if first effect is greater than the second, the metal acquires a negative charge with respect to solution and if the second is greater than the first, it acquires positive charge with respect to solution, thus in both the cases a potential difference is set-up.

The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons, i.e., it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). The magnitude of potential depends on the following factors:

- (i) Nature of the electrode,
- (ii) Concentration of the ions in solution,
- (iii) Temperature.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

(i) Oxidation potential: When electrode is negatively charged with respect to solution, i.e., it acts as anode. Oxidation occurs.



(ii) Reduction potential: When electrode is positively charged with respect to solution, i.e., it acts as cathode. Reduction occurs.



It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode**. The emf of the resulting cell is measured experimentally. The emf of the cell is equal to the sum of potentials on the two electrodes.

$$\begin{aligned}\text{Emf of the cell} &= E_{\text{Anode}} + E_{\text{Cathode}} \\ &= \text{Oxidation potential of anode} \\ &\quad + \text{Reduction potential of cathode}\end{aligned}$$

Knowing the value of reference electrode, the value of other electrode can be determined.

12.15 STANDARD ELECTRODE POTENTIAL

In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25°C (298 K) is called **standard electrode potential**.

According to the IUPAC convention, the reduction potential alone can be called as the electrode potential (E°), i.e., the given value of electrode potential can be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential. Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus,

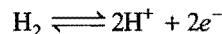
$$\text{Standard reduction potential} = - \text{Standard oxidation potential}$$

$$\text{or} \quad \text{Standard oxidation potential} = - \text{Standard reduction potential}$$

12.16 REFERENCE ELECTRODE (Standard Hydrogen Electrode, SHE or NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and

sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 M . Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives an equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.



The temperature of the cell is maintained at 25°C . By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly $\pm 0.000\dots$ volt.

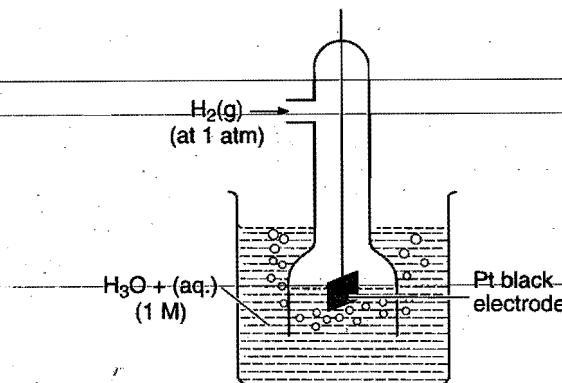


Fig. 12.11 Hydrogen electrode

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	Electrode potential
$\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$	0.0 V (Anode)
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.0 V (Cathode)

12.17 MEASUREMENT OF ELECTRODE POTENTIAL

The measurement of electrode potential of a given electrode is made by constituting a voltaic cell, i.e., by connecting it with a standard hydrogen electrode (SHE) through a salt bridge. 1 M solution is used in hydrogen half-cell and the temperature is maintained at 25°C . The emf of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter, i.e., a valve voltmeter. The reading of the voltmeter gives the electrode potential of the electrode in question with respect to the hydrogen electrode. The standard electrode potential of a metal may be determined as it is the potential difference in volt developed in a cell consisting of two electrodes: the pure metal is in contact with a molar solution of one of its ions and the standard hydrogen electrode.

