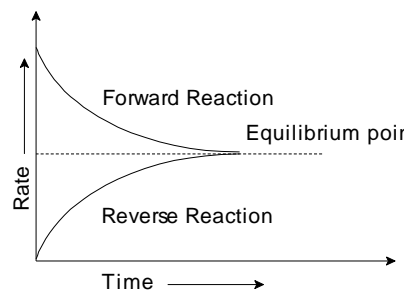
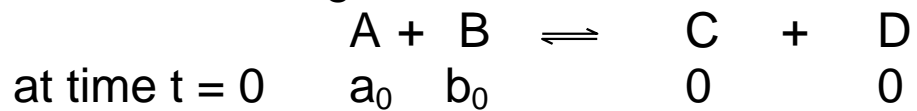


CONCEPT OF CHEMICAL EQUILIBRIUM

Let we have a general reversible reaction,



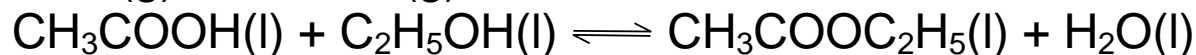
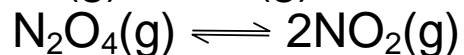
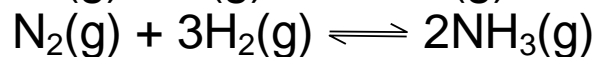
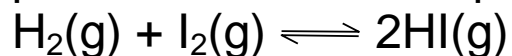
Characteristics of Chemical Equilibrium

- The equilibrium is dynamic i.e. the reaction continues in both forward and reverse directions. The rate of forward reaction equals to the rate of reverse reaction.
- The observable properties of the system such as pressure, concentration, density remains invariant with time.
- The chemical equilibrium can be approached from either side.
- A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium.

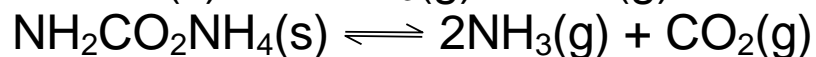
Types of Equilibria

There are mainly two types of equilibria:

- (a) **Homogeneous:** Equilibrium is said to be homogeneous if reactants and products are in same phase.

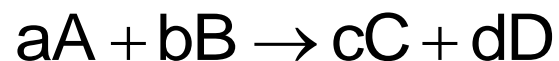


- (b) **Heterogeneous:** Equilibrium is said to be heterogeneous if reactants and products are in different phases



LAW OF MASS ACTION

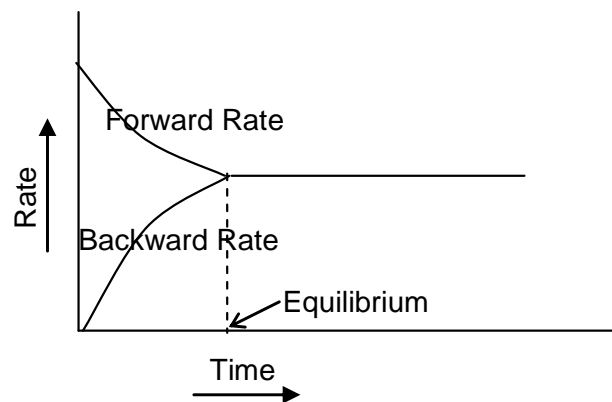
Guldberg and Waage established a relationship between rate of chemical reaction and the concentration of the reactants or, with their partial pressure in the form of law of mass action.



$$\text{rate of reaction} \propto [A]^a \cdot [B]^b$$

$$\text{rate of reaction} = K[A]^a[B]^b$$

Unit of rate constant (K) = $[\text{moles/lit}]^{1-n} \text{time}^{-1}$ (where n is order of reaction.)



Note:

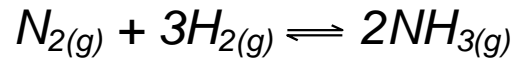
Active mass is the molar concentration of the reacting substances actually participating in the reaction.

Hence

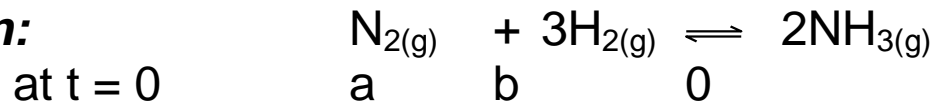
$$\text{Active mass} = \frac{\text{number of moles}}{\text{volume in litres}}$$

Active mass of solid is taken as unity.

Eg. 1. Calculate the partial pressure of each component in the following equilibria



Solution:



$$n_{\text{total}} = a - x + b - 3x + 2x = (a + b - 2x)$$

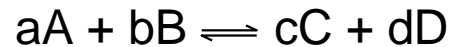
Partial pressure:

$$P_{N_2} = \frac{n_{N_2}}{n_T} \times P_T = \frac{(a - x)}{(a + b - 2x)} \times P_T$$

$$P_{H_2} = \frac{n_{H_2}}{n_T} \times P_T = \frac{(b - 3x)}{(a + b - 2x)} \times P_T$$

$$P_{NH_3} = \frac{n_{NH_3}}{n_T} \times P_T = \frac{2x}{(a + b - 2x)} \times P_T$$

Law of Chemical Equilibrium



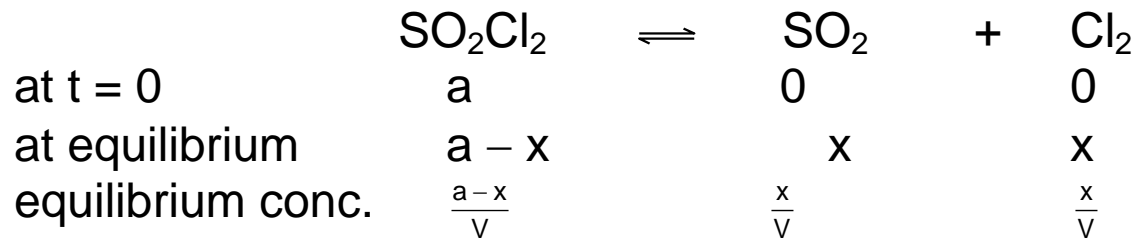
then, from Law of mass action

$$\Rightarrow K_1 [A]^a [B]^b = K_2 [C]^c [D]^d$$

$$\Rightarrow \frac{K_1}{K_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$K_c = K_1/K_2$, an equilibrium constant in terms of active masses of reacting species.

For the reaction

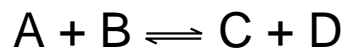


So, $[\text{SO}_2\text{Cl}_2] = \frac{a-x}{V}$; $[\text{SO}_2] = \frac{x}{V} = [\text{Cl}_2]$

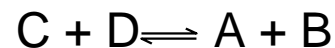
So, $K_c = \frac{\left(\frac{x}{V}\right) \times \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V} \Rightarrow K_c = \frac{x^2}{(a-x) \times V}$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT (K_c)

- (i) K_c for a particular reaction at given temperature has a constant value.
- (ii) Value of K_c always depends on nature of reactants and the temperature, but independent of presence of catalyst or, of inert material.
- (iii) Its value is always independent of the initial concentration of reactants as well as the products.
- (iv) The value of K_c indicates the proportion of products/product formed at equilibrium. Large K_c value means large proportions of product.
- (v) When the reaction is reversed, equilibrium constant for reverse reaction will also be inversed. $K'_c = \frac{1}{K_c}$

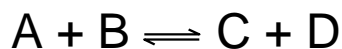


$$K_c = \frac{[C][D]}{[A][B]}$$



$$K'_c = \frac{[A][B]}{[C][D]} = \frac{1}{K_c}$$

- (vi) If the coefficients of reactants of products are halved or, doubled then accordingly, value of K'_c will change.

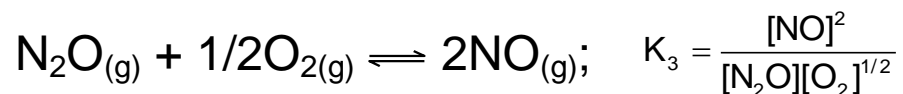
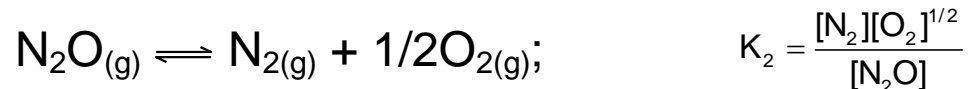
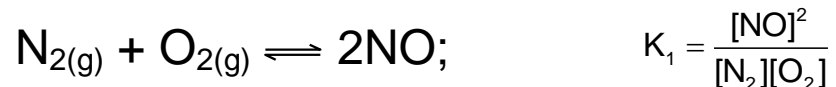


$$K_c = \frac{[C][D]}{[A][B]}$$

for $2A + 2B \rightleftharpoons 2C + 2D$

$$K'_c = \frac{[C]^2[D]^2}{[A]^2[B]^2} = \left\{ \frac{[C][D]}{[A][B]} \right\}^2 = K_c^2$$

(vii) When a number of equilibrium reactions are added, the equilibrium constant, for overall reaction is the product of equilibrium constants of respective reactions.

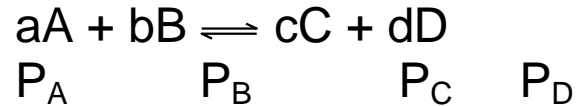


$$\frac{K_3}{K_2} = \frac{[NO]^2}{[N_2O][O_2]^{1/2}} \times \frac{[N_2O]}{[N_2][O_2]^{1/2}} = \frac{[NO]^2}{[N_2][O_2]} = K_1$$

i.e. $\frac{K_3}{K_2} = K_1$

Equilibrium constant in terms of partial pressures

Let us consider a general reaction



$$\Rightarrow K_p = \frac{K_1}{K_2} = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

RELATION BETWEEN K_p AND K_c

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{\{(c+d)-(a+b)\}}$$

Where $\Delta n_g = \{(c + d) - (a + b)\}$ = change in the numbers of gaseous moles.

Hence,

$$K_p = K_c \cdot (RT)^{\Delta n_g}$$
$$\Delta n > 0; \quad K_p > K_c$$

$$\text{When } \Delta n = 0; \quad K_p = K_c$$
$$\Delta n < 0; \quad K_p < K_c$$

Note:

Similarly we can find equilibrium constant (K_x) in terms of mole fraction and can find out its relation with K_p and K_c .

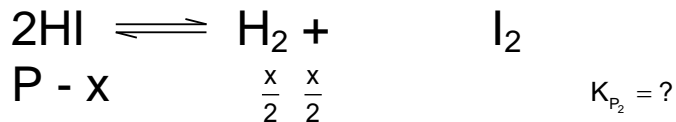
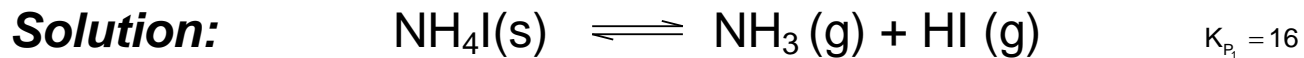
Eg. 2. At 27°C K_p value for reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 0.1 atm, calculate its K_c value.

Solution:

$$K_p = K_c(RT)^{\Delta n}$$
$$\Delta n = 1$$
$$K_c = \frac{K_p}{RT} = \frac{0.1}{0.082 \times 300} = 4 \times 10^{-3}$$

Eg. 3. Solid NH_4I dissociates according to the reaction at 400 K

$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$; $K_p = 16 \text{ atm}$. In presence of catalyst HI dissociates in H_2 and I_2 as $2HI \rightleftharpoons H_2 + I_2$. If partial pressure of H_2 at this temp is 1 atm in the container when both the equilibrium exist simultaneously, calculate K_p value of second equilibrium (for the dissociation of HI).



Here $\frac{x}{2} = 1 \text{ atm}$

$\therefore x = 2 \text{ atm}$

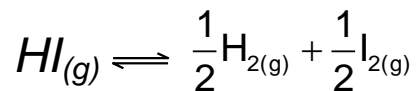
$P(P - 2) = 16$

$\therefore P = 5.1$

Eg. 4. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on addition of graphite. What is the value of K_p if the total pressure at equilibrium is 0.8 atm?



