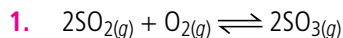


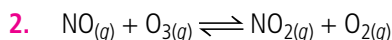
# Equilibrium

## Topic 1



Applying law of chemical equilibrium,

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(1.9)^2}{(0.6)^2(0.82)} = 12.229 \text{ L mol}^{-1}$$



$$K_c = \frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}][\text{O}_3]} = 6.3 \times 10^{14}$$

For the reverse reaction,

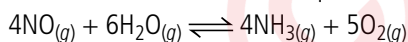
$$K'_c = \frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2][\text{O}_2]} = \frac{1}{K_c} = \frac{1}{6.3 \times 10^{14}} = 1.587 \times 10^{-15}$$

3. For the concentration of pure solid or pure liquid,

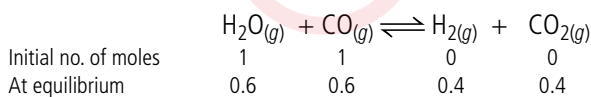
$$\begin{aligned} \text{Molar conc.} &= \frac{\text{Moles of the substance}}{\text{Volume of the substance}} \\ &= \frac{\text{Mass/Molar mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Molar mass}} \\ &= \frac{\text{Density}}{\text{Molecular mass}} \end{aligned}$$

Since density of pure solid or liquid is constant at constant temperature and molar mass is also constant therefore, their molar concentrations are constant and therefore can be ignored while writing the equilibrium constant expression.

4. The balanced chemical equation is



5. From the above reaction,



$$\therefore [\text{H}_2\text{O}] = \frac{0.6}{10} \text{ mol L}^{-1} = 0.06 \text{ mol L}^{-1}$$

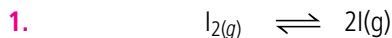
$$[\text{CO}] = \frac{0.6}{10} \text{ mol L}^{-1} = 0.06 \text{ mol L}^{-1}$$

$$[\text{H}_2] = \frac{0.4}{10} = 0.04 \text{ mol L}^{-1}$$

$$\text{and } [\text{CO}_2] = \frac{0.4}{10} = 0.04 \text{ mol L}^{-1}$$

$$K_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{\frac{0.4}{10} \times \frac{0.4}{10}}{\frac{0.6}{10} \times \frac{0.6}{10}} = 0.44$$

## Topic 2



Initial moles            1                    0

Moles at equilibrium   1 - x                    2x

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

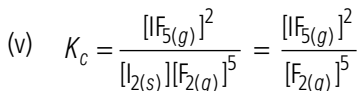
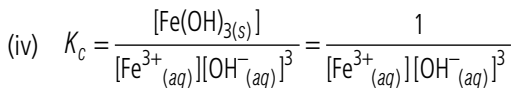
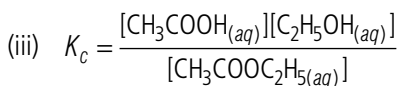
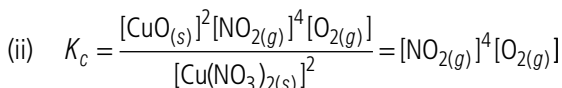
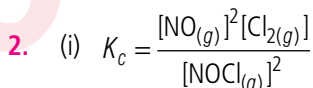
$$\text{But } \frac{2x}{1+x} = 0.4 \text{ (given)} \therefore x = \frac{1}{4}$$

$$\text{So, mole fraction of I}_2 = \frac{1 - \frac{1}{4}}{1 + \frac{1}{4}} = \frac{\frac{3}{4}}{\frac{5}{4}} = 0.6$$

$$\text{Mole fraction of I} = \frac{2 \times \frac{1}{4}}{1 + \frac{1}{4}} = \frac{\frac{1}{2}}{\frac{5}{4}} = 0.4$$

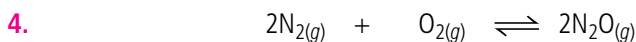
$$p_1 = 0.4 \times 10^5 \text{ Pa}, p_{\text{I}_2} = 0.6 \times 10^5 \text{ Pa}$$

$$K_p = \frac{p_{\text{I}}^2}{p_{\text{I}_2}} = \frac{(0.4 \times 10^5)^2}{(0.6 \times 10^5)} = 2.67 \times 10^4$$



3. (i)  $K_p = K_c(RT)^{\Delta n_g}$ ,  $\Delta n_g = (2 + 1) - 2 = 1$   
 $1.8 \times 10^{-2} = K_c(0.0821 \times 500)$ ,  $K_c = 4.38 \times 10^{-4}$

(ii)  $\Delta n_g = 1$ ,  $K_c = \frac{K_p}{(RT)} = \frac{167}{(0.0821 \times 1073)} = 1.896$



Initial no. of moles :            0.482                    0.933                    0

At eqm. no. of moles :        (0.482 - x)            (0.933 - x/2)            x

Molar conc.                     $\frac{0.482 - x}{10}$                      $\frac{0.933 - (x/2)}{10}$                      $\frac{x}{10}$

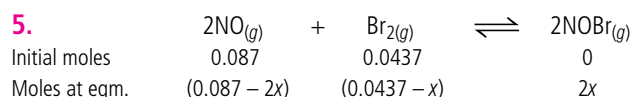
As  $K_c = 2.0 \times 10^{-37}$  is very small, this means that the consumed/reacted amount of  $N_2$  and  $O_2$  ( $x$ ) is very very small. Hence, at equilibrium, we have,

$$[N_2] = 0.0482 \text{ mol L}^{-1}, [O_2] = 0.0933 \text{ mol L}^{-1}, [N_2O] = 0.1x$$

$$\therefore K_c = \frac{(0.1x)^2}{(0.0482)^2(0.0933)} = 2.0 \times 10^{-37} \text{ (given)}$$