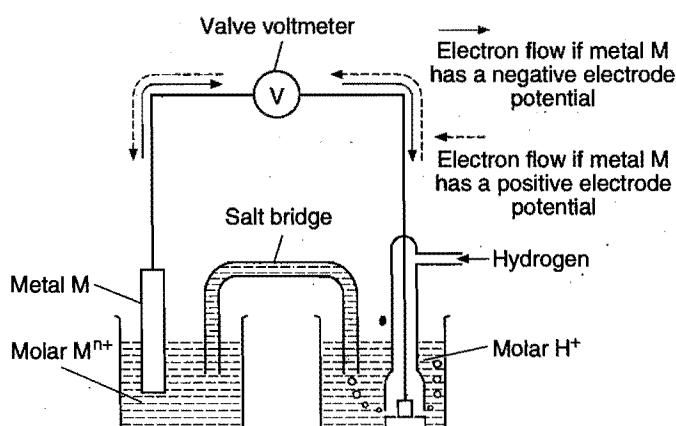
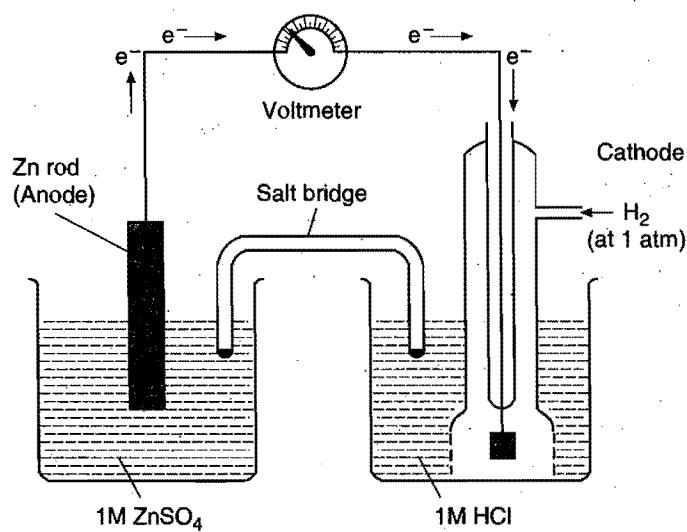
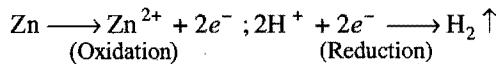
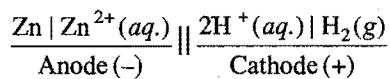


Fig. 12.12

(i) Determination of standard electrode potential of

Zn / Zn²⁺ electrode: A zinc rod is dipped in 1 M zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. Both the electrodes are connected with a voltmeter as shown in Fig. 12.13. The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal-electrode or the electrons are moving from zinc rod to hydrogen electrode. The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

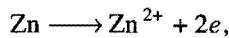
Fig. 12.13 Zn-H₂ electrochemical cell

The emf of the cell is 0.76 volt

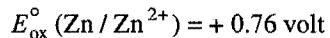
$$E_{\text{Cell}} = E_{\text{Anode}}^\circ + E_{\text{Cathode}}^\circ$$

$$0.76 = E_{\text{Anode}}^\circ + 0 \text{ or } E_{\text{Anode}}^\circ = +0.76 \text{ V}$$

As the reaction on the anode is oxidation, i.e.,



E_{Anode}° is the standard oxidation potential of zinc. This potential is given the positive sign.



So, standard reduction potential of Zn, i.e., $E^\circ (\text{Zn}^{2+} / \text{Zn})$

$$= -E_{\text{ox}}^\circ = -(+0.76)$$

$$= -0.76 \text{ volt}$$

The emf of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.

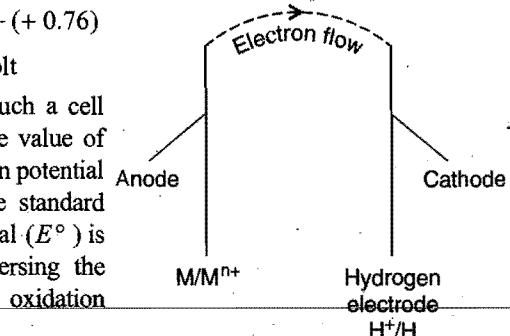
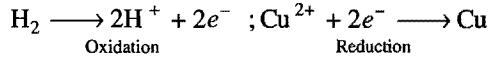
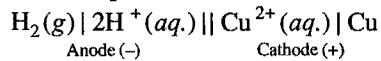


Fig. 12.14

(ii) Determination of standard electrode potential of Cu²⁺ / Cu, electrode:

A copper rod is dipped in 1 M solution of CuSO₄. It is combined with hydrogen electrode through a salt bridge. Both the electrodes are joined through a voltmeter. The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, i.e., the electrons are moving from hydrogen electrode to copper electrode. The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as



The emf of the cell is 0.34 volt.

$$E_{\text{Cell}}^\circ = E_{\text{Anode}}^\circ + E_{\text{Cathode}}^\circ$$

$$0.34 = 0 + E_{\text{Cathode}}^\circ$$

Since, the reaction on the cathode is reduction, i.e., $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$, E_{Cathode}° is the standard reduction potential of copper. This is given the +ve sign.