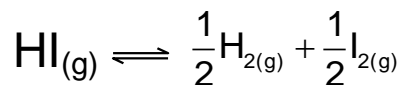
Eg. 5. Given that the equilibrium constant for the reaction, $\text{H}_{2(\text{g})} + \text{I}_{2(\text{g})} \rightleftharpoons 2\text{HI}_{(\text{g})}$ is 50 at 700K. Calculate the equilibrium constant for the reaction.



Solution: We have $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 50$$

The new equilibria is



$$K'_c = \frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]} = \frac{1}{\sqrt{K_c}}$$

$$= \frac{1}{\sqrt{50}} = \frac{\sqrt{2}}{10} = 0.141$$

Eg. 6. One mole of N_2 is mixed with 3 moles of H_2 in a 4 litre container. If 25% of N_2 is converted into NH_3 by the following reaction

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. Calculate K_c and K_p of the reaction. (Temperature = 227°C and $R = 0.08231$).

Solution: We have $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Percentage N_2 reacted, 25%

$$\therefore x = 0.25$$

$$\text{Now, } (a - x) = 1 - 0.25 = 0.75$$

$$b - 3x = 3 - 0.75 = 2.25$$

$$\therefore \frac{(a-x)}{V} = \frac{0.75}{4} = 0.1875$$

$$\left(\frac{b-3x}{V}\right) = \frac{2.25}{4} = 0.5625$$

$$\left(\frac{2x}{V}\right) = \frac{0.50}{4} = 0.125$$

$$\therefore K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.125)^2}{(0.1875)(0.5625)^3}$$

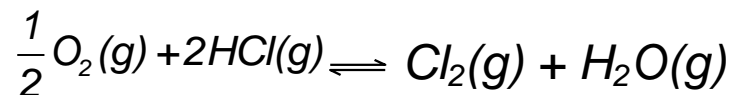
$$= 1.48 \times 10^{-5} \text{ L}^2 \text{ mol}^{-2}$$

$$\text{Now, } K_p = K_c \cdot (RT)^{\Delta n} = 1.48 \times 10^{-5} \times [0.0821 \times (227 + 273)]^2$$

$$\frac{1.48 \times 10^{-5}}{\{0.082 \times (500)\}^2}$$

$$= 8.78 \times 10^{-9}$$

Eg. 7. The value of K_p for the reaction $2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g) \rightleftharpoons 4\text{HCl}(g) + \text{O}_2(g)$ is 0.035 atm at 400°C , when the partial pressures are expressed in atmosphere. Calculate K_c for the reaction,



Solution: $K_P = K_C (RT)^{\Delta n}$

$$\Delta n = \text{moles of product} - \text{moles of reactants} = 5 - 4 = 1$$

$$R = 0.082 \text{ L atm/mol K,}$$

$$T = 400 + 273 = 673 \text{ K}$$

$$\therefore 0.035 = K_C (0.082 \times 673)$$

$$K_C = 6.342 \times 10^{-4} \text{ mol l}^{-1}$$

$$\therefore K'_C \text{ for the reverse reaction would be } \frac{1}{K_C}.$$

$$\therefore K'_C = \frac{1}{6.342 \times 10^{-4}} = 1576.8 \text{ (mol l}^{-1}\text{)}^{-1}$$

When a reaction is multiplied by any number n (integer or a fraction) the K'_C or K'_P becomes $(K_C)^n$ or $(K_P)^n$ of the original reaction.

$$\therefore K_C \text{ for } \frac{1}{2}O_2(g) + 2HCl(g) \rightleftharpoons Cl_2(g) + H_2O(g)$$

$$\text{is } \sqrt{1576.8} = \mathbf{39.7 \text{ (mol.l}^{-1}\text{)}^{-1/2}}$$

Eg. 8. K_p for the equilibrium, $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ at 1000°C is 0.4. If $CO(g)$ at a pressure of 1 atm and excess $FeO(s)$ are placed in a container at 1000°C , what are the pressures of $CO(g)$ and $CO_2(g)$ when equilibrium is attained?

Solution: Assuming ideal gas behaviour, partial pressures are proportional to the no. of moles present. Since moles of CO₂ formed equals moles of CO consumed, the drop in partial pressure of CO will equal the partial pressure of CO₂ produced. Let the partial pressure of CO₂ at equilibrium be 'x' atm. Then, partial pressure of CO will be (1 - x) atm.

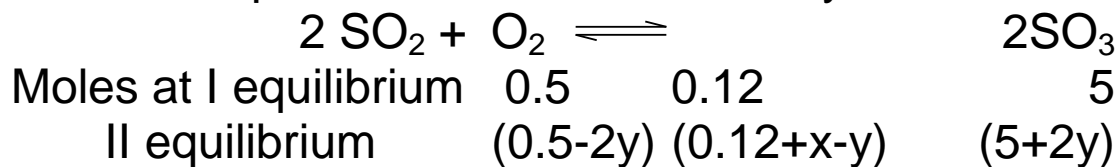
$$\text{Since } K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{x}{1-x} = 0.4 \Rightarrow x = 0.286$$

$$\begin{aligned} \text{Hence } P_{\text{CO}} &= 1-x \\ &= \mathbf{0.714 \text{ atm.}} \end{aligned}$$

Eg. 9. At 800 K a reaction mixture contained 0.5 mole of SO₂, 0.12 mole of O₂ and 5 mole of SO₃ at equilibrium. K_c for the equilibrium 2SO₂ + O₂ ⇌ 2SO₃ is 833 lit/ mole. If the volume of the container is 1 litre, calculate how much O₂ is to be added at this equilibrium in order to get 5.2 moles of SO₃ at the same temperature.

Solution: Suppose x mole of O₂ is added by which equilibrium shifts to right hand side and y mole of O₂ changes to SO₃.

The new equilibrium concentration may be



$$5 + 2y = 5.2$$

$$\therefore y = 0.1$$

$$\begin{aligned}
 K_c &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(5+2y)^2}{(0.5-2y)^2 (0.12+x-y)} \\
 &= 833
 \end{aligned}$$

Substituting y = 0.1 (V = 1 lit)

We get x = 0.34 mole

THE REACTION QUOTIENT 'Q'

Consider the equilibrium



At equilibrium $\frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]} = K_C$. When the reaction is not at equilibrium this ratio is called 'Q_C' i.e., Q_C is the general term used for the above given ratio at any instant of time. And at equilibrium Q_C becomes K_C.

Similarly, $\frac{P_{\text{Cl}_2} P_{\text{PCl}_3}}{P_{\text{PCl}_5}}$ is called Q_P and at equilibrium it becomes K_P.

- If the reaction is at equilibrium, Q = K_C
- A net reaction proceeds from left to right (forward direction) if Q < K_C.
- A net reaction proceeds from right to left (the reverse direction) if Q > K_C

Eg. 10. For the reaction,

$A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$ at 25°C, in a 2 litre vessel contains 1, 2, 3 moles of respectively. Predict the direction of the reaction if

- K_C for the reaction is 3
- K_C for the reaction is 6
- K_C for the reaction is 4.5

Solution: $A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$

$$\text{Reaction quotient } Q = \frac{[C]^2}{[A][B]} = \frac{\left(\frac{3}{2}\right)^2}{\frac{1}{2} \times \frac{2}{2}} = \frac{9}{2} = 4.5$$

- (a) $\therefore Q > K_c$, therefore backward reaction will be followed
(b) $\therefore Q < K_c$
 \therefore The forward reaction is followed
(c) $Q = K_c$
 \therefore The reaction is at equilibrium

Eg. 11. For the reaction : $A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(aq)} + D_{(aq)}$, the net rate of consumption of B at 25°C and at any time 't' is as given below

$$-\frac{d[B]}{dt} = \{4 \times 10^{-4} [A] [B] - 1.33 \times 10^{-5} [C] [D]\} \text{ mol L}^{-1} \text{ min}^{-1}$$

Predict whether the reaction will be spontaneous in the direction as written in reaction mixture in which each A, B, C and D is having a concentration of 1 mol L^{-1} ?

Solution: $K = \frac{K_1}{K_2}$
 $= \frac{4 \times 10^{-4}}{1.33 \times 10^{-5}} = 30$

$$Q = \frac{[C][D]}{[A][B]}$$
$$= \frac{1 \times 1}{1 \times 1} = 1 < K$$

Since $Q < K$, so the above reaction is spontaneous in the forward direction.

LE CHATELIER'S PRINCIPLE

“When an equilibrium is subjected to either a change in concentration, temperature or, in external pressure, the equilibrium will shift in that direction where the effects caused by these changes are nullified”.

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Effect of Concentration

Temperature Effect

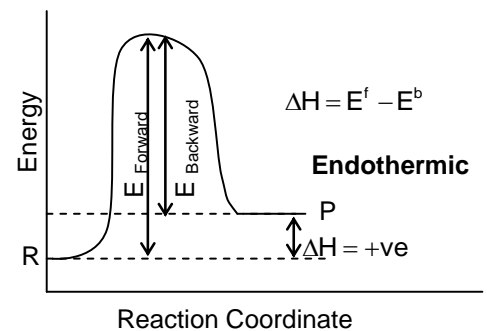
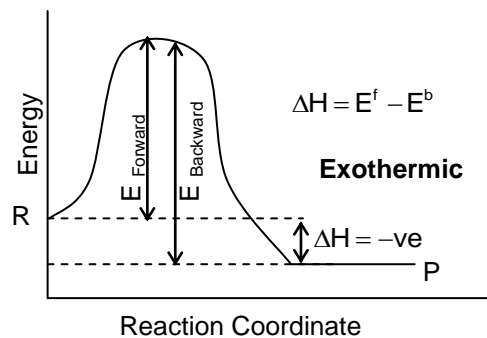
The effect of change in temperature on an equilibrium cannot be immediately seen because on changing temperature the equilibrium constant itself changes. So first we must find out as to how the equilibrium constant changes with temperature.

According to the Arrhenius equation,

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

From the equation,

$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ it is clear that



R = Reactant, P = Product

Eg. 12. Under what conditions will the following reactions go in the forward direction?

- (i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 23 \text{ k cal.}$
- (ii) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 45 \text{ k cal.}$
- (iii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43.2 \text{ k cal.}$
- (iv) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) + 27.8 \text{ k cal.}$
- (v) $C(s) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) + X \text{ k cal.}$
- (vi) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - X \text{ k cal.}$
- (vii) $N_2O_4(g) \rightleftharpoons 2NO_2(g) - 14 \text{ k cal.}$

Solution:

- (i) Low T, High P, excess of N_2 and H_2 .
- (ii) Low T, High P, excess of SO_2 and O_2 .
- (iii) High T, any P, excess of N_2 and O_2
- (iv) Low T, High P, excess of NO and O_2
- (v) Low T, Low P, excess of C and H_2O
- (vi) High T, Low P, excess of PCl_5
- (vii) High T, Low P, excess of N_2O_4 .

Eg. 13. The equilibrium constant K_p for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is $1.6 \times 10^{-4} \text{ atm}^{-2}$ at 400°C . What will be the equilibrium constant at 500°C if heat of the reaction in this temperature range is -25.14 k cal ?

Solution: Equilibrium constants at different temperature and heat of the reaction are related by the equation, $\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

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

$$\log K_{P_2} = \frac{-25140}{2.303 \times 2} \left[\frac{773 - 673}{773 \times 673} \right] + \log 1.64 \times 10^{-4}$$

$$\log K_{P_2} = -4.835$$

$$\therefore K_{P_2} = 1.462 \times 10^{-5} \text{ atm}^{-2}$$

Effect of change of Pressure

The effect of change of pressure on chemical equilibrium can be done by the formula.

$$K_p = Q_p \times P^{(\Delta n)}$$

Case A: When $\Delta n = 0$

$$K_p = Q_p$$

And equilibria is independent of pressure.