On solving this gives,  $x = 6.6 \times 10^{-20}$

$$\therefore [N_2O] = 0.1x = 6.6 \times 10^{-21} \text{ mol L}^{-1}$$



$$\text{But } 2x = 0.0518 \quad \therefore x = 0.0259$$

$$(n_{NO})_{eq} = 0.087 - 0.0518 = 0.0352 \text{ mol}$$

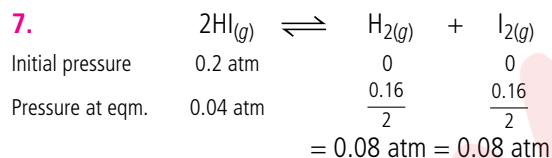
$$(n_{Br_2})_{eq} = 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

$$6. \quad K_p = K_c(RT)^{\Delta n_g} \text{ or } K_c = \frac{K_p}{(RT)^{\Delta n_g}}$$

$$\Delta n_g = 2 - (2 + 1) = -1, T = 450 \text{ K,}$$

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

$$\therefore K_c = \frac{2.0 \times 10^{10}}{(0.083 \times 450)^{-1}} = 2.0 \times 10^{10} \times (0.083 \times 450) = 7.47 \times 10^{11}$$

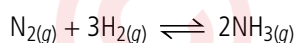


According to law of chemical equilibrium,

$$K_p = \frac{p_{H_2} \times p_{I_2}}{p_{HI}^2} = \frac{0.08 \times 0.08}{(0.04)^2} = \frac{0.0064}{0.0016} = 4$$

$$\therefore K_p = 4$$

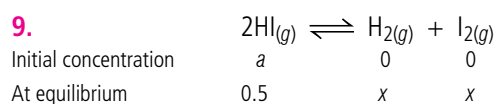
8. The reaction is :



$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{8.13}{20} \text{ mol L}^{-1}\right)^2}{\left(\frac{1.57}{20} \text{ mol L}^{-1}\right)\left(\frac{1.92}{20} \text{ mol L}^{-1}\right)^3} = 2.38 \times 10^3$$

As  $Q_c \neq K_c$ , the reaction mixture is not in equilibrium.

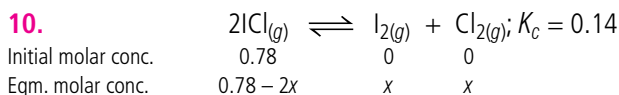
As  $Q_c > K_c$ , the net reaction will be in the backward direction.



$$K_c = \frac{[H_2][I_2]}{[HI]^2} \text{ or, } \frac{1}{54.8} = \frac{x \times x}{(0.5)^2} \text{ or } x^2 = \frac{0.25}{54.8}$$

$$\Rightarrow x = 0.068$$

$$\therefore [H_2] = [I_2] = 0.068 \text{ mol L}^{-1}$$



Applying law of chemical equilibrium,

$$K_c = \frac{[I_2][Cl_2]}{[Cl]^2} \Rightarrow 0.14 = \frac{x \cdot x}{(0.78 - 2x)^2}$$

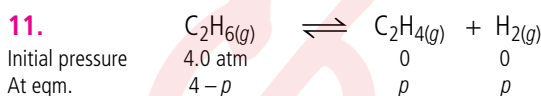
$$x^2 = 0.14(0.78 - 2x)^2$$

$$\text{or } \frac{x}{0.78 - 2x} = \sqrt{0.14} = 0.374$$

$$\text{or } x = 0.292 - 0.748x \text{ or } 1.748x = 0.292 \text{ or } x = 0.167$$

Hence at equilibrium,  $[I_2] = [Cl_2] = 0.167 \text{ M}$

$$[Cl] = 0.78 - (2 \times 0.167) = 0.446 \text{ M}$$



Applying law of chemical equilibrium,

$$K_p = \frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} \Rightarrow 0.04 = \frac{p^2}{4 - p}$$

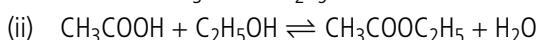
$$\text{or, } p^2 = 0.16 - 0.04p \text{ or } p^2 + 0.04p - 0.16 = 0$$

$$\therefore p = \frac{-0.04 \pm \sqrt{0.0016 - 4(-0.16)}}{2} = \frac{-0.04 \pm 0.80}{2}$$

$$\text{Taking positive value, } p = \frac{0.76}{2} = 0.38$$

$$\therefore [C_2H_6]_{eq} = (4 - 0.38) \text{ atm} = 3.62 \text{ atm}$$

$$12. \text{ (i) } Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$



Initially :

$$n_{CH_3COOH} = 1.00; n_{C_2H_5OH} = 0.180 \text{ and } n_{CH_3COOC_2H_5} = n_{H_2O} = 0$$

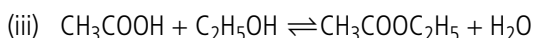
At equilibrium :

$$n_{CH_3COOH} = (1.00 - 0.171) = 0.829,$$

$$n_{C_2H_5OH} = (0.180 - 0.171) = 0.009$$

$$n_{CH_3COOC_2H_5} = 0.171, n_{H_2O} = 0.171$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\left(\frac{0.171}{V}\right)^2}{\left(\frac{0.829}{V}\right)\left(\frac{0.009}{V}\right)} = 3.92$$



Initially :

$$n_{CH_3COOH} = 1.00 \text{ mol, } n_{C_2H_5OH} = 0.500 \text{ mol,}$$

$$n_{CH_3COOC_2H_5} = n_{H_2O} = 0$$

At equilibrium,

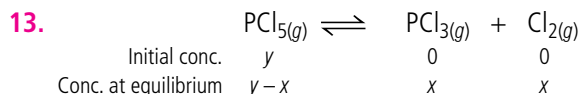
$$n_{CH_3COOH} = (1.00 - 0.214) = 0.786 \text{ mol,}$$

$$n_{C_2H_5OH} = (0.500 - 0.214) = 0.286 \text{ mol,}$$

$$n_{CH_3COOC_2H_5} = 0.214 \text{ mol; } n_{H_2O} = 0.214 \text{ mol}$$

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{\left(\frac{0.214}{V}\right)^2}{\left(\frac{0.786}{V}\right)\left(\frac{0.286}{V}\right)} = 0.204$$

As  $Q_c < K_c$ , the equilibrium has not reached. The reaction tends to proceed right, towards products.