E° , i.e., standard reduction potential of Cu²⁺ / Cu = 0.34 volt

So, E_{ox}° (standard oxidation potential of copper) = -0.34 volt

The emf of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

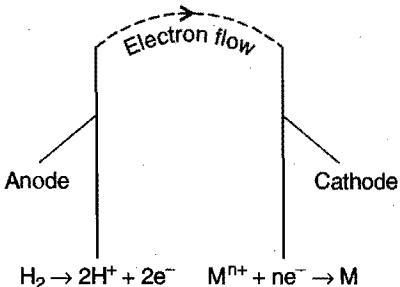


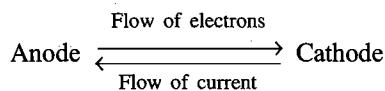
Fig. 12.15

It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode in question with a standard hydrogen electrode and measuring the emf of the cell constituted.

12.18 EMF OF A GALVANIC CELL

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). The potentials of these half-cells are always different. On account of this difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential, i.e., from cathode to anode. The direction of the flow of electrons is from anode to cathode.



The difference in potentials of the two half-cells is known as the **electromotive force (emf) of the cell or cell potential**.

The emf of the cell or cell potential can be calculated from the values of electrode potentials of the two half-cells constituting the cell. The following three methods are in use:

(i) When oxidation potential of anode and reduction potential of cathode are taken into account:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= \text{Oxidation potential of anode} \\ &\quad + \text{Reduction potential of cathode} \\ &= E_{\text{ox}}^{\circ} (\text{anode}) + E_{\text{red}}^{\circ} (\text{cathode}) \end{aligned}$$

(ii) When reduction potentials of both electrodes are taken into account:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= \text{Standard Reduction potential of cathode} \\ &\quad - \text{Standard Reduction potential of anode} \\ &= E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ} \\ &= E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} \end{aligned}$$

(iii) When oxidation potentials of both electrodes are taken into account:

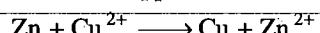
$$\begin{aligned} E_{\text{cell}}^{\circ} &= \text{Oxidation potential of anode} \\ &\quad - \text{Oxidation potential of cathode} \\ &= E_{\text{ox}}^{\circ} (\text{anode}) - E_{\text{ox}}^{\circ} (\text{cathode}) \end{aligned}$$

Difference between emf and potential difference: The potential difference is the difference between the electrode potentials of the two electrodes of the cell under any condition while emf is the potential generated by a cell when there is zero electron flow, i.e., it draws no current. The points of difference are given ahead:

Emf	Potential difference
1. It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation.
2. It is the maximum voltage that the cell can deliver.	It is always less than the maximum value of voltage which the cell can deliver.
3. It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

12.19 REVERSIBLE AND IRREVERSIBLE CELLS

Daniell cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,



stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.



Such a cell is termed a **reversible cell**. Thus, the following are the two main conditions of reversibility:

(i) The chemical reaction of the cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Any other cell which does not obey the above two conditions is termed as **irreversible**. A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is irreversible. Similarly, the cell



is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,



is not reversed but the cell reaction becomes



12.20 SOME OTHER REFERENCE ELECTRODES

Since, a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as secondary reference electrodes. These are convenient to handle and are prepared easily. Two important secondary reference electrodes are described here.

(i) **Calomel electrode:** It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

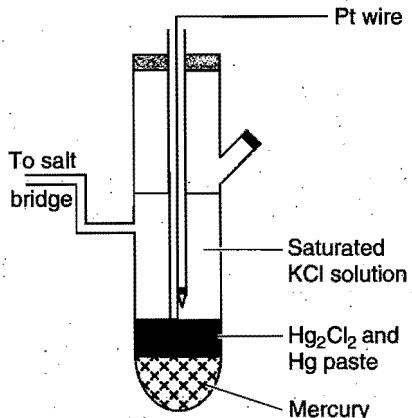
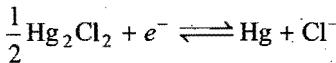


Fig. 12.16 Calomel electrode

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE). The electrode reaction when the electrode acts as cathode is:



The reduction potentials of the calomel electrodes on hydrogen scale at 298 K are as follows:

Saturated KCl	0.2415 V
1.0 N KCl	0.2800 V
0.1 N KCl	0.3338 V

The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

(ii) **Silver-silver chloride electrode:** This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without inserting liquid junctions.

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K. The electrode is represented as:



The electrode reaction is:



12.21 PREDICTION FOR OCCURRENCE OF A REDOX REACTION

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative. The free energy is related to cell emf in the following manner:

$$\Delta G^\circ = -nFE^\circ$$

where, n is the number of electrons involved, F is the value of Faraday and E° is the cell emf. ΔG can be negative if E° is positive.