Case B: When $\Delta n = -ve$

$$K_p = Q_p \cdot P^{-\Delta n} = \frac{Q_p}{P^{\Delta n}}$$

Here with increase in external pressure, will shift the equilibrium towards forward direction to maintain K_p . Similarly, decrease in pressure will shift the equilibrium in the reverse direction.

Case C: When $\Delta n = +ve$

$$K_p = Q_p \cdot P^{\Delta n} \text{ and, effect will be opposite to that of Case 'B'}$$

EFFECT OF CATALYST ON EQUILIBRIUM

Since the catalyst is associated with forward as well as reverse direction reaction. So, at equilibrium, rate of forward reaction will be equal to rate of reverse reaction and hence catalyst effect will be same on both forward as well as reverse. Hence catalyst never effect the point of equilibrium but it reduces the time to attain the equilibrium.

Effect on equilibrium due to the addition of inert gases

Following are the cases, where this effect in different manner.

Case A: When $\Delta n = 0$ and total volume change at equilibrium remain constant.

So, addition of inert gases will increase the number of moles in the mixture but partial pressure of each component remains constant. Hence equilibrium remains unaffected.

Case B: When $\Delta n = +ve$ and $\Delta V_T \neq 0$

The total volume will increase with addition of inert gases. This will shift the equilibrium in forward direction.

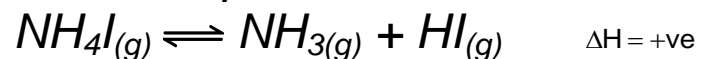
Case C: When $\Delta n = -ve$ and $\Delta V_T \neq 0$

In this case, the addition of inert gases will increase the total volume and the reaction will shift in reverse direction.

Dependence of K_p or K_c on Temperature

With the increase of temperature, equilibrium favours forward reaction in case of an endothermic ($\Delta H > 0$) reaction while it favours backward reaction in the case of an exothermic ($\Delta H < 0$) reaction.

Eg. 14. For the equilibrium



What will be the effect on the equilibrium constant on increasing the temperature.

Solution: Since the forward reaction is endothermic, so increasing the temperature, the forward reaction is favoured. Thereby the equilibrium constant will increase.

Eg. 15. K_p for the reaction $2\text{BaO}_{2(s)} \rightleftharpoons 2\text{BaO}_{(s)} + \text{O}_{2(g)}$ is 1.6×10^{-4} atm, at 400°C . Heat of reaction is -25.14 kcal. What will be the no. of moles of O_2 gas produced at 500°C temperature, if it is carried in 2 litre reaction vessel?

Solution: We know that

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{K_{p_2}}{1.6 \times 10^{-4}} = \frac{-25.14}{2.330 \times 2 \times 10^{-3}} \left[\frac{773 - 673}{773 \times 673} \right]$$

$$\Rightarrow K_{p_2} = 1.46 \times 10^{-5} \text{ atm}$$

$$\therefore K_{p_2} = p_{\text{O}_2} = 1.46 \times 10^{-5} \text{ atm}$$

Since, $PV = nRT$

$$1.46 \times 10^{-5} \times 2 = n \times 0.0821 \times 773$$

$$\therefore n = \frac{1.46 \times 10^{-5} \times 2}{0.0821 \times 773} = 4.60 \times 10^{-7}$$

Standard Free Energy Change of a Reaction and its Equilibrium Constant

$\Delta G^0 = - 2.303 RT \log K_c$ and $\Delta G^0 = - 2.303 RT \log K_p$ (in case of ideal gases)

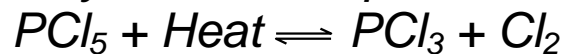
Now, we know that thermodynamically,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

here ΔH^0 is standard enthalpy of reaction, and ΔS^0 is standard entropy change

- (i) When $\Delta G^0 = 0$, then, $K_c = 1$
- (ii) When, $\Delta G^0 > 0$, i.e. +ve, then $K_c < 1$, in this case reverse reaction is feasible showing thereby a less concentration of products at equilibrium rate.
- (iii) When $\Delta G^0 < 0$, i.e. -ve, then, $K_c > 1$; In this case, forward reaction is feasible showing thereby a large concentrations of product at equilibrium state.

Eg. 16. A system is in equilibrium as



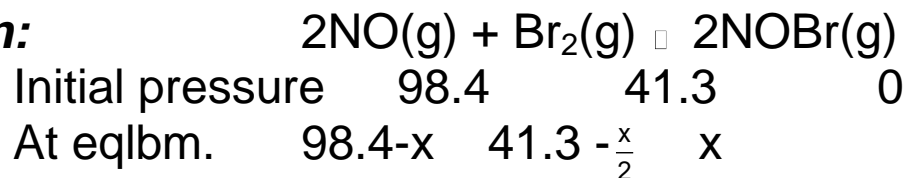
Why does the temperature of the system decrease, when PCl_3 are being removed from the equilibrium mixture at constant volume?

Solution: When PCl_3 are being removed from the system, the reaction moves to the right. This consumes heat and therefore, temperature is decreased.

Eg. 17. *NO and Br₂ at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300K. At equilibrium the total pressure was 110.5 torr.*

Calculate the value of the equilibrium constant and the standard free energy change at 300K for the reaction $2\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{NOBr}(\text{g})$.

Solution:



The total pressure at equilibrium is 110.5 torr.

$$\therefore 98.4-x + 41.3 - \frac{x}{2} + x = 110.5$$

$$x = 58.4 \text{ torr}$$

Now, 1 atm = 760.4 torr,

$$\therefore x = 7.68 \times 10^{-2} \text{ atm.}$$

$$p_{\text{NOBr}} = 7.68 \times 10^{-2} \text{ atm} ; \quad p_{\text{NO}} = 98.4-x = 40 \text{ torr} = 5.26 \times 10^{-2} \text{ atm.}$$

$$p_{\text{Br}_2} = 41.3 - \frac{x}{2} = 12.1 \text{ torr} = 1.59 \times 10^{-2} \text{ atm.}$$

$$K_p = \frac{[p_{\text{NOBr}}]^2}{[p_{\text{NO}}]^2 [p_{\text{Br}_2}]} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})^2 (1.59 \times 10^{-2})} = 134 \text{ atm}^{-1}$$

$$\Delta G^\circ = -2.303 RT \log K = -2.303 (1.99) (300) (\log 134)$$

$$= -2.92 \text{ k cal} = -12.2 \text{ kJ.}$$

[If R is used as 1.99 cal/mol K , then ΔG° will be in cal. If R is used as 8.314 J/mol K , then ΔG° will be in Joules. But K_p must always be in $(\text{atm})^{\Delta n}$.]

Dependence of Degree of Dissociation on Density Measurements

For a reaction at equilibrium V is a constant and ρ is a constant. \therefore vapour

Density $\propto \frac{1}{n}$

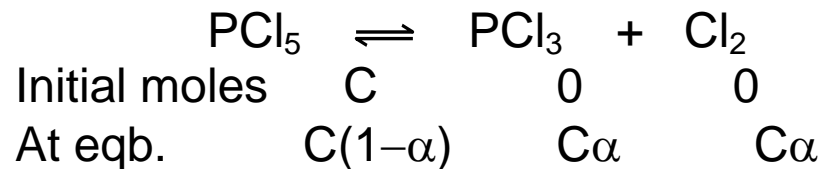
$$\therefore \frac{\text{Total moles at equilibrium}}{\text{Initial total moles}} = \frac{\text{vapour density initial}}{\text{vapour density at equilibrium}} = \frac{D}{d} = \frac{M}{m}$$

(\because molecular weight = $2 \times \text{V.D}$)

Here M = molecular weight initial

m = molecular weight at equilibrium

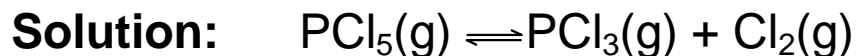
Let us take a reaction



$$\therefore \frac{C(1+\alpha)}{C} = \frac{D}{d}; \quad 1+\alpha = \frac{D}{d} = \frac{M}{m}$$

Knowing D and d , α can be calculated and so for M and m .

Eg. 18. When PCl_5 is heated it dissociates into PCl_3 and Cl_2 . The density of the gas mixture at 200°C and at 250°C is 70.2 and 57.9 respectively. Find the degree of dissociation at 200°C and 250°C .



We are given the vapour densities at equilibrium at 200°C and 250°C .

The initial vapour density will be the same at both the temperatures as it would be $\frac{M_{\text{PCl}_5}}{2}$.

$$\therefore \text{Initial vapour density} = \frac{(31 + 5 \times 35.5)}{2} = 104.25$$

Vapour density at equilibrium at $200^\circ\text{C} = 70.2$

$$\begin{aligned} \therefore \frac{\text{Total moles at equilibrium}}{\text{Total moles initial}} &= 1 + \alpha = \frac{\text{Vapour density initial}}{\text{Vapour density at equilibrium}} \\ &= \frac{104.25}{70.2} = 1.485 \end{aligned}$$

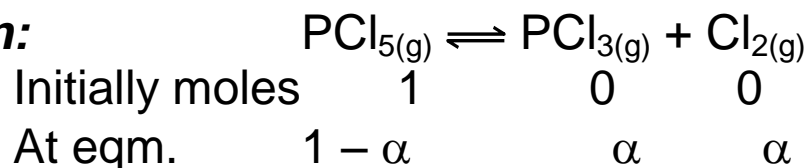
$$\therefore \alpha = 0.485$$

$$\text{At } 250^\circ\text{C}, \quad 1 + \alpha = \frac{104.25}{57.9} = 1.8$$

$$\therefore \alpha = 0.8$$

Eg. 19. The degree of dissociation of PCl_5 is 60%, then find out the observed molar mass of the mixture.

Solution:



Where α = degree of dissociation = 0.6

Total moles at equilibrium = $1 + \alpha$ = observed mole

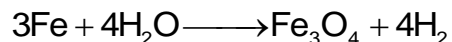
$$\frac{\text{observed moles}}{\text{Theoretical moles}} = \frac{\text{molecular weight theoretical}}{\text{molecular weight observed}}$$

$$\Rightarrow \frac{1 + \alpha}{1} = \frac{206.5}{\text{molecular weight observed}}$$

$$\Rightarrow \text{molecular weight observed} = \frac{206.5}{1 + \alpha} = \frac{206.5}{1.6} = 129.06$$

Objective:

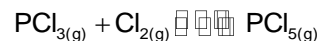
Prob 1. Reaction between iron and steam is reversible if it is carried out



- (A) at constant T (B) at constant P
(C) in an open vessel (D) in a closed vessel

Sol. In open vessel H_2 gas will escape.
 \therefore (D)

Prob 2. For the reaction



The value of K_c at 250°C is 26. The value of K_p at this temperature will be

- (A) 0.61 (B) 0.57
(C) 0.83 (D) 0.46

Sol. $K_p = K_c (\text{RT})^{\Delta n} = 26 \times (0.082 \times 523)^{-1} = 0.61$
 \therefore (A)

Prob 3. In a reversible reaction, two substances are in equilibrium. If the concentration of each one is doubled, the equilibrium constant will be
(A) Reduced to half, its original value
(B) becomes (original)/4
(C) doubled
(D) constant

Sol. K_c or K_p do not depend on concentration, but only on temperature.
 \therefore (D)

Prob 4. The equilibrium constant for the reaction,



In presence of a catalyst, equilibrium is attained ten times faster.
Therefore, the equilibrium constant, in presence of the catalyst at 2000K is

- (A) 40×10^{-4} (B) 4×10^{-4}
(C) 4×10^{-5} (D) difficulty to compute

Sol. Equilibrium is constant at constant temperature for a reaction
 \therefore (B)

Prob 5. 64g of HI are present in a 2 litre vessel. The active mass of HI is:

- (A) 0.5 (B) 0.25
(C) 1 (D) none

Sol. Molecular mass of HI = 128

$$[\text{HI}] = [\text{HI}] = \frac{64}{128} \times \frac{1}{2} = 0.25$$

∴ (B)

Prob 6. For which of the following K_p may be equal to 0.5 atm

- (A) $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ (B) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$
(C) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ (D) $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$

Sol. For $K_p = 0.5$ atm

$\Delta n = 1$ (since the unit is atm)

and $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

$\Delta n = 1$

∴ (B)

Prob 7. 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 at the final temperature is

- (A) 80 (B) 60
(C) 40 (D) 70

Sol. $N_2O_4 \rightleftharpoons 2NO_2$
 1 0 at initial
 $1 - \alpha$ 2α at equilibrium

$$\therefore \frac{V.D._{initial}}{V.D._{final}} = \frac{n_{final}}{n_{initial}}$$

$$\frac{46}{25.4} = \frac{1 + \alpha}{1}$$

$$1.8 = 1 + \alpha \Rightarrow \alpha = 0.8 \text{ or } 80\%$$

\therefore (A)

Prob 8. If pressure is applied to the following equilibrium, liquid \rightleftharpoons vapours the boiling point of liquid

- (A) will increase (B) will decrease
(C) may increase or decrease (D) will not change

Sol. Boiling point of a liquid is the temperature at which vapour pressure became equal to atm pressure. If the pressure is applied to the above equilibrium the reaction will go to the backward direction, i.e. vapour pressure decrease hence the boiling point increase.