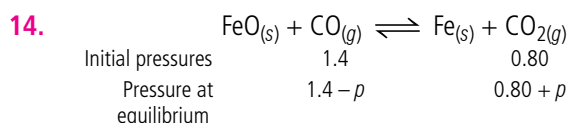
But  $y-x = 0.5 \times 10^{-1} \text{ mol L}^{-1}$

$$\therefore K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{x \cdot x}{(y-x)}$$

$$\text{or } K_c = \frac{x^2}{0.5 \times 10^{-1}} = 8.3 \times 10^{-3}$$

$$\Rightarrow x = 2.04 \times 10^{-2} \text{ mol L}^{-1}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = 2.04 \times 10^{-2} \text{ mol L}^{-1}$$



$\therefore$  At equilibrium,  $p_{\text{CO}_2} = (0.80 + p) \text{ atm}$ ,

$$p_{\text{CO}} = (1.4 - p) \text{ atm}$$

$$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \Rightarrow 0.265 = \frac{0.80 + p}{1.4 - p}$$

$$\text{or, } 0.265(1.4 - p) = 0.80 + p$$

$$\text{or, } 0.371 - 0.265p = 0.80 + p$$

$$\text{or, } 1.265p = -0.429 \text{ or, } p = -0.339 \text{ atm}$$

$$\therefore (p_{\text{CO}})_{\text{eq}} = (1.4 + 0.339) \text{ atm} = 1.739 \text{ atm}$$

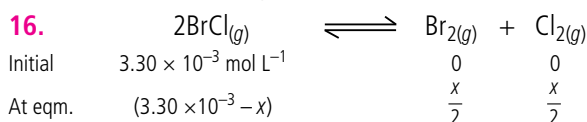
$$(p_{\text{CO}_2})_{\text{eq}} = (0.80 - 0.339) \text{ atm} = 0.461 \text{ atm}$$

**15.**  $Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$

Given  $K_c = 0.061$

As  $Q_c \neq K_c$ , reaction is not in equilibrium.

As  $Q_c < K_c$ , reaction will proceed in the forward direction.



$$K_c = \frac{(x/2)(x/2)}{(3.30 \times 10^{-3} - x)^2} = 32 \text{ (Given)}$$

$$\therefore \frac{x^2}{4(3.30 \times 10^{-3} - x)^2} = 32$$

$$\text{or, } \frac{x}{2(3.30 \times 10^{-3} - x)} = \sqrt{32} = 5.66$$

$$\text{or, } x = 11.32(3.30 \times 10^{-3} - x)$$

$$\text{or, } 12.32x = 11.32 \times 3.30 \times 10^{-3}$$

$$\text{or, } x = 3.0 \times 10^{-3}$$

$$\therefore \text{ At eqm., } [\text{BrCl}] = (3.30 \times 10^{-3} - 3.0 \times 10^{-3}) \\ = 0.30 \times 10^{-3} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$$

**17.** Let the total mass of the mixture of CO and CO<sub>2</sub> is 100 g, then mass of CO = 90.55 g and mass of CO<sub>2</sub> = 100 - 90.55 = 9.45 g

$$\text{Moles of CO} = \frac{90.55}{28} = 3.234$$

$$\text{Moles of CO}_2 = \frac{9.45}{44} = 0.215$$

$$\text{Mole fraction of CO} = \frac{3.234}{3.234 + 0.215} = 0.938$$

$$\text{Mole fraction of CO}_2 = \frac{0.215}{3.234 + 0.215} = 0.062$$

$$\therefore p_{\text{CO}} = \text{mole fraction} \times \text{total pressure}$$

$$= 0.938 \times 1 \text{ atm} = 0.938 \text{ atm}$$

$$p_{\text{CO}_2} = 0.062 \times 1 \text{ atm} = 0.062 \text{ atm}$$

$$K_p \text{ for the reaction } \text{C}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons 2\text{CO}_{(g)}$$

$$K_p = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} = \frac{(0.938)^2}{0.062} = 14.19$$

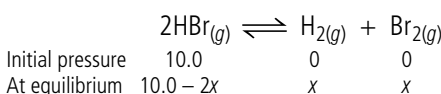
$$\text{Now } \Delta n_g = 2 - 1 = 1, K_p = K_c(RT)^{\Delta n_g}$$

$$\text{or } K_c = \frac{K_p}{RT} = \frac{14.19}{0.0821 \times 1127} = 0.153$$

**18.**  $\text{H}_{2(g)} + \text{Br}_{2(g)} \rightleftharpoons 2\text{HBr}_{(g)}$ ;  $K_p = 1.6 \times 10^5$

For the reaction  $2\text{HBr}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{Br}_{2(g)}$

$$K_p = \frac{1}{1.6 \times 10^5} = 6.25 \times 10^{-6}$$



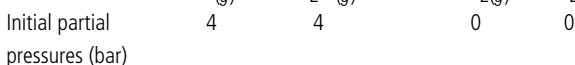
$$\therefore K_p = \frac{p_{\text{H}_2} \times p_{\text{Br}_2}}{p_{\text{HBr}}^2}$$

$$6.25 \times 10^{-6} = \frac{x^2}{(10.0 - 2x)^2} \text{ or } \frac{x}{10.0 - 2x} = 2.5 \times 10^{-3}$$

and  $x = 2.5 \times 10^{-2}$  So,  $p_{\text{H}_2} = p_{\text{Br}_2} = 2.5 \times 10^{-2} \text{ bar}$

$$p_{\text{HBr}} = 10.0 - 5.0 \times 10^{-2} \approx 10.0 \text{ bar}$$

**19.**  $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_2_{(g)}$



Applying law of chemical equilibrium,

$$K_p = \frac{p_{\text{CO}_2} \cdot p_{\text{H}_2}}{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}$$

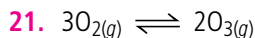
$$10.1 = \frac{p \cdot p}{(4-p)(4-p)} = \frac{p}{4-p} = \sqrt{10.1}$$

$$\frac{p}{4-p} = 3.178 \Rightarrow p = 3.04 \text{ bar}$$

20. (a) Since  $K_c$  is very small, there will be appreciable concentration of the reactants.