When E° is positive, the cell reaction is spontaneous and serves as a source of electrical energy.

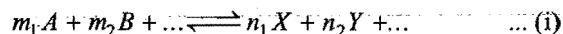
To predict whether a particular redox reaction will occur or not, write down the redox reaction into two half reactions, one involving oxidation reaction and the other involving reduction reaction. Write the oxidation potential value for oxidation reaction and reduction potential value for reduction reaction. Add these two values, if the algebraic summation gives a positive value, the reaction will occur, otherwise not.

[Note : The true conditions for operating voltaic cells are :

$$\Delta G < 0, E > 0]$$

12.22 ELECTRODE AND CELL POTENTIALS – NERNST EQUATION

The electrode potential and the emf of the cell depend upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potentials with concentration of ions in solution can be obtained from thermodynamic considerations. For a general reaction such as



occurring in the cell, the Gibbs free energy change is given by the equation

$$\Delta G = \Delta G^\circ + 2.303RT \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \dots}{a_A^{m_1} \times a_B^{m_2} \dots} \quad \dots (ii)$$

where, 'a' represents the activities of reactants and products under a given set of conditions and ΔG° refers to free energy change for the reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction is related to the electrical work that can be obtained from the cell, i.e., $\Delta G = -nFE_{\text{cell}}$ and $\Delta G^\circ = -nFE^\circ$. On substituting these values in eq. (ii), we get

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + 2.303RT \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \dots}{a_A^{m_1} \times a_B^{m_2} \dots} \quad \dots (iii)$$

$$\text{or } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \dots}{a_A^{m_1} \times a_B^{m_2} \dots} \quad \dots (iv)$$

This equation is known as Nernst equation.

Putting the values of $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$ and $F = 96500 \text{ C}$, eq. (iv) reduces to

$$E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \dots}{a_A^{m_1} \times a_B^{m_2} \dots} \quad \dots (v)$$

$$= E^\circ - \frac{0.0591}{n} \log_{10} \frac{[\text{Products}]}{[\text{Reactants}]} \quad \dots (vi)$$

Potential of single electrode (Anode): Consider the general oxidation reaction,



Applying Nernst equation,

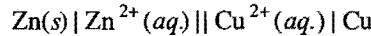
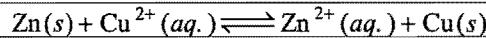
$$E_{\text{ox}} = E_{\text{ox}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

where, E_{ox} is the oxidation potential of the electrode (anode), E_{ox}° is the standard oxidation potential of the electrode.

[Note: The concentration of pure solids and liquids are taken as unity.]

$$E_{\text{ox}} = E_{\text{ox}}^{\circ} - \frac{0.0591}{n} \log_{10} [M^{n+}]$$

Let us consider a Daniell cell to explain the above equations. The concentrations of the electrolytes are not 1 M.



Potential at zinc electrode (Anode)

$$E_{\text{ox}} = E_{\text{ox}}^{\circ} - \frac{0.0591}{n} \log_{10} [\text{Zn}^{2+}]$$

Potential at copper electrode (Cathode)

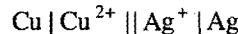
$$E_{\text{red}} = E_{\text{red}}^{\circ} + \frac{0.0591}{n} \log_{10} [\text{Cu}^{2+}]$$

Emf of the cell

$$\begin{aligned} E_{\text{cell}} &= E_{\text{ox}} + E_{\text{red}} \\ &= (E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ}) - \frac{0.0591}{n} \log_{10} \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right] \\ &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log_{10} \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right] \end{aligned}$$

The value of $n = 2$ for both zinc and copper.

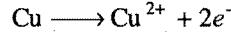
Let us consider an example, in which the values of n for the two ions in the two half-cells are not same. For example, in the cell



The cell reaction is:



The two half-cell reactions are:



The second equation is multiplied by 2 to balance the number of electrons.



Note : Oxidation potential is E_{M/M^+}° while reduction potential is represented as $E_{M^+/M}^{\circ}$. The value of $E_{\text{Zn}/\text{Zn}^{2+}}^{\circ}$ (oxidation potential of Zn) is + 0.76 volt and the value of $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$ (reduction potential of copper) is + 0.34 volt. The electrode having lower value of reduction potential acts as an anode while that having higher value of reduction potential acts as cathode.