∴ **(A)**

Prob 9. For the reaction

$A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)}$ at 250°C , a 3 litre vessel contains 1, 2, 4 mole of A, B and C respectively. If K_C for the reaction is 10, the reaction will proceed in

(A) Forward direction (B) Backward direction

(C) In either direction (D) In equilibrium

Sol.
$$Q = \frac{[C]^3}{[A][B]} = \frac{4^3 \times 3 \times 3}{3^3 \times 1 \times 2} = 10.66$$

∴ $[C] = \frac{4}{3}$

$[A] = \frac{1}{3} \Rightarrow [B] = \left(\frac{2}{3}\right) \because K_C = 10, \text{ and } Q > K_C$

∴ reaction will proceed in backward direction

∴ **(B)**

Prob 10. If $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}_{(s)} + 2\text{H}_2\text{O}_{(l)}$ $K_p = 1.086 \times 10^{-4} \text{ atm}^2$ at 25°C . The efflorescent nature of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can be noticed when vapour pressure of H_2O in atmosphere is

- (A) $> 7.29 \text{ mm}$ (B) $< 7.92 \text{ mm}$
 (C) $\geq 7.92 \text{ mm}$ (D) None

Sol. An efflorescent salt is one that loses H_2O to atmosphere.

For the reaction



$$K_p = (p'_{\text{H}_2\text{O}})^2 = 1.086 \times 10^{-4}$$

$$p'_{\text{H}_2\text{O}} = 1.042 \times 10^{-2} \text{ atm} = 7.92 \text{ mm}$$

\therefore If $p'_{\text{H}_2\text{O}}$ at $25^\circ\text{C} < 7.92 \text{ mm}$ only then, reaction will proceed in forward direction.

\therefore **(B)**

Prob 11. The enthalpies of two reaction are ΔH_1 and ΔH_2 (both positive) with $\Delta H_2 > \Delta H_1$. If the temperature of reacting system is increased from T_1 to T_2 , predict which of the following alternatives is correct?

- (A) $\frac{K'_1}{K_1} = \frac{K'_2}{K_2}$ (B) $\frac{K'_1}{K_1} > \frac{K'_2}{K_2}$

$$(C) \frac{K'_1}{K_1} < \frac{K'_2}{K_2}$$

(D) None

Sol. As the temperature of reacting system is increased the equilibrium constant of reaction is also increased for endothermic reactions so for two reactions on increasing the temperature by equal amounts

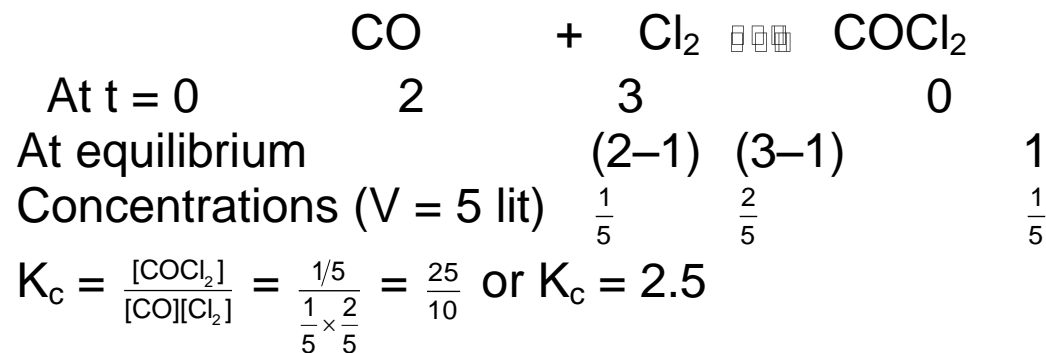
$$\frac{K'_1}{K_1} < \frac{K'_2}{K_2}$$

Hence, **(C)** is correct.

Prob 12. At a certain temperature 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ in a 5 lit vessel. At equilibrium if one mole of CO is present then equilibrium constant for the reaction is:

- (A) 2 (B) 2.5
(C) 3.0 (D) 4

Sol.



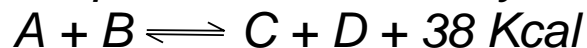
Hence, **(B)** is correct.

Prob 13. The reaction: $3\text{O}_2 \rightleftharpoons 2\text{O}_3$, $\Delta H = + 69,000$ calories is favoured by:

- (A) high temperature and low pressure (B) high temperature and high pressure
(C) low temperature and high pressure (D) low temperature and low pressure

Sol. According to Le Chatalier principle formation of ozone is favoured by high temperature (endothermic reaction) and high pressure. Hence, **(B)** is correct.

Prob 14. The equilibrium constant at 323°C is 1000. What would be its value in the presence of a catalyst in the forward reaction?



- (A) $1000 \times \text{concentration of catalyst}$ (B) 1000
(C) $\frac{1000}{\text{concentration of catalyst}}$ (D) impossible to tell

Sol. The equilibrium constant varies only with temperature. At constant temperature it will not vary. Hence, **(B)** is correct.

Prob 15. Which of the following reactions represent a heterogenous equilibrium?



Sol. In heterogenous equilibrium, physical state of all the reactants and products are not same.
Hence, **(B)** is correct.

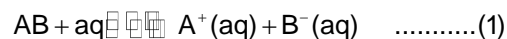
DEGREE OF IONISATION 'α'

$$\alpha = \frac{\text{Number of molecules dissociated as ions}}{\text{Total number of molecules dissolved}}$$

$$= \frac{\text{Number of moles dissociated}}{\text{Total number of moles dissolved}}$$

Ostwald dilution law (Ionisation of weak electrolytes)

It is the law of mass action as applied to weak electrolytes like CH_3COOH , NH_4OH , HCN , etc.



Initial conc.

when $t = 0$ C 0 0

Conc. at

equilibrium C - Cα Cα Cα

Apply the law of mass action to equilibrium (1)

$$K = \frac{[\text{A}^+(\text{aq})][\text{B}^-(\text{aq})]}{[\text{AB}]}$$

$$= \frac{C\alpha \times C\alpha}{[C - C\alpha]}$$

$$= \frac{C\alpha^2}{1 - \alpha}$$

For weak electrolyte, $\alpha \ll 1, \Rightarrow 1 - \alpha \approx 1$ i.e. $\alpha < 5\%$

$$K = C\alpha^2$$

or $\alpha = \sqrt{\frac{K}{C}} \quad \dots\dots\dots (2)$

If one mole of electrolyte is dissolved in V litre of solution i.e. $c = \frac{1}{V}$

$$\alpha = \sqrt{KV} \dots \dots \dots (3)$$

Thus “**degree of dissociation of a weak electrolyte is proportional to the square root of dilution**”. This is called Ostwald law.

Note:

If $\alpha > 5\%$ then we can not neglect α from denominator.

$$K = \frac{C\alpha^2}{(1-\alpha)}$$

α can be calculate by quadratic equation ($ax^2 + bx + c = 0$)

$$C\alpha^2 - (1-\alpha)K = 0$$

$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

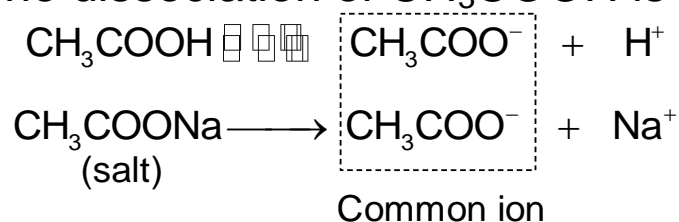
Here $b = -(1-\alpha)$

$a = C$ and $c = 0$

COMMON ION EFFECT

“The degree of dissociation of weak electrolyte is suppressed by the addition of strong electrolyte containing a common ion is called common ion effect”.

Example: To the solution of weak acid CH_3COOH if its salt CH_3COONa is added. The dissociation of CH_3COOH is suppressed.



Eg. 1. Give reason that acetic acid is less acidic in sodium acetate solution than in sodium chloride solution.

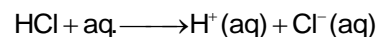
Solution: Ionisation of acetic acid is suppressed in sodium acetate due to common ion effect. While in sodium chloride, no such effect is noticed.

THEORY OF ACID AND BASE

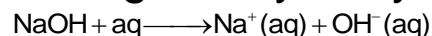
Arrhenious concept: According to Arrhenious

Acid:

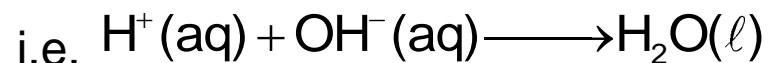
it gives H^+ in water.



Base: A base is a substance which gives hydroxyl ion (OH^-) in water.



Neutralisation reaction involves the combination of H^+ ion from acid and OH^- ion from base.



Limitations of Arrhenious concept

This theory is limited to aqueous solution only.

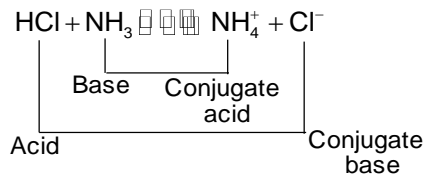
Bronsted Lowry concept (proton donor acceptor concept):

Acid: Acid is a substance that donates proton (H^+).

Base: Base is a substance that accepts proton (H^+).

Acid $\rightleftharpoons H^+$ + conjugated base

Base + H^+ \rightleftharpoons conjugated acid



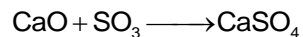
HPO_4^{2-} , $H_2PO_3^-$, HSO_3^- are amphiprotic or amphoteric.

e.g. $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

Limitations

- (i) It can not explain the acidic character of substance like BF_3 , $AlCl_3$ etc. which do not have any H^+ but known to be acids.
- (ii) It can not explain the reaction between the acidic oxides like CO_2 , SO_2 , SO_3 etc. and basic oxides like CaO , BaO , MgO etc. taking place in absence of solvent.



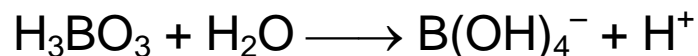
Eg. 2. Which is the stronger base towards a proton NH_2^- or PH_2^- and why?

Solution: Bond energy ($\text{N—H} > \text{P—H}$) ionisation suggests that NH_2^- will be stronger base. This is constituent with the relative strengths of the respective conjugate acids: $\text{NH}_3 < \text{PH}_3$.

Eg. 3. H_3BO_3 isacid

- (A) Monobasic (B) Dibasic
(C) Tribasic (D) None

Solution: H_3BO_3 is monobasic acid



Hence, **(A)** is correct.

Eg. 4. Which of the following is the strongest acid?