(b) Since  $K_c$  is very large, there will be appreciable concentration of the products.

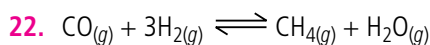
(c) Since  $K_c = 1.8$ , the concentration of reactants and products will be in comparable amounts.



$$K_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3} \Rightarrow 2.0 \times 10^{-50} = \frac{[\text{O}_3]^2}{(1.6 \times 10^{-2})^3}$$

$$[\text{O}_3]^2 = 2.0 \times 10^{-50} \times (1.6)^3 \times 10^{-6}$$

$$[\text{O}_3] = \sqrt{2.0 \times (1.6)^3 \times 10^{-28}} = 2.864 \times 10^{-28} \text{ mol L}^{-1}$$



Applying law of chemical equilibrium,

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \Rightarrow 3.90 = \frac{[\text{CH}_4] \times 0.02}{0.30 \times (0.1)^3}$$

$$[\text{CH}_4] = \frac{3.9 \times 0.3 \times 0.1 \times 0.1 \times 0.1}{0.02} = \frac{39 \times 3}{2} \times 10^{-3}$$

$$= 58.5 \times 10^{-3} = 5.85 \times 10^{-2} \text{ mol/L}$$

### Topic 3

1. (a) Initially vapour pressure decreases because the same amount of vapour are now distributed in larger space.

(b) Rate of evaporation remains constant at constant temperature in a closed vessel while that of condensation falls initially.

(c) On restoration of the equilibrium again, rate of evaporation = rate of condensation the vapour pressure becomes the same. The final vapour pressure will be same as it was originally because vapour pressure depends upon the temperature and not upon the volume of the container.

2. (a)  $\Delta G^\circ = \sum \Delta_f G^\circ(\text{Products}) - \sum \Delta_f G^\circ(\text{Reactants})$

$$= \Delta_f G^\circ(\text{NO}_2) - [\Delta_f G^\circ(\text{NO}) + \frac{1}{2} \Delta_f G^\circ(\text{O}_2)]$$

$$= 52.0 - \left( 87.0 + \frac{1}{2} \times 0 \right) = -35.0 \text{ kJ mol}^{-1}$$

(b)  $-\Delta G^\circ = 2.303 RT \log K$

$$\text{Hence, } -(-35000) = 2.303 \times 8.314 \times 298 \times \log K$$

$$\text{or } \log K = 6.1341 \text{ or } K = \text{antilog}(6.1341)$$

$$\text{or } K = 1.361 \times 10^6$$

3. Applying Le Chatelier's principle, on decreasing the pressure, equilibrium shifts to the direction in which number of moles of gaseous substances is more. Thus, moles of reaction products will increase in reaction (a), decrease in reaction (b) and remain same ( $n_p = n_r$ , for gaseous substances) in reaction (c).

4. Reactions will be affected in those in which ( $n_p \neq n_r$ , for gaseous substances) Hence, reactions (i), (iii), (iv), (v) and (vi) will be affected. By applying Le Chatelier's principle, we can predict the direction.

(i)  $n_p = 2, n_r = 1$  i.e.,  $n_p > n_r$ , reaction will go in the backward direction.

(ii)  $n_p = 3, n_r = 3$  i.e.,  $n_p = n_r$ , reaction will not be affected by pressure.

(iii)  $n_p = 2, n_r = 1$  i.e.,  $n_p > n_r$ , reaction will go in the backward direction.

(iv)  $n_p = 1, n_r = 3$  i.e.,  $n_p < n_r$ , reaction will go in the forward direction.

(v)  $n_p = 1, n_r = 0$  i.e.,  $n_p > n_r$ , reaction will go in the backward direction.

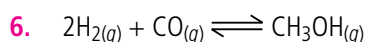
(vi)  $n_p = 10, n_r = 9$  i.e.,  $n_p > n_r$ , reaction will go in the backward direction.

5. (a)  $K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2}^3}{p_{\text{CH}_4} \times p_{\text{H}_2\text{O}}}$

(b) (i)  $K_p$  remains constant on increasing pressures. By Le Chatelier's principle, on increasing pressure, equilibrium will shift in the backward direction where number of moles decreases.

(ii) As the given reaction is endothermic, the value of  $K_p$  increases with increase in temperature. By Le Chatelier's principle, equilibrium will shift in the forward direction with increasing temperature for endothermic reaction.

(iii)  $K_p$  remains constant, equilibrium composition will not be disturbed by the presence of catalyst but equilibrium will be attained quickly.



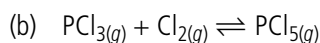
(a) Addition of  $\text{H}_2$ : The equilibrium will shift in the forward direction.

(b) Addition of  $\text{CH}_3\text{OH}$ : The equilibrium will shift in the backward direction.

(c) Removal of  $\text{CO}$ : The equilibrium will shift in the backward direction.

(d) Removal of  $\text{CH}_3\text{OH}$ : The equilibrium will shift in the forward direction.

7. (a)  $K_c = \frac{[\text{PCl}_3(g)][\text{Cl}_2(g)]}{[\text{PCl}_5(g)]}$



$$\therefore K'_c = \frac{[\text{PCl}_5(g)]}{[\text{PCl}_3(g)][\text{Cl}_2(g)]} = \frac{1}{8.3 \times 10^{-3}} = 120.48$$

(c) (i)  $K_c$  remains unchanged, as  $K_c$  is independent of concentration.

(ii)  $K_c$  remains unchanged as  $K_c$  is independent of pressure.

(iii) As the given reaction is endothermic,  $K_c$  will increase with increase of temperature.

## Topic 4

**1. Conjugate acid-base pair :** The pairs of acids and bases which are formed from each other by the gain or loss of a proton are called conjugate acid-base pairs.

Species	Conjugate acid	Conjugate base
HNO <sub>2</sub>	—	NO <sub>2</sub> <sup>-</sup>
CN <sup>-</sup>	HCN	—
HClO <sub>4</sub>	—	ClO <sub>4</sub> <sup>-</sup>
F <sup>-</sup>	HF	—
OH <sup>-</sup>	H <sub>2</sub> O	O <sup>2-</sup>
CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	—
S <sup>2-</sup>	HS <sup>-</sup>	—

**2.** BF<sub>3</sub>, H<sup>+</sup> and NH<sub>4</sub><sup>+</sup> are Lewis acids because they can accept a lone pair of electron.