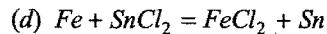
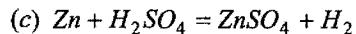
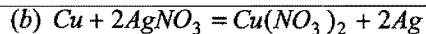
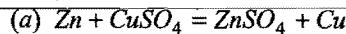
$$E_{\text{ox}} = E_{\text{ox}}^{\circ} - \frac{0.0591}{2} \log_{10} [\text{Cu}^{2+}]$$

$$E_{\text{red}} = E_{\text{red}}^{\circ} + \frac{0.0591}{2} \log_{10} [\text{Ag}^+]^2$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{ox}} + E_{\text{red}} = E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \\ &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \end{aligned}$$

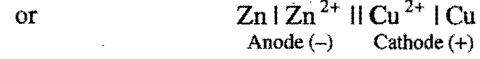
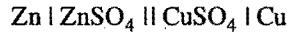
::: SOME SOLVED EXAMPLES :::

Example 31. Construct the cells in which the following reactions are taking place. Which of the electrodes shall act as anode (negative electrode) and which one as cathode (positive electrode)?



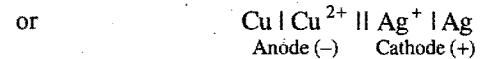
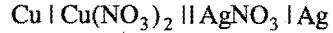
Solution: It should always be kept in mind that the metal which goes into solution in the form of its ions undergoes oxidation and thus acts as negative electrode (anode) and the element which comes into the free state undergoes reduction and acts as positive electrode (cathode):

(a) In this case Zn is oxidised to Zn^{2+} and thus acts as anode (negative electrode) while Cu^{2+} is reduced to copper and thus acts as cathode (positive electrode). The cell can be represented as



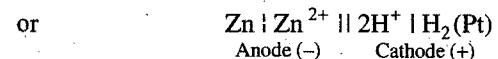
Anode (-) Cathode (+)

(b) In this case Cu is oxidised to Cu^{2+} and Ag^+ is reduced to Ag. The cell can be represented as



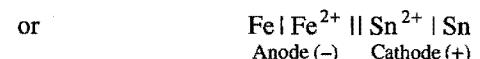
Anode (-) Cathode (+)

(c) In this case, Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2 . The cell can be represented as:



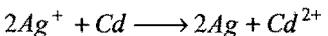
Anode (-) Cathode (+)

(d) Here, Fe is oxidised to Fe^{2+} and Sn^{2+} is reduced to Sn. The cell can be represented as:



Anode (-) Cathode (+)

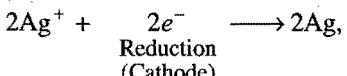
Example 32. Consider the reaction,



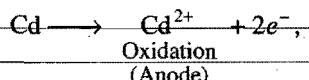
The standard electrode potentials for $\text{Ag}^+ \rightarrow \text{Ag}$ and $\text{Cd}^{2+} \rightarrow \text{Cd}$ couples are 0.80 volt and -0.40 volt respectively.

- (i) What is the standard potential E° for this reaction?
- (ii) For the electrochemical cell, in which this reaction takes place which electrode is negative electrode?

Solution: (i) The half reactions are:



$$E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ volt} \quad (\text{Reduction potential})$$



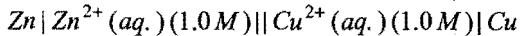
$$E_{\text{Cd}^{2+}/\text{Cd}}^\circ = -0.40 \text{ volt} \quad (\text{Reduction potential})$$

$$\text{or} \quad E_{\text{Cd}/\text{Cd}^{2+}}^\circ = +0.40 \text{ volt}$$

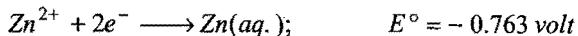
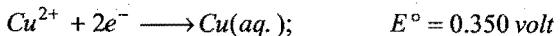
$$E^\circ = E_{\text{Cd}/\text{Cd}^{2+}}^\circ + E_{\text{Ag}^+/\text{Ag}}^\circ = 0.40 + 0.80 = 1.20 \text{ volt}$$

(ii) The negative electrode is always the electrode whose reduction potential has smaller value or the electrode where oxidation occurs. Thus, Cd electrode is the negative electrode.