- (A) HClO_4 (B) HBrO_4
(C) HIO_4 (D) HNO_3

Solution: The acidic character of oxy acids decreases down the group and increases along the period. Also acidity increases with increase in oxidation number of central atom.
Hence, **(A)** is correct.

Lewis concept of acids and base: According to this concept

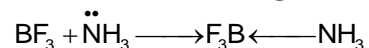
Acid – electron pair acceptor and Base – electron pair donor

All electrophiles are Lewis acids e.g. AlCl_3 , BF_3 , H^+ etc.

All nucleophiles are Lewis base e.g. $\ddot{\text{N}}\text{H}_3$, H_2O , R-NH_2 , R-OH , F^- , OH^- , Br^- etc.

Example: BF_3 is an acid as it can accept an electron pair and NH_3 is a base as it donate an electron pair.

The neutralisation reaction involves the donation of electron pair from base to acid resulting the formation of coordinate bond.



Type of Lewis acids

(i) Molecules having incomplete octet of central atom e.g. BF_3 , AlCl_3 , MgCl_2 , BCl_3 etc.

(ii) Simple cations Ca^{2+} , Ag^+ , H^+ , Fe^{3+} etc.

(iii) Molecules having vacant d-orbitals of central atom e.g. SnCl_4 , PF_5 , SiF_4 , RX_3 , TiCl_4 etc.

(iv) Molecules containing multiple bond between the two atoms of different electronegativity.



Type of Lewis bases

- (i) Neutral molecules like H_2O , NH_3 , R-OH , R-NH_2 etc. having atleast one lone pair of electrons.
- (ii) All negative ions like OH^- , Cl^- , Br^- , NH_2^- etc.

Eg. 5. Which salt undergoes hydrolysis?

- (A) CH_3COONa (B) KNO_3
 (C) NaCl (D) K_2SO_4

Solution:

Salt of strong acid and strong base does not undergo hydrolysis.

Hence, **(A)** is correct.

Eg. 6. The conjugate acid of PO_4^{3-} is

- (A) H_3PO_4 (B) $H_2PO_4^-$
(C) HPO_4^{2-} (D) HPO_3^{2-}

Solution: Conjugate acid and base differs by one proton hence the conjugate acid of PO_4^{3-} is HPO_3^{2-}
Hence, **(D)** is correct.

Eg. 7. The conjugate base of hydrazoic acid is

- (A) NH_3 (B) N_3H
(C) N_3^- (D) N_2^-

Solution: $N_3H \xrightarrow{-H^+} N_3^-$
Hence, **(C)** is correct.

RELATIVE STRENGTH OF WEAK ACIDS AND BASES



Initially	C	0	0
At equilibrium	C - Cα	Cα	Cα

$$K_a = \frac{C\alpha \times C\alpha}{C - C\alpha} = \frac{C\alpha^2}{1 - \alpha}$$

($1 - \alpha \approx 1$ assuming α is very small).

$$\therefore K_a = C\alpha^2$$

Similarly for base NH_4OH

$$K_b = C\alpha^2$$

For two acids having equi-molar concentrations

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly for two base

$$\frac{\text{Strength of base I}}{\text{Strength of base II}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

SELF IONIZATION OF WATER (IONIC PRODUCT OF WATER)

Pure water is a weak electrolyte and itself ionises as



Applying law of mass action

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad \text{or} \quad K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

where K is called dissociation constant.

Since the ionisation of water is very small it means very few H_2O molecule are dissociated into H^+ and OH^- ions i.e.

$$[\text{H}_2\text{O}] = \text{constant} = \frac{1000}{18} = 55.55 \text{ mole/litre}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

K_w is called ionic product of water.

pH SCALE

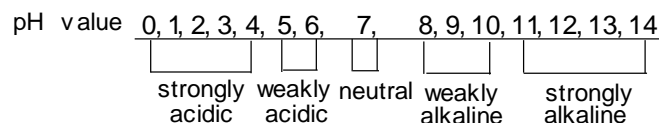
Sorenson gave the best way of expressing the acidic or basic nature of solution. This is a logarithmic scale in which hydrogen ion concentration ranges from 10^{-14} to 1 mole/litre.

pH may be defined as logarithm of reciprocal of $[H_3O^+]$.

or negative logarithm of hydronium ion concentration.

$$pH = -\log [H_3O^+]$$

$$pH = -\log [H^+]$$



In similar manner, we can define pOH scale as

$$pOH = -\log [OH^-]$$

$$[H^+][OH^-] = 10^{-14} \text{ at } 25^\circ\text{C}$$

$$-\log [H^+] - \log [OH^-] = 14$$

$$pH + pOH = 14$$

Limitations of pH scale

- (i) pH value of solutions do not give immediate idea of their relative strength.
(ii) pH value can be negative too.

Eg. 8. Which of the following concentration has the largest degree of dissociation for a weak acid?

- (A) 1.0 M (B) 0.5 M
(C) 0.10 M (D) 0.01 M

Solution: (D)

Eg. 9. Which of the following solutions can be titrated with HCl as well as NaOH?

- (A) Glycine (B) Pyruvic acid
(C) Triethyl amine (D) Aniline

Solution: (A)

- Eg. 10.** The dissociation constant of monobasic acids A, B and C are 10^{-4} , 10^{-6} and 10^{-10} respectively. The concentration of each monobasic acid is 0.1 M. Which of the following has been arranged in increasing order of pH?
- (A) $A < B < C$ (B) $C < A < B$
(C) $B < C < A$ (D) $B < A < C$

Solution: (A)

- Eg. 11.** Among the following, which causes the greatest change in pH on addition to 50 mL of a 0.2 M malonic acid solution?
- (A) Addition of 25 mL of 0.02 M malonic acid
(B) Addition of 25 mL of 0.02 M NaOH solution
(C) Addition of 25 mL of 0.02 M HCl solution
(D) Addition of 50 mL of 0.2 M acetic acid

Solution: (B)

Determination of pH of acids and bases

(A) Strong Acid

A strong acid is defined as a substance which completely dissociates to give all the maximum possible H^+ ions that it is capable of giving.

For example



Therefore $[HCl] = [H^+]$

If we have to find the pH of 10^{-4} M HCl,

$$[HCl] = [H^+]$$

$$\therefore pH = -\log 10^{-4} = 4.$$

Now to find the pH of 10^{-7} M HCl,

Assuming that a is the amount of H^+ (or OH^-) coming from water.

In the case of 10^{-7} M HCl, the total $[H^+]$ will be $(10^{-7} + a)$ if a is the amount of H^+ coming from water.

Since $[OH^-] = a'$.

$$[H^+]_T \times [OH^-]_T = (10^{-7} + a') \times a' = 10^{-14} \quad \text{-----} \quad (2)$$

Where $[H^+]_T$ is the total H^+ coming from both acid and water.

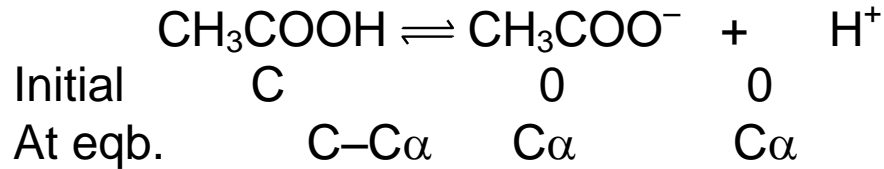
Therefore a' (the $[H^+]$ coming from water in the presence of 10^{-7} M HCl) can be calculated from equation (2)

and therefore the total $[H^+]$ would be equal to $[H^+]_T = a' + 10^{-7}$ and

$$pH = -\log [H^+]_T$$

Note: In order to figure out when to take the contribution of water, it should be noted that when $[H^+]_A \geq 10^{-6}$ M, water contribution need not be taken and when $[H^+]_A < 10^{-6}$ M, water contribution should be taken.

(B) Weak Acids



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Generally, for weak acids `α' is very small and to a reasonable approximation we can neglect α in comparison to 1.

$$K_a = C\alpha^2;$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}}; \text{Since } [\text{H}^+]_A = C\alpha = C \times \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$$

Where $[\text{H}^+]_A$ is the $[\text{H}^+]$ coming from the weak acid. Again if $[\text{H}^+]_A < 10^{-6}$ M, we must take into account H^+ coming from water.

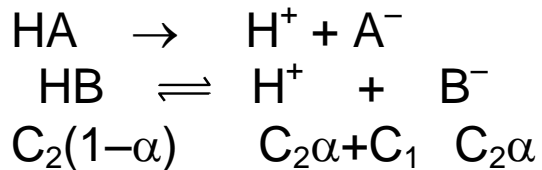
Let us follow the above discussion and calculate the pH of 10^{-6} M CH_3COOH with

$K_a = 1.8 \times 10^{-5}$. Following the above procedure

$$[\text{H}^+]_A = \sqrt{1.8 \times 10^{-5} \times 10^{-6}} = 4.24 \times 10^{-6}$$

$$\begin{aligned}\Rightarrow \text{pH} &= -\log 4.24 \times 10^{-6} \\ &= 6 - \log 4.24 = 6 - 0.6274 = 5.37\end{aligned}$$

(C) Strong Acid + Weak Acid



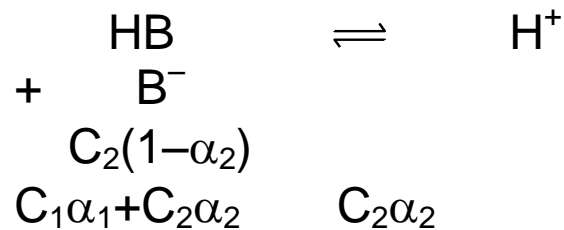
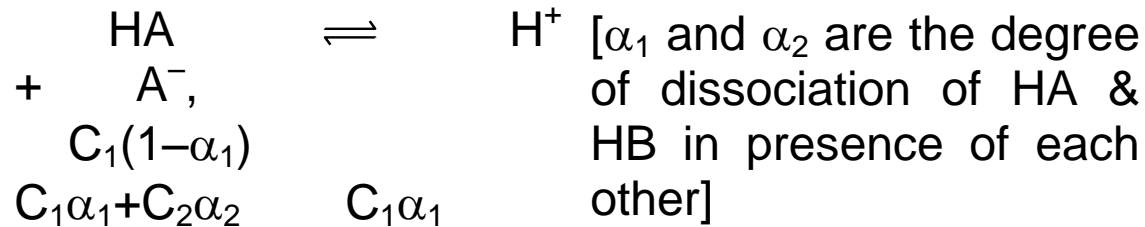
[α is the degree of dissociation of HB in the presence of HA]

$$[\text{HB}] = \text{C}_2(1-\alpha); \quad [\text{B}^-] = \text{C}_2\alpha; \quad [\text{H}^+]_{\text{T}} = \text{C}_2\alpha + \text{C}_1$$

$$\text{Therefore } K_a = \frac{[\text{H}^+]_{\text{T}}[\text{B}^-]}{[\text{HB}]} = \frac{(\text{C}_2\alpha + \text{C}_1) \text{C}_2\alpha}{\text{C}_2(1-\alpha)}$$

Solving this equation we can get the value of α and then determine the $[\text{H}^+]$ and find the pH.