**3. Bronsted acid**                      **Conjugate base**

HF	F <sup>-</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>
HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>

**4. Bronsted base**                      **Conjugate acid**

NH <sub>2</sub> <sup>-</sup>	NH <sub>3</sub>
NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>
HCOO <sup>-</sup>	HCOOH

**5. Species**                      **Conjugate acid**                      **Conjugate base**

H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	OH <sup>-</sup>
HCO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> CO <sub>3</sub>	CO <sub>3</sub> <sup>2-</sup>
HSO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> SO <sub>4</sub>	SO <sub>4</sub> <sup>2-</sup>
NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>	NH <sub>2</sub> <sup>-</sup>

**6.** (a) OH<sup>-</sup> : OH<sup>-</sup> is a Lewis base because it can donate lone pair of electrons.

(b) F<sup>-</sup> : F<sup>-</sup> is a Lewis base because it can donate lone pair of electrons.

(c) H<sup>+</sup> : H<sup>+</sup> is a Lewis acid because it can accept lone pair of electrons.

(d) BCl<sub>3</sub> : BCl<sub>3</sub> is a Lewis acid because it is electron deficient and can accept a lone pair of electrons.

**7.** [H<sup>+</sup>] = 3.8 × 10<sup>-3</sup> M

$$\text{pH} = -\log[\text{H}^+] = -\log(3.8 \times 10^{-3})$$

$$= 3 \log 10 - \log 3.8 = 3 - 0.5797 = 2.4203 \approx 2.42$$

**8.** We know that  $\text{pH} = -\log[\text{H}^+]$

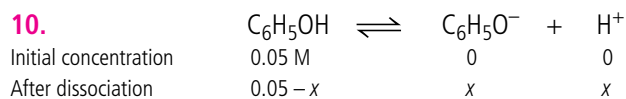
$$\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-3.76) = 1.738 \times 10^{-4} \text{ M}$$

**9.**  $K_b = \frac{K_w}{K_a}$

$$\text{For F}^-, K_b = \frac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

$$\text{For HCOO}^-, K_b = \frac{10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

$$\text{For CN}^-, K_b = \frac{10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$



$$\therefore K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10} \text{ (Given)}$$

$$\text{or } \frac{x^2}{0.05} = 1.0 \times 10^{-10} \quad [\because (0.05 - x) \approx 0.05]$$

$$\text{or } x^2 = 5 \times 10^{-12} \text{ or } x = 2.23 \times 10^{-6} \text{ M}$$

In presence of 0.01 M C<sub>6</sub>H<sub>5</sub>ONa, suppose y is the amount of phenol dissociated, then at equilibrium

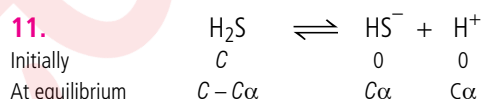
$$[\text{C}_6\text{H}_5\text{OH}] = 0.05 - y \approx 0.05 \text{ M}$$

$$[\text{C}_6\text{H}_5\text{O}^-] = 0.01 + y \approx 0.01 \text{ M}, [\text{H}^+] = y \text{ M}$$

$$\therefore K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10} \quad \text{(Given)}$$

$$\text{or } y = 5 \times 10^{-10}$$

$$\therefore \alpha = \frac{y}{C} = \frac{5 \times 10^{-10}}{0.05} = 1 \times 10^{-8}$$

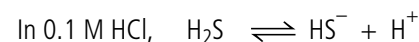


$$K_a = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]} = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \therefore (1-\alpha) \approx 1 \quad (\because \alpha \ll 1)$$

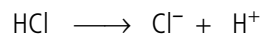
$$\text{and } [\text{HS}^-] = C\alpha = \sqrt{K_a C}$$

$$[\text{HS}^-] = \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.54 \times 10^{-5} \text{ M}$$

$$\therefore [\text{HS}^-] = 9.54 \times 10^{-5} \text{ M}$$



Initially	0.1 M	0	0
At equilibrium	(0.1 - x)	x	x



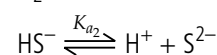
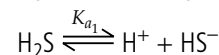
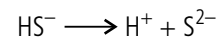
$$0.1 + n \approx 0.1 \text{ M} \quad 0.1 \text{ M} \quad 0.1 \text{ M}$$

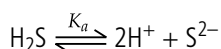
$$K_a = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 9.1 \times 10^{-8}$$

$$\Rightarrow K_a = \frac{0.1 \times [\text{HS}^-]}{0.1} = 9.1 \times 10^{-8} \Rightarrow [\text{HS}^-] = 9.1 \times 10^{-8} \text{ M}$$

∴ The concentration of HS<sup>-</sup> has decreased in 0.1 M HCl.

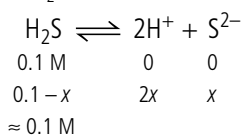
To calculate the concentration of S<sup>2-</sup> ion:





Overall dissociation constant of  $\text{H}_2\text{S}$

$$K_a = K_{a_1} \times K_{a_2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20}$$



$$K_a = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

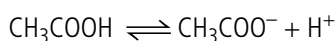
$$\Rightarrow 1.092 \times 10^{-20} = \frac{(2x)^2 x}{0.1} \Rightarrow x = 6.5 \times 10^{-8} \text{ M}$$

In presence of 0.1 M HCl,

$$K_a = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$1.092 \times 10^{-20} = \frac{(0.1)^2[\text{S}^{2-}]}{(0.1)} \Rightarrow [\text{S}^{2-}] = 1.092 \times 10^{-19} \text{ M}$$

$$12. \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.74 \times 10^{-5}}{5 \times 10^{-2}}} = 0.0186$$