Example 33. Consider the cell,



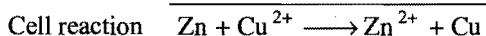
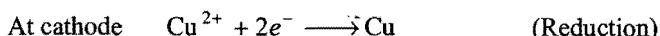
The standard electrode potentials are:



(i) Write down the cell reaction.

(ii) Calculate the emf of the cell.

Solution: (i) Reduction potential of Zn is less than copper, hence Zn acts as anode and copper as cathode.



$$(ii) E_{\text{cell}}^\circ = E_{\text{Zn}/\text{Zn}^{2+}}^\circ + E_{\text{Cu}^{2+}/\text{Cu}}^\circ$$

= Oxi. potential of zinc + Red. potential of copper

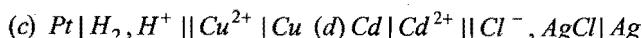
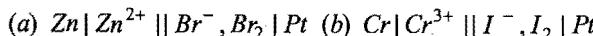
$$E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.763 \text{ (Reduction potential)}$$

$$E_{\text{Zn}/\text{Zn}^{2+}}^\circ = +0.350 \text{ (Oxidation potential)}$$

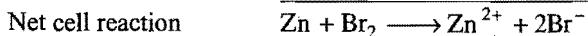
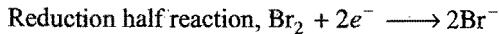
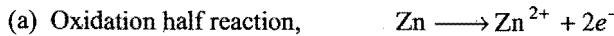
$$\text{and} \quad E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.350 \text{ (Reduction potential)}$$

$$\text{So, } E_{\text{cell}}^\circ = 0.763 + 0.350 = 1.113 \text{ volt}$$

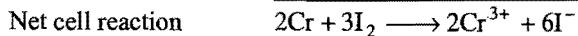
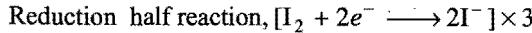
Example 34. Write the electrode reactions and the net cell reactions for the following cells. Which electrode would be the positive terminal in each cell?



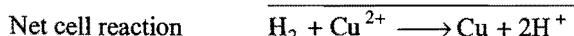
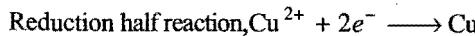
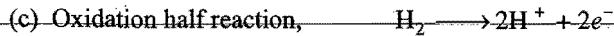
Solution:



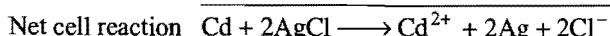
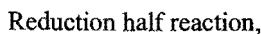
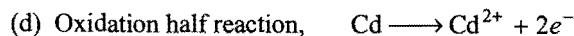
Positive terminal—Cathode Pt



Positive terminal—Cathode Pt



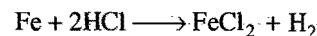
Positive terminal—Cathode Cu



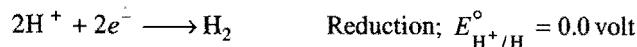
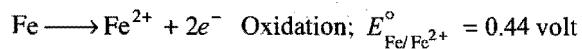
Positive terminal—Cathode Ag

Example 35. Will Fe be oxidised to Fe^{2+} by reaction with 1.0 M HCl? E° for Fe/Fe^{2+} = +0.44 volt.

Solution: The reaction will occur if Fe is oxidised to Fe^{2+} .



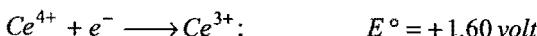
Writing two half reactions,



$$\text{Adding; emf} = 0.44 \text{ volt}$$

Since, emf is positive, the reaction shall occur.

Example 36. The values of E° of some of the reactions are given below:



On the basis of the above data, answer the following questions:

- (a) Whether Fe^{3+} oxidises Ce^{3+} or not?
 (b) Whether I_2 displaces chlorine from KCl ?
 (c) Whether the reaction between FeCl_3 and SnCl_2 occurs or not?

Solution: (a) Chemical reaction,



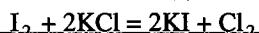
Two half reactions,



$$\text{Adding; emf} = -0.84 \text{ volt}$$

Since, emf is negative, the reaction does not occur, i.e., Fe^{3+} does not oxidise Ce^{3+} .

(b) Chemical reaction,



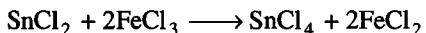
Half reactions,



$$\text{Adding; emf} = -0.82 \text{ volt}$$

Since, emf is negative, the reaction does not occur, i.e., I_2 does not displace Cl_2 from KCl .