(D) Two Weak Acids



$$[\text{HA}] = \text{C}_1(1-\alpha_1); \quad [\text{A}^-] = \text{C}_1\alpha_1; \quad [\text{HB}] = \text{C}_2(1-\alpha_2);$$

$$[\text{B}^-] = \text{C}_2\alpha_2 \quad \text{and} \quad [\text{H}^+] = \text{C}_1\alpha_1 + \text{C}_2\alpha_2$$

$$K_{a_1} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(\text{C}_1\alpha_1 + \text{C}_2\alpha_2)\text{C}_1\alpha_1}{\text{C}_1(1-\alpha_1)}$$

$$K_{a_2} = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} = \frac{(\text{C}_1\alpha_1 + \text{C}_2\alpha_2)\text{C}_2\alpha_2}{\text{C}_2(1-\alpha_2)}$$

Eg. 12. 0.2 (M) solution of monobasic acid is dissociated to 0.95% Calculate its dissociation constant. Given $\alpha = 0.0095$; $C = 0.2 \text{ mole lit}^{-1}$

Solution: $K_a = C\alpha^2 = 0.2 \times (0.0095)^2 = 1.8 \times 10^{-5}$

Eg. 13. Calculate pH for (i) 0.01 (N) Ca(OH)_2 , (ii) 10^2 (M) HCl

Solution: (i) $\text{Ca(OH)}_2 \longrightarrow \text{Ca}^{2+} + 2\text{OH}^-$
 $\begin{array}{ccc} 10^{-2}\text{N} & 0 & 0 \\ 0 & 10^{-2} & 2 \times 10^{-2} \end{array}$
 $\therefore [\text{OH}] = 10^{-2} \times 2 \text{ gm equivalent / lit} = 10^{-2} \text{ gm mole / lit}$
 $\text{pOH} = 2, \text{ pH} = 12$

(ii) $\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$
 $[\text{H}^+] = 10^2 \text{ (M) or pH} = -2.$
 This is not possible because pH range is 0–14.
 $\text{pH} = -\log_{10} a_{\text{H}^+}$

Where a_{H^+} = activity = molar concentration \times activity coefficient

\therefore Unless and unit activity coefficient is given it is not possible to calculate pH of solution.

Eg. 14. *If the H^+ ion concentration of a solution is increased to ten times its initial value, its pH will*

- (A) increase by one (B) remains changed
(C) decrease by one (D) increase by ten

Solution: (C)

Eg. 15. *What will be the H^+ ion concentration in a solution prepared by mixing 50.0 mL of 0.20 M NaCl, 25 mL of 0.10 M NaOH and 25.0 mL of 0.30 M HCl?*

- (A) 0.5 M (B) 0.05 M
(C) 0.02 M (D) 0.10 M

Solution: (B)

Eg. 16. Determine the pH of the solution that results from the addition of 20.00 mL of 0.01 M $\text{Ca}(\text{OH})_2$ to 30.00 mL of 0.01 M HCl

- (A) 11.30 (B) 10.53
(C) 2.70 (D) 8.35

Solution: (A)

Eg. 17. To 250.0 mL of M/50 H_2SO_4 , 4 g of solid NaOH is added and the resulting solution is diluted to 1.0 L. The pH of the resulting solution is

- (A) 12.00 (B) 11.25
(C) 11.95 (D) 12.15

Solution: (D)

Eg. 18. A given weak acid (0.10 M) had $pK_a = 6$. The pH of the solution is
(A) 2.5 (B) 3.5
(C) 4.5 (D) 6.5

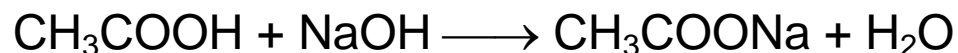
Solution: (B)

Eg. 19. The pH of 10^{-10} M H_2SO_4 will be almost
(A) four (B) seven
(C) six (D) zero

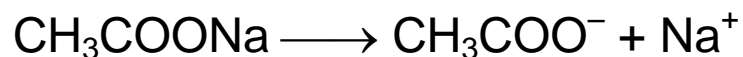
Solution: (B)

DETERMINATION OF pH DUE TO HYDROLYSIS

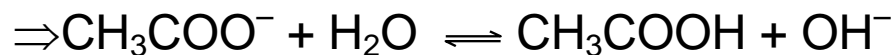
(a) Salt of a Weak Acid and Strong Base



CH_3COONa being a strong electrolyte, completely dissociates into its constituent ions.

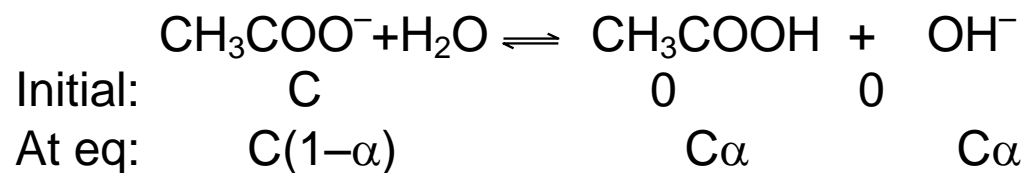


Now, the ions produced would react with H_2O . This process is called hydrolysis



$$\therefore K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

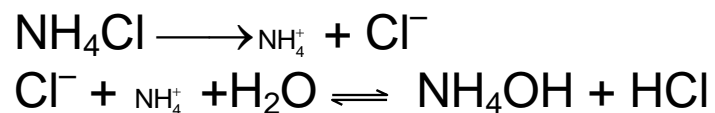
$$K_h = \frac{K_w}{K_a} \Rightarrow K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a}$$



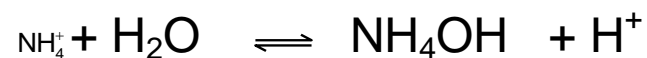
$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \sqrt{\frac{K_w K_a}{C}}$$

$$\text{or } \text{pH} = -\log [\text{H}^+] = -\log \left(\sqrt{\frac{K_w \cdot K_a}{C}} \right) = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

(b) **Salt of a Weak Base and a Strong Acid**



,



Initial: C 0 0

At eqb: C(1- α) C α C α

Where α is the degree of hydrolysis of NH_4^+ .

$$K_h = \frac{[\text{NH}_4\text{OH}] [\text{H}^+]}{[\text{NH}_4^+]}$$

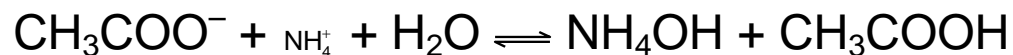
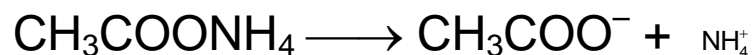
Multiplying and dividing by OH^- and rearranging,

$$K_h = \frac{K_w}{K_b}$$

$$\text{Since } [H^+] = C\alpha, [H^+] = C \sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{K_w C}{K_b}}$$

$$\text{or pH} = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

(c) Salt of a Weak Acid and Weak Base



Initial: C C 0 0

At equilibrium: C(1-α) C(1-α) Cα Cα

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}]}{[\text{NH}_4^+][\text{CH}_3\text{COO}^-]}$$

$$\therefore K_h = \frac{K_w}{K_a K_b}$$

Substituting the concentration terms,

$$K_h = \frac{K_w}{K_a K_b} = \frac{C\alpha \times C\alpha}{C(1-\alpha) C(1-\alpha)} = \frac{(C\alpha)^2}{[C(1-\alpha)]^2} = \frac{\alpha^2}{(1-\alpha)^2}$$

$$\therefore \frac{\alpha}{1-\alpha} = \sqrt{\frac{K_w}{K_a K_b}}$$

$$[H^+] = K_a \times \left(\frac{\alpha}{1-\alpha} \right) = \sqrt{\frac{K_w K_a}{K_b}}$$

$$\text{or pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

Eg. 20. Calculate the pH at the equivalence point between the titration of 0.1 M, 25 ml CH_3COOH with 0.05 M NaOH solution. K_a (CH_3COOH) = 1.8×10^{-5}

Solution: Volume of NaOH required to reach equivalence point

$$= \frac{0.1 \times 25}{0.05} = 50 \text{ mL.}$$

\therefore Concentration of salt formed = $\frac{\text{millimoles of acid}}{\text{total volume}}$

$$= \frac{25 \times 0.1}{75} = \frac{0.1}{3}$$

$$\text{Since } [\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{10^{-14} \times 1.8 \times 10^{-5}}{\frac{0.1}{3}}}$$

$$\therefore \text{pH} = 8.63$$

Eg. 21. When 0.2 M CH_3COOH is neutralised with 0.2 M NaOH in 0.5 litre of water the resulting solution is slightly alkaline. Calculate pH of resulting solution $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$.

Solution:



$$K_h = \frac{Cx^2}{1-x} = Cx^2, x \ll 1$$

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\text{So, } K_h = Cx^2 = 5.5 \times 10^{-10}$$

$$x^2 = 55 \times 10^{-10}$$

$$\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{Cx} = \frac{10^{-14}}{7.42 \times 10^{-6}} = 1.3477 \times 10^{-9} \text{M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.3477 \times 10^{-9}) = 8.87$$

Eg. 22. Calculate amount of ammonium chloride required to dissolve in 500 ml water to have $\text{pH} = 4.5$ (K_b for $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$).

Solution: $[H^+] = 10^{-pH} = 10^{-4.5} = 3.162 \times 10^{-5} \text{ M}$



$$K_h = Ch^2$$

$$\therefore h = \frac{K_h}{Ch} = \frac{K_h}{[H^+]} = \frac{5.5 \times 10^{-10}}{3.162 \times 10^{-5}} = 1.74 \times 10^{-5}$$

$$\therefore C = \frac{[H^+]}{h} = \frac{3.162 \times 10^{-5}}{1.74 \times 10^{-5}} = 1.8 \text{ mol/L}$$

500 ml of H_2O contains $\frac{1.8}{2} = 0.9$ mole

Mass in gm = $0.9 \times 53.5 = 48.15$ gm

Eg. 23. Calcium lactate $Ca(Lac)_2$ is salt of weak organic acid. A saturated solution of $Ca(Lac)_2$ contains 0.13 mole of this salt in 0.5 litre solution. The pOH of this solution is 5.60. Assuming a complete dissociation of salt, calculate K_a of lactic acid.

Solution: $Ca(Lac)_2 \rightleftharpoons Ca^{2+} + 2Lac^{-1}$
 $\quad\quad\quad 0.13 \times 2 \quad\quad\quad 2 \times 2 \times 0.13$



$$K_h = \frac{x^2}{0.52-x} = \frac{x^2}{0.52} \text{ as } x \text{ is small}$$

$$[OH^{-1}] = 10^{-5.6} = 2.5 \times 10^{-6} = x$$

$$K_h = \frac{2.51 \times 10^{-6} \times 2.5 \times 10^{-6}}{0.52} = 12.12 \times 10^{-12}$$

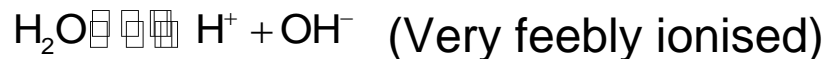
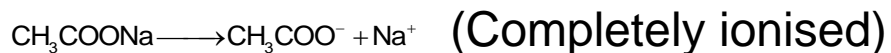
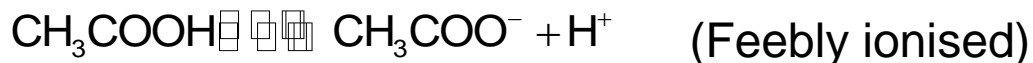
$$K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{12.12 \times 10^{-12}} = 8.26 \times 10^{-4}$$

BUFFER SOLUTIONS

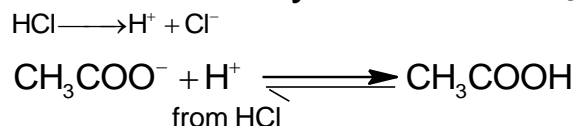
A buffer solution is a solution which resists a change in its pH when such a change is caused by the addition of a small amount of acid or base. This does not mean that the pH of the buffer solution does not change (we make this assumption while doing numerical problems).

(i) **Acidic buffer:** It is the solution of a weak acid and its salts with strong base.

e.g. (CH₃COOH + CH₃COONa), (Phthalic acid + Potassium acid phthalate),
(Boric acid + Borax)

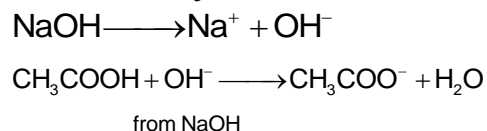


Addition of acid: If a drop of HCl is added, H⁺ ion from HCl combine with CH₃COO⁻ ion to form feebly ionised CH₃COOH molecule.



Addition of base

If a drop of NaOH is added, OH⁻ ion from NaOH combine with CH₃COOH molecule to form feebly ionised H₂O molecule.