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

$$\text{or, } [\text{H}^+] = \sqrt{K_a[\text{CH}_3\text{COOH}]}$$

$$= \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4} \text{ M}$$

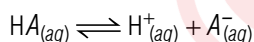
$$[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 9.33 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(9.33 \times 10^{-4}) = 4 - 0.97 = 3.03$$

$$13. \quad \text{pH} = -\log[\text{H}^+]$$

$$\therefore [\text{H}^+] = \text{antilog}(-4.15)$$

$$[\text{H}^+] = 7.08 \times 10^{-5} \text{ M}$$



$$\therefore [\text{H}^+] = [\text{A}^-] = 7.08 \times 10^{-5} \text{ M}$$

$$\text{and } \alpha = \frac{[\text{H}^+]}{C} = \frac{7.08 \times 10^{-5}}{0.01} = 7.08 \times 10^{-3}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.01(7.08 \times 10^{-3})^2}{1-7.08 \times 10^{-3}} = 5.05 \times 10^{-7}$$

$$\text{p}K_a = -\log K_a = -\log(5.05 \times 10^{-7}) = 6.29$$

$$14. \quad (\text{a}) \text{HCl} + \text{aq} \rightarrow \text{H}^+ + \text{Cl}^-$$

$$\therefore [\text{H}^+] = [\text{HCl}] = 3 \times 10^{-3} \text{ M}$$

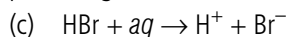
$$\text{pH} = -\log(3 \times 10^{-3}) = 2.52$$

$$(\text{b}) \text{NaOH} + \text{aq} \rightarrow \text{Na}^+ + \text{OH}^-$$

$$\therefore [\text{OH}^-] = 5 \times 10^{-3} \text{ M}$$

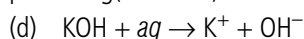
$$\therefore [\text{H}^+] = \frac{10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log(2 \times 10^{-12}) = 11.70$$



$$\therefore [\text{H}^+] = 2 \times 10^{-3} \text{ M,}$$

$$\text{pH} = -\log(2 \times 10^{-3}) = 2.70$$



$$\therefore [\text{OH}^-] = 2 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$$

$$\text{pH} = -\log(5 \times 10^{-12}) = 11.30$$

$$15. \quad (\text{a}) \text{Molar mass of TlOH} = 221.4 \text{ g mol}^{-1}$$

$$\therefore n_{\text{TlOH}} = \frac{2 \text{ g}}{221.4 \text{ g mol}^{-1}} = 9.03 \times 10^{-3} \text{ mol}$$

$$[\text{OH}^-] = [\text{TlOH}] = \frac{9.03 \times 10^{-3} \text{ mol}}{2 \text{ L}} = 4.51 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(4.51 \times 10^{-3}) = 2.35 \text{ and}$$

$$\text{pH} = 14 - 2.35 = 11.65$$

$$(\text{b}) n_{\text{Ca(OH)}_2} = \frac{0.3 \text{ g}}{74 \text{ g mol}^{-1}} = 4.05 \times 10^{-3} \text{ mol}$$

$$[\text{OH}^-] = 2[\text{Ca(OH)}_2] = 2 \times \frac{4.05 \times 10^{-3} \text{ mol}}{0.5 \text{ L}}$$

$$= 1.62 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log(1.62 \times 10^{-2}) = 1.79 \text{ and}$$

$$\text{pH} = 14 - 1.79 = 12.21$$

$$(\text{c}) n_{\text{NaOH}} = \frac{0.3 \text{ g}}{40 \text{ g mol}^{-1}} = 7.5 \times 10^{-3} \text{ mol}$$

$$[\text{OH}^-] = [\text{NaOH}] = \frac{7.5 \times 10^{-3} \text{ mol}}{0.2 \text{ L}} = 0.0375 \text{ M}$$

$$\text{pOH} = -\log(0.0375) = 1.43 \text{ and}$$

$$\text{pH} = 14 - 1.43 = 12.57$$

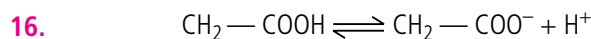
$$(\text{d}) M_1V_1 = M_2V_2$$

$$13.6 \text{ mol L}^{-1} \times 1 \text{ mL} = M \times 1000 \text{ mL}$$

$$M_{\text{HCl}} = 0.0136 \text{ mol L}^{-1}$$

$$[\text{H}^+] = [\text{HCl}] = 0.0136 \text{ M}$$

$$\therefore \text{pH} = -\log(0.0136) = 1.87$$



Initial molar conc.	C	0	0
Eqm. molar conc.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$C = 0.1 \text{ M, } \alpha = 0.132, [\text{H}^+] = C\alpha = 0.0132 \text{ M}$$

$$\text{pH} = -\log(0.0132) = 1.8794$$

$$K_a = C\alpha^2 \text{ or } K_a = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

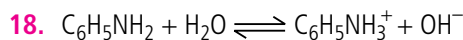
$$\text{p}K_a = -\log K_a = -\log(1.74 \times 10^{-3}) = 2.7595$$

$$17. \quad [\text{H}^+] = \text{antilog}(-9.95) = 1.12 \times 10^{-10} \text{ M}$$

$$\therefore [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.12 \times 10^{-10}} = 8.92 \times 10^{-5} \text{ M}$$

$$\text{But } K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{(8.92 \times 10^{-5})^2}{0.005} = 1.59 \times 10^{-6}$$

$$pK_b = -\log K_b = -\log(1.59 \times 10^{-6}) = 5.80$$



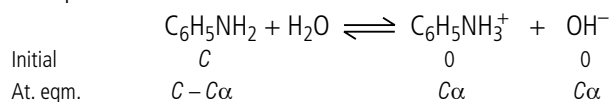
$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{[\text{OH}^-]^2}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$[\text{OH}^-] = \sqrt{K_b[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$= \sqrt{(4.27 \times 10^{-10})(10^{-3})} = 6.534 \times 10^{-7} \text{ M}$$

$$p\text{OH} = -\log(6.534 \times 10^{-7}) = 6.18$$

$$\therefore \text{pH} = 14 - 6.18 = 7.82$$



$$K_b = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \quad (\because \alpha \ll 1)$$

$$\therefore \alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{4.27 \times 10^{-10}}{10^{-3}}} = 6.53 \times 10^{-4}$$