(c) Chemical reaction,



Half reactions,



$$\text{Adding; emf} = +0.61 \text{ volt}$$

Since, emf is positive, the reaction will occur.

Example 37. Calculate the electrode potential at a copper electrode dipped in a 0.1 M solution of copper sulphate at 25°C . The standard electrode potential of Cu^{2+}/Cu system is 0.34 volt at 298 K.

Solution: We know that, $E_{\text{red}} = E_{\text{red}}^\circ + \frac{0.0591}{n} \log_{10} [\text{ion}]$

Putting the values of $E_{\text{red}}^\circ = 0.34 \text{ V}$, $n = 2$ and $[\text{Cu}^{2+}] = 0.1 \text{ M}$

$$E_{\text{red}} = 0.34 + \frac{0.0591}{2} \log_{10} [0.1]$$

$$= 0.34 + 0.02955 \times (-1)$$

$$= 0.34 - 0.02955 = 0.31045 \text{ volt}$$

Example 38. What is the single electrode potential of a half-cell for zinc electrode dipping in 0.01 M ZnSO_4 solution at 25°C ? The standard electrode potential of Zn/Zn^{2+} system is 0.763 volt at 25°C .

Solution: We know that, $E_{\text{ox}} = E_{\text{ox}}^\circ - \frac{0.0591}{n} \log_{10} [\text{ion}]$

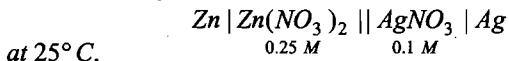
Putting the value of $E_{\text{ox}}^\circ = 0.763 \text{ V}$, $n = 2$ and $[\text{Zn}^{2+}] = 0.01 \text{ M}$,

$$E_{\text{ox}} = 0.763 - \frac{0.0591}{2} \log_{10} [0.01]$$

$$= 0.763 - 0.02955 \times (-2)$$

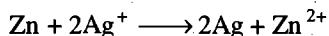
$$= (0.763 + 0.0591) \text{ volt} = 0.8221 \text{ volt}$$

Example 39. The standard oxidation potential of zinc is 0.76 volt and of silver is -0.80 volt. Calculate the emf of the cell:



at 25°C .

Solution: The cell reaction is



$$E_{\text{ox}}^\circ \text{ of Zn} = 0.76 \text{ volt}$$

$$E_{\text{red}}^\circ \text{ of Ag} = -0.80 \text{ volt}$$

$$E_{\text{cell}}^\circ = E_{\text{ox}}^\circ \text{ of Zn} + E_{\text{red}}^\circ \text{ of Ag} = 0.76 + 0.80 = 1.56 \text{ volt}$$

$$\text{We know that, } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{0.25}{0.1 \times 0.1}$$

$$= 1.56 - \frac{0.0591}{2} \times 1.3979$$

$$= (1.56 - 0.0413) \text{ volt}$$

$$= 1.5187 \text{ volt}$$

Alternative method: First of all, the single electrode potentials of both the electrodes are determined on the basis of given concentrations.

$$E_{\text{ox}} \text{ (Zinc)} = E_{\text{ox}}^\circ - \frac{0.0591}{2} \log 0.25$$

$$= 0.76 + 0.0177 = 0.7777 \text{ volt}$$

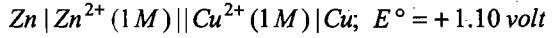
$$E_{\text{red}} \text{ (Silver)} = E_{\text{red}}^\circ + \frac{0.0591}{1} \log 0.1$$

$$= 0.80 - 0.0591 = 0.7409 \text{ volt}$$

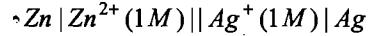
$$E_{\text{cell}} = E_{\text{ox}} \text{ (Zinc)} + E_{\text{red}} \text{ (Silver)}$$

$$= 0.7777 + 0.7409 = 1.5186 \text{ volt}$$

Example 40. The emf (E°) of the following cells are:



Calculate the emf of the cell:



$$E_{\text{cell}} = E_{\text{ox}} \text{ (Zn/Zn}^{2+}) + E_{\text{red}} \text{ (Ag}^+/\text{Ag})$$

With the help of the following two cells, the above equation can be obtained:



or $\text{Cu} | \text{Cu}^{2+}(1 \text{ M}) \parallel \text{Ag}^+(1 \text{ M}) | \text{Ag}; \quad E^\circ$ will be +0.46 volt