Thus small addition of H⁺ and OH⁻ to buffer solution makes no appreciable change in pH of the buffer.

Calculation of pH of acidic buffer

This is called Hendersons equation.

Basic Buffers

$$\text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$$

This is called Hendersons equation.

Eg. 24. CH_3COOH (50 ml, 0.1M) is titrated against 0.1M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml and 60 ml of NaOH. K_a of CH_3COOH is 2×10^{-5} .

Solution: (i) When 0 ml of NaOH is added, the pH is due to acetic acid,

$$\therefore [\text{H}^+] = \sqrt{K_a \times C} = \sqrt{2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6}}$$

$$\text{pH} = -\log \sqrt{2 \times 10^{-6}} = -\frac{1}{2} [\log 2 - 6] = 3 - 0.15 = \mathbf{2.85}$$

(ii) When 10 ml of NaOH is added, it reacts with CH_3COOH to produce salt and water. The solution is then a buffer.

$$\begin{aligned} \therefore \text{pH} &= \text{pK}_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} \\ &= 4.699 + \log \frac{10 \times 0.1}{50 \times 0.1 - 10 \times 0.1} = 4.699 + \log \frac{1}{4} = \mathbf{4.0969} \end{aligned}$$

(iii) When 20 ml of NaOH is added.

$$\text{pH} = \text{pK}_a + \log \frac{20 \times 0.1}{50 \times 0.1 - 20 \times 0.1} = 4.699 + \log \frac{2}{3} = \mathbf{4.5229}$$

(iv) When 25 ml of NaOH is added,

$$\text{pH} = 4.699 + \log \frac{25 \times 0.1}{50 \times 0.1 - 25 \times 0.1} = \mathbf{4.699}$$

(v) When 40 ml of NaOH is added,

$$\text{pH} = 4.699 + \log \frac{40 \times 0.1}{50 \times 0.1 - 40 \times 0.1} = 4.699 + \log 4 = \mathbf{5.3011}$$

(vi) When 50 ml of NaOH is added,

Here, if we use the buffer equation, pH would be = ∞

But we can't use the buffer equation as there is no acid. Therefore we used the hydrolysis equation.

$$\therefore [\text{H}^+] = \sqrt{\frac{K_w K_a}{C}}$$

$$C = \frac{0.1}{2} \left[\because \text{Total Volume is 100 ml and millimoles of salt is } 50 \times 0.1 \right]$$

$$\Rightarrow [\text{H}^+] = \sqrt{\frac{10^{-14} \times 2 \times 10^{-5} \times 2}{0.1}} = \text{pH} = \mathbf{8.699}$$

(vii) When 60 ml of NaOH is added, the excess OH^- ion from NaOH would suppress the hydrolysis of CH_3COO^- ion. So we can ignore the contribution of OH^- ion from the hydrolysis of CH_3COO^- ion.

$$\therefore [\text{OH}^-] = \frac{0.1 \times 10}{110} \text{ [10 ml of OH}^- \text{ ion is in excess]} = \frac{1}{110}$$

$$\text{pOH} = 2.0414$$

$$\therefore \text{pH} = 14 - 2.0414 = \mathbf{11.9586}$$

Eg. 25. How much water should be added to 10.00 g of acetic acid to give a hydrogen ion concentration equal to $1.0 \times 10^{-3} \text{ M}$ (given $\text{pK}_a = 4.74$).

- (A) 130 ml (B) 230 ml
(C) 30 ml (D) 330 ml

Solution: (D)

Eg. 26. The pH of an HCl solution is 2.0. Sufficient water is added to it, to make the pH of the new solution equal to 5.0. The decrease in the hydrogen ion concentration is

- (A) 10 times (B) 7 times
(C) 1000 times (D) 100 times

Solution: (C)

Eg. 27. Calculate the pH of a solution prepared by mixing 20 mL of a strong acid solution of pH 3.0 and 3.0 mL of a strong base of pH 10.0.

- (A) 2.5 (B) 3.5

(C)

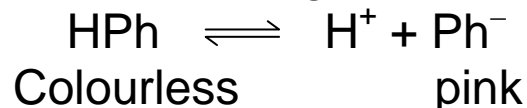
4.5 (D) 6.5

Solution:

(C)

OSTWALD THEORY OF INDICATORS

An indicator generally a weak organic acid or weak organic bases is a substance which is used to determine the end point in a titration. They change their colours within a certain pH range generally the colour change is due to shifting of indicator equilibrium, eg, for phenolphthalein (HPh).



and shifting of this equilibrium from left to right produces pink colours

$$K_{\text{In}} = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]} \text{ and } \text{pH} = \text{p}K_{\text{In}} + \frac{[\text{Ph}^-]}{[\text{HPh}]}$$

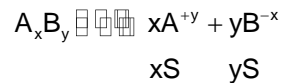
At equilibrium point $[\text{Ph}^-] = [\text{HPh}]$

$$\therefore \text{pH} = \text{p}K_{\text{In}}. \text{ also } K_{\text{In}} = [\text{H}^+]$$

Where K_{In} is the ionization constant of the indicator

SOLUBILITY PRODUCT

Consider a binary electrolyte A_xB_y with solubility S mole/litre.



$$K_{eq} = \frac{[A^{+y}]^x [B^{-x}]^y}{[A_xB_y]}$$

$$K_{eq}[A_xB_y] = [A^{+y}]^x [B^{-x}]^y$$

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y = x^x y^y S^{(x+y)}$$

K_{sp} is called solubility product.

Solubility product may be defines as “**the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature**”.

From solubility product, we may conclude that;

Case I: If, [ionic product] < K_{sp}

Then, the solution is unsaturated i.e. more solute go into the solution.

Case II: If, [ionic product] = K_{sp}

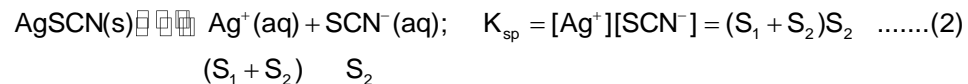
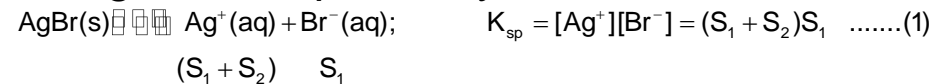
The solution is just saturated i.e. no more solute can be dissolved.

Case III: If, [ionic product] > K_{sp}

The solution is supersaturated i.e. precipitation takes place.

Simultaneous solubility

Solubility of two sparingly soluble salt having common ion dissolved in same solution is called simultaneous solubility. Let S_1 and S_2 be the simultaneous solubility of AgBr and AgSCN respectively.



Thus simultaneous solubility of AgBr and AgSCN can be calculated by the above two expression.

Fractional Precipitation

It is the technique used to separate two or more ions from a solution by adding a selective reagent that precipitates first one ion and then the second.

Considering a solution of 0.1 M Ba^{2+} and 0.1 M Sr^{2+} . If $\text{K}_2\text{Cr}_2\text{O}_4$ is added to this solution as a precipitating agent. K_{sp} of BaCrO_4 is 1.2×10^{-10}

and K_{sp} of SrCrO_4 is 3.5×10^{-5}

Concentration of CrO_4^{2-} required to precipitate $\text{BaCrO}_4 = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9} \text{ M}$

Concentration of CrO_4^{2-} required to ppt. $\text{SrCrO}_4 = \frac{3.5 \times 10^{-5}}{0.1} = 3.5 \times 10^{-4}$

Since the required concentration of CrO_4^{2-} is low so BaCrO_4 will ppt. first.

On addition of chromate ions to the solution, BaCrO_4 starts precipitating in the solution when concentration reaches $1.2 \times 10^{-9} \text{ M}$. On adding further chromate ions to the solution when concentration reaches upto 3.5×10^{-4} , then SrCrO_4 also start precipitating in the solution.

$[\text{Ba}^{2+}]$ left when SrCrO_4 starts precipitating $= \frac{K_{\text{sp}} \text{BaCrO}_4}{[\text{CrO}_4^{2-}]} = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}}$
 $= 3.4 \times 10^{-7} \text{ M}$

$$\% (\text{Ba}^+) \text{ left} = \frac{3.4 \times 10^{-7}}{0.1} \times 100 = 0.00034\%$$

Calculation of solubilities of salts

We shall now discuss the solubilities of different types of salts under various conditions.

(i) **Solubilities of AgCl (salt of a strong acid and strong base) in water**

AgCl would dissolve in water as,



At saturation point,



If the solubility of the salt is x moles / l

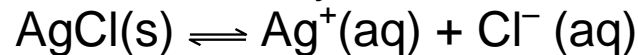
$$\therefore [\text{Ag}^+] = x\text{M}, [\text{Cl}^-] = x\text{M}$$

$$\Rightarrow x^2 = K_{\text{sp}}$$

$$\text{or } x = \sqrt{K_{\text{sp}}}$$

(ii) **Solubility of AgCl in a solution that is having 0.1M in AgNO₃**

AgCl would dissolve and finally reach saturation.



The K_{sp} of AgCl is approximately 10^{-10} . If AgCl were to be dissolved in water (pure), its solubility would have been 10^{-5} M (previous section). In the presence of 0.1M AgNO₃ its solubility will decrease due to common ion effect. This means that $[\text{Ag}^+]$ from AgCl would be less than 10^{-5} M. Hence, we can ignore the contribution of Ag^+ from AgCl.

If the solubility of AgCl is x' moles / l in the presence of 0.1M AgNO₃, then

$$[\text{Ag}^+] = 0.1 \text{ M}, [\text{Cl}^-] = x' \text{ M}$$

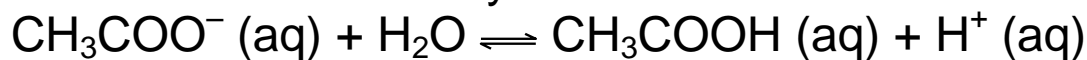
$$\therefore x' = \frac{K_{sp}}{0.1} = 10^{-9} \text{ moles / l}$$

(iii) **Solubility of CH₃COOAg (salt of weak acid and strong base) in water**

CH₃COOAg dissolves and reaches saturation. Since it is a salt of weak acid and strong base, it would hydrolyse. If the solubility of the salt is x moles/ l then



At eqb: $x - y$ x



At eqb: $x - y$ y y

Where y is the amount of CH₃COO⁻ ion that is hydrolysed.

$$\therefore (x - y) x = K_{sp}$$

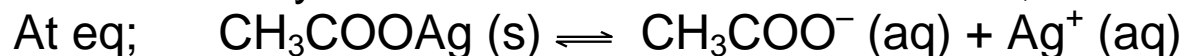
$$\frac{y^2}{(x - y)} = \frac{K_w}{K_a}$$

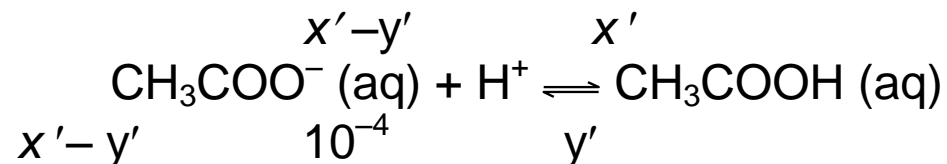
Knowing the values of K_{sp} and K_a , solubility of the salt can be calculated.

(iv) **Solubility of CH₃COOAg (salt of a weak acid and strong base) in an acid buffer of pH = 4** (assuming that the buffer does not have any common ion by CH₃COOAg):

CH₃COOAg would dissolve and reach equilibrium. It would then be hydrolysed.