$$pK_b = -\log(4.27 \times 10^{-10}) = 9.37$$

$$pK_a + pK_b = 14 \quad (\text{for a pair of conjugate acid and base})$$

$$\therefore pK_a = 14 - 9.37 = 4.63$$

$$\text{i.e. } -\log K_a = 4.63 \quad \text{or, } \log K_a = -4.63$$

$$\text{or, } K_a = \text{antilog}(-4.63) = 2.34 \times 10^{-5}$$

$$\text{pH} = 7.82, \alpha = 6.53 \times 10^{-4}, K_a = 2.34 \times 10^{-5}$$

19.  $pK_a = 4.74$

$$-\log(K_a) = 4.74$$

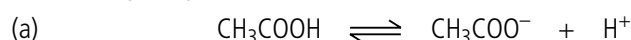
$$K_a = \text{antilog}(-4.74) = 1.820 \times 10^{-5}$$

$$C\alpha^2 = 1.82 \times 10^{-5}$$

$$\Rightarrow \alpha^2 = \frac{1.82 \times 10^{-5}}{C} = \frac{1.82 \times 10^{-5}}{0.05} = 3.64 \times 10^{-4}$$

$$\alpha^2 = 3.64 \times 10^{-4}$$

$$\Rightarrow \alpha = 1.9 \times 10^{-2}$$



Initial molar conc.	$C$	$0$	$0$
Eqm. molar conc.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{C}$$

$$[\text{H}^+] = 0.01 \text{ M}$$

$$1.82 \times 10^{-5} = \frac{C\alpha}{C} \times 0.011$$

$$\Rightarrow \alpha = \frac{1.82 \times 10^{-5}}{0.01} = 1.82 \times 10^{-3}$$

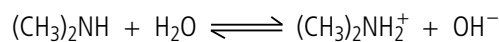
(b)  $[\text{H}^+] = 0.1 \text{ M}$

$$1.82 \times 10^{-5} = \frac{C\alpha}{C} \times 0.1 = \alpha \times 0.1 \Rightarrow \alpha = 1.82 \times 10^{-4}$$

20.  $K_a = 5.4 \times 10^{-4}, C = 0.02 \text{ M}, K_a = C\alpha^2$

$$\alpha^2 = \frac{K_a}{C} = \frac{5.4 \times 10^{-4}}{0.02} = 270 \times 10^{-4}$$

$$\alpha = 0.164$$



Initially :	$C$	$0$	$0$
At eqm. :	$C(1-\alpha)$	$C\alpha$	$C\alpha$

But  $[\text{OH}^-] = 0.1 \text{ M}$

$$K_a = \frac{C\alpha \times [\text{OH}^-]}{C(1-\alpha)} \Rightarrow 5.4 \times 10^{-4} = \frac{C\alpha \times 0.1}{C(1-\alpha)}$$

But  $\alpha \ll 1$ ,

$\therefore \alpha$  is neglected in the denominator.

$$\Rightarrow \alpha = \frac{5.4 \times 10^{-4}}{0.1} = 5.40 \times 10^{-3} = 0.0054$$

$$\% \text{ ionisation} = 100\alpha = 100 \times 0.0054 = 0.54$$

21. (a)  $\text{pH} = 6.83$

$$\therefore [\text{H}^+] = \text{antilog}(-6.83) = 1.48 \times 10^{-7} \text{ M}$$

(b)  $\text{pH} = 1.2$

$$\therefore [\text{H}^+] = \text{antilog}(-1.2) = 6.30 \times 10^{-2} \text{ M}$$

(c)  $\text{pH} = 7.38$

$$\therefore [\text{H}^+] = \text{antilog}(-7.38) = 4.17 \times 10^{-8} \text{ M}$$

(d)  $\text{pH} = 6.4$

$$\therefore [\text{H}^+] = \text{antilog}(-6.4) = 3.98 \times 10^{-7} \text{ M}$$

22. For milk,  $\text{pH} = 6.8$

$$\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-6.8)$$

$$= 1.58 \times 10^{-7} \text{ M}$$

For black coffee,  $\text{pH} = 5.0$

$$\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-5.0)$$

$$= 1 \times 10^{-5} \text{ M}$$

For tomato juice,  $\text{pH} = 4.2$

$$\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-4.2) = 6.31 \times 10^{-5} \text{ M}$$

For lemon juice,  $\text{pH} = 2.2$

$$\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-2.2)$$

$$= 6.31 \times 10^{-3} \text{ M}$$

For egg white,  $\text{pH} = 7.8$

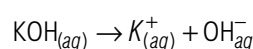
$$\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-7.8) = 1.58 \times 10^{-8} \text{ M}$$

23. Molar mass of  $\text{KOH} = 56.0 \text{ g mol}^{-1}$

$$\therefore \text{No. of moles of KOH} = \frac{0.561 \text{ g}}{56.0 \text{ g mol}^{-1}}$$

$$= 0.01 \text{ mol}$$

$$\text{and conc. of KOH} = \frac{0.01}{0.2 \text{ L}} \text{ mol} = 0.05 \text{ mol/L}$$





$$[K^+] = [OH^-] = 0.05 \text{ M}$$

$$\text{and } [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.05} = 2.0 \times 10^{-13}$$

$$\therefore \text{pH} = -\log(2.0 \times 10^{-13}) = 12.70$$

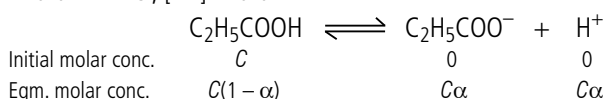
$$24. K_a = 1.32 \times 10^{-5}; C = 0.05 \text{ M};$$

$$\alpha = \sqrt{\frac{K_a}{C}} \text{ or } \alpha = \sqrt{\frac{1.32 \times 10^{-5}}{5 \times 10^{-2}}} = 1.62 \times 10^{-2}$$

$$[H^+] = C\alpha = 0.05 \times 1.62 \times 10^{-2} = 8.1 \times 10^{-4}$$

$$\text{pH} = -\log(8.1 \times 10^{-4}) = 3.09$$

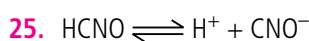
$$\text{In } 0.01 \text{ M HCl, } [H^+] = 0.01 \text{ M}$$