If the solubility of the salt is x' M in this solution, then





Since the solution is a buffer, the pH will be maintained.

$$\therefore (x' - y') x' = K_{\text{sp}}$$

$$\frac{y'}{10^{-4} \times (x' - y')} = \frac{1}{K_a}$$

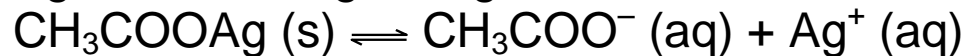
Since in presence of basic buffer, the degree of hydrolysis will be suppressed by already existing OH^- ions, therefore the approximated formula which can be used is

$$x'^2 = K_{\text{sp}} (\text{CH}_3\text{COOAg}) \text{ (neglecting } y'')$$

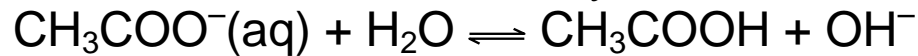
Knowing K_{sp} and K_a , the solubility can be calculated.

(v) Solubility of CH_3COOAg in an buffer solution of pH = 9

Following the same logic as give in the earlier section,



At eqb: $\frac{x'' - y''}{10^{-5}} = \frac{x''}{y''}$



At eqb: $\frac{x'' - y''}{y''} = 10^{-5}$

Where x'' M is the solubility of the salt and y'' the extent to which it is hydrolysed.

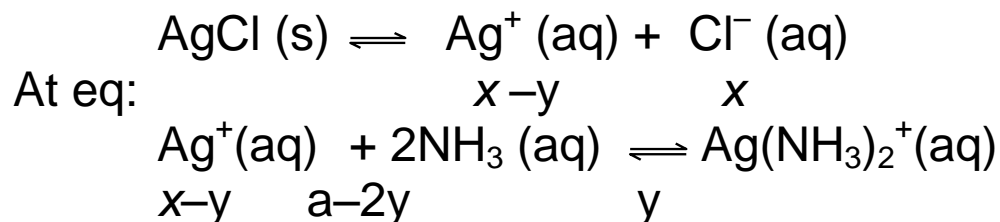
$$\therefore (x'' - y'') x'' = K_{sp}$$

$$\frac{y'' \times 10^{-5}}{(x'' - y'')} = \frac{K_w}{K_a}$$

Knowing, K_{sp} and K_a , the solubility can be calculated.

(vi) **Solubility of AgCl in an aqueous solution containing NH_3**

Let the amount of NH_3 initially be 'a' M. If the solubility of the salt is x moles/ l, then



Where y is the amount of Ag^+ which has reacted with NH_3 .

$$\therefore (x - y) x = K_{sp}$$

$$\frac{y}{(x - y) (a - 2y)^2} = K_f \text{ (formation constant of } Ag(NH_3)_2^+ \text{)}$$

Knowing K_{sp} and K_f , the solubility can be calculated.

Eg. 28. *The solubility of $BaSO_4$ in water is 2.3×10^{-4} gm/100 mL. Calculate the percentage loss in weight when 0.2 gm of $BaSO_4$ is washed with (a) 1lt of water (b) 1lt of 0.01N Na_2SO_4 .*

Solution: (a) Solubility is in general expressed in gm/lit,
 so solubility of $\text{BaSO}_4 = 2.3 \times 10^{-3} \text{ g /lt}$
 Loss in weight of $\text{BaSO}_4 = \text{amount of } \text{BaSO}_4 \text{ soluble}$
 $\Rightarrow \% \text{loss} = \frac{2.3 \times 10^{-3}}{0.2} \times 100 = 1.15\%$

(b) Now $0.01 \text{ N N Na}_2\text{SO}_4 \equiv 0.01 \text{ N } \text{NSO}_4^{2-} \text{ ions}$
 $\equiv 0.005 \text{ M } \text{SO}_4^{2-} \text{ ions}$

Now presence of SO_4^{2-} prior to washing BaSO_4 will suppress the solubility of BaSO_4 (due to common ion effect). The suppression will be governed by K_{sp} value of BaSO_4 . So first calculate K_{sp} of BaSO_4 .

Solubility of BaSO_4 in fresh water $= 2 \times 10^{-3} \text{ g/lt}$
 $\equiv \frac{2.3 \times 10^{-3}}{233.4} = \text{Mol/lt} = 9.85 \times 10^{-6} \text{ M}$

$$K_{\text{sp}} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = (9.85 \times 10^{-6})^2 = 9.71 \times 10^{-11}$$

Now let x be solubility in mol/lt

$\Rightarrow [\text{Ba}^{2+}]$ in solution $= x \text{ mol/lt}$ and $[\text{SO}_4^{2-}]$ in solution

$= (x + 0.005) \text{ mol/lt}$

Ionic product $= [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = (x) (x + 0.005)$

$K_{\text{sp}} = \text{Ionic Product at equilibrium (saturation)}$

$$\Rightarrow 9.71 \times 10^{-11} = (x) (x + 0.005) \Rightarrow x^2 + 0.005x - 9.71 \times 10^{-11} = 0$$

$$\Rightarrow x = \frac{9.71 \times 10^{-11}}{0.005} = 1.94 \times 10^{-8} \text{ mol/lit} = 1.94 \times 10^{-8} \times 233.4 \text{ g/lit}$$

$$\Rightarrow 4.53 \times 10^{-6} \text{ gm of BaSO}_4 \text{ are washed away}$$

$$\Rightarrow \text{percentage loss} = \frac{4.53 \times 10^{-6} \times 100}{0.2} = 2.26 \times 10^{-3} \%$$

Eg. 29. *Two weak solutions are isohydric when their*

(A) *hydrogen ion concentrations are the same before mixing*

(B) *hydrogen ion concentrations are the same before and after mixing*

(C) *degrees of dissociation are the same*

(D) *chemical properties are the same*

Solution: (A)

Objective:

Prob 1. *If the degree of ionization of water be 1.8×10^{-9} at 298K. Its ionization constant will be*

$$(A) 1.8 \times 10^{-16}$$

$$(C) 1 \times 10^{-16}$$

$$(B) 1 \times 10^{-14}$$

$$(D) 1.67 \times 10^{-14}$$

Sol. $K_a = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$

∴(A)

Prob 2. When a solution of benzoic acid was titrated with NaOH the pH of the solution when half the acid neutralized was 4.2. Dissociation constant of the acid is

$$(A) 6.31 \times 10^{-5}$$

$$(C) 8.7 \times 10^{-8}$$

$$(B) 3.2 \times 10^{-5}$$

$$(D) 6.42 \times 10^{-4}$$



After 0.5 0.5

neutralization

It is a buffer solution of weak acid and its salt

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$pK_a = 4.2$$

$$K_a = 6.31 \times 10^{-5}$$

∴(A)

Prob 3. 10^{-2} mole of NaOH was added to 10 litre of water. The pH will change by

(A) 4

(B) 3

(C) 11

(D) 7

Sol. Old pH = 7

$$\text{New } [\text{OH}^-] = 10^{-2} \times \frac{1}{10} = 10^{-3}$$

New pH = 11

Change in pH = 4

∴(A)

Prob 4. If an aqueous solution at 25°C has twice as many OH⁻ ion as pure water will be its pOH

(A) 6.699

(B) 7.307

(C) 7

(D) 6.98

Sol. $[\text{OH}^-] = 2 \times 10^{-7}$

$$\text{pOH} = 14 - \text{pH} \text{ or } -\log [\text{OH}^-]$$

\therefore (A)

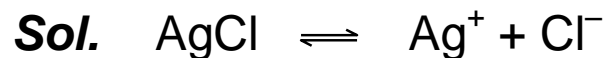
Prob 5. Solubility of AgCl in water, 0.01M CaCl₂, 0.01M NaCl and 0.05M AgNO₃ are S₁, S₂, S₃ and S₄ respectively then.

(A) $S_1 < S_2 < S_3 < S_4$

(B) $S_1 > S_3 > S_2 > S_4$

(C) $S_1 > S_2 = S_3 > S_4$

(D) $S_1 > S_3 > S_4 < S_2$

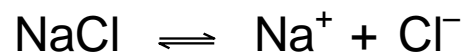


In CaCl₂



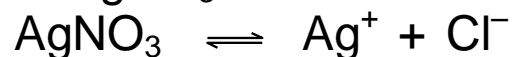
$$0.01 \quad 0.01 \quad 2 \times 0.01$$

In NaCl



$$0.01 \quad 0.01 \quad 0.01$$

In AgNO₃



$$0.05 \quad 0.05 \quad 0.05$$

common ion effect is maximum in AgNO₃

So, $S_1 > S_3 > S_2 > S_4$

\therefore (B)

Prob 6. What would be the pH of an ammonia solution if that of an acetic acid solution of equal strength is 3.2? Assume dissociation constant for NH_3 & acetic acid are equal.

(A) 3.2

(B) 6.4

(C) 9.6

(D) 10.8

Sol. pH of CH_3COOH = pOH of NH_3 solution $\therefore K_a = K_b$
 \therefore pH of NH_3 solution = $14 - 3.2 = 10.8$

Prob 7. pH of $\text{Ba}(\text{OH})_2$ solution is 12. Its solubility product is

(A) 10^{-6}M^3

(B) $4 \times 10^{-6}\text{M}^3$

(C) $0.5 \times 10^{-7}\text{M}^3$

(D) $5 \times 10^{-7}\text{M}^3$

Sol. Since pH = 12 \therefore pOH = $14 - 12 = 2$

$\therefore [\text{OH}^-] = 10^{-2}\text{M}$

We know $\text{Ba}(\text{OH})_2 \rightleftharpoons \text{Ba}^{++} + 2\text{OH}^-$

$\therefore [\text{Ba}^{++}] = \frac{10^{-2}}{2}\text{M}$

$\therefore K_{\text{SP}} = [\text{Ba}^{++}] [\text{OH}^-]^2 = \left(\frac{10^{-2}}{2}\right) \times (10^{-2})^2 = 5 \times 10^{-7}\text{M}^3$

∴(D)

Prob 8. The hydrolysis constant for $ZnCl_2$ will be

(A) $K_h = \frac{K_w}{K_b}$

(B) $K_h = \frac{K_w^2}{K_b}$

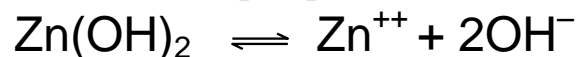
(C) $K_h = \frac{K_w^2}{K_b^2}$

(D) $K_h = \frac{K_b}{K_w^2}$

Where K_b is effective dissociation constant of base Zn^{++}

Sol. $Zn^{++} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$

$$\therefore K_h = \frac{[Zn(OH)_2] [H^+]^2}{[Zn^{++}]} \quad \dots (1)$$



$$\therefore K_b = \frac{[Zn^{++}] [OH^-]^2}{[Zn(OH)_2]}, \quad K_w = [H^+] [OH^-]$$

$$\therefore \frac{K_w^2}{K_b} = K_h$$

∴ (B)

Prob 9. $M(OH)_x$ has $K_{SP} 4 \times 10^{-12}$ and solubility $10^{-4}M$. Then the value of x is

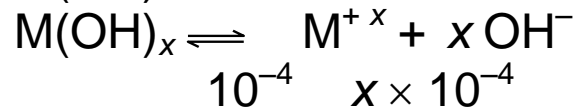
(A) 1

(B) 2

(C) 3

(D) -4

Sol. $M(OH)_x$ will ionize in the way



$$\therefore K_{sp} = [M^{+x}] [OH^-]^x \therefore (10^{-4}) (x \times 10^{-4})^x = 4 \times 10^{-12}$$

by inspection we get this relation will hold good when $x = 2$

\therefore **(B)**

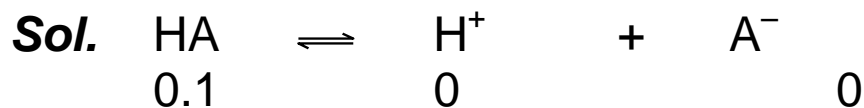
Prob 10. *The pH of an aqueous solution of 0.1M solution of a weak monoprotic acid which is 1% ionised is*

(A) 1

(B) 2

(C) 3

(D) 11



$$0.1 \left(1 - \frac{1}{100}\right) \quad \frac{1 \times 0.1}{100} \qquad \qquad \frac{1 \times 0.1}{100}$$

$$[H^+] = 10^{-3} \therefore \text{pH} = 3$$

\therefore **(C)**