Applying law of chemical eqm.

$$K_a = \frac{[C_2H_5COO^-][H^+]}{[C_2H_5COOH]} = \frac{C\alpha \times 0.01}{C(1-\alpha)}, K_a = \frac{C\alpha \times 0.01}{C}$$

$$1.32 \times 10^{-5} = 0.01\alpha \Rightarrow \alpha = 1.32 \times 10^{-3}$$



$$\text{pH} = 2.34 \text{ or } \log[H^+] = -2.34$$

$$\text{or, } [H^+] = \text{antilog}(-2.34) = 4.57 \times 10^{-3} \text{ M}$$

$$[CNO^-] = [H^+] = 4.57 \times 10^{-3} \text{ M}$$

$$K_a = \frac{(4.57 \times 10^{-3})(4.57 \times 10^{-3})}{0.1} = 2.09 \times 10^{-4}$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.09 \times 10^{-4}}{0.1}} = 0.0457$$

$$26. \text{ Degree of hydrolysis, } h = \sqrt{\frac{K_w}{K_a \cdot C}}$$

$$= \sqrt{\frac{1 \times 10^{-14}}{4.5 \times 10^{-4} \times 0.04}} = 2.36 \times 10^{-5}$$

$$\text{pH} = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$= \frac{1}{2}[-\log 10^{-14} + (-\log 4.5 \times 10^{-4}) + \log(4 \times 10^{-2})] = 7.975$$

27. Pyridinium hydrochloride is a salt of weak base and strong acid. Therefore,

$$\text{pH} = 7 - \frac{1}{2}(\log C + pK_b)$$

where  $K_b$  = dissociation constant of pyridine

$$3.44 = 7 - \frac{1}{2}(\log 0.02 + pK_b)$$

$$-3.56 = -\frac{1}{2}(-1.70 + pK_b) \Rightarrow -7.12 = 1.70 - pK_b$$

$$pK_b = 1.70 + 7.12 = 8.82$$

$$K_b = \text{antilog}(-8.82) = 1.513 \times 10^{-9}$$

28. NaCN, NaNO<sub>2</sub>, KF solutions are basic, as they are salts of strong base and weak acid.

NaCl, KBr solutions are neutral, as they are salts of strong acid and strong base.

NH<sub>4</sub>NO<sub>3</sub> solution is acidic, as it is a salt of strong acid and weak base.

29. pH of acid solution,

$$[H^+] = \sqrt{K_a \times C}$$

$$K_a = 1.35 \times 10^{-3}, C = 0.1 \text{ M}$$

$$[H^+] = \sqrt{1.35 \times 10^{-3} \times 0.1} = \sqrt{1.35 \times 10^{-4}} = 1.16 \times 10^{-2}$$

$$\text{pH} = -\log[H^+] = -\log(1.16 \times 10^{-2}) = 2 - 0.064 = 1.936$$

Sodium salt of chloroacetic acid is salt of weak acid and strong base. Hence,

$$\text{pH} = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$K_a = 1.35 \times 10^{-3}$$

$$pK_a = -\log K_a = -\log(1.35 \times 10^{-3}) = -(0.1303 - 3) = 2.8697$$

$$pK_w = -\log 10^{-14} = 14$$

$$C = 0.1 \text{ M, } \log C = \log(0.1) = -1$$

$$\text{pH} = \frac{1}{2}[14 + 2.8697 - 1] = 7.935$$

30. We know that

$$[H^+] = \sqrt{K_w} = \sqrt{2.7 \times 10^{-14}} = 1.643 \times 10^{-7} \text{ M}$$

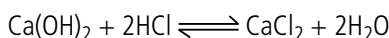
$$\therefore \text{pH} = -\log[H^+] = -\log(1.643 \times 10^{-7}) \\ = 7 - 0.2156 = 6.78$$

31. (a) 10 mL of 0.2 M Ca(OH)<sub>2</sub>

$$= 10 \times 0.2 \text{ millimoles} = 2 \text{ millimoles of Ca(OH)}_2$$

$$25 \text{ mL of } 0.1 \text{ M HCl} = 25 \times 0.1 \text{ millimoles}$$

$$= 2.5 \text{ millimoles of HCl}$$



1 millimole of Ca(OH)<sub>2</sub> reacts with 2 millimoles of HCl

$\therefore$  2.5 millimoles of HCl will react with 1.25 millimoles of Ca(OH)<sub>2</sub>

$\therefore$  Ca(OH)<sub>2</sub> left = 2 - 1.25 = 0.75 millimoles (HCl is the limiting reactant.)

$$\text{Total volume of the solution} = 10 + 25 \text{ mL} = 35 \text{ mL}$$

$$\therefore \text{Molarity of Ca(OH)}_2 \text{ in the mixture solution} = \frac{0.75}{35} \text{ M} \\ = 0.0214 \text{ M}$$

$$\therefore [OH^-] = 2 \times 0.0214 \text{ M} = 0.0428 \text{ M} = 4.28 \times 10^{-2} \text{ M}$$

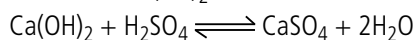
$$\text{pOH} = -\log(4.28 \times 10^{-2}) = 2 - 0.6314 = 1.3686 \approx 1.37$$

$$\therefore \text{pH} = 14 - 1.37 = 12.63$$

(b) 10 mL of 0.01 M H<sub>2</sub>SO<sub>4</sub> = 10 × 0.01 millimole

$$= 0.1 \text{ millimole}$$

10 mL of 0.01 M Ca(OH)<sub>2</sub> = 10 × 0.01 millimole = 0.1 millimole



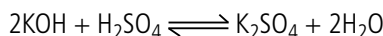


1 mole of  $\text{Ca}(\text{OH})_2$  reacts with 1 mole of  $\text{H}_2\text{SO}_4$

$\therefore$  0.1 millimole of  $\text{Ca}(\text{OH})_2$  will react completely with 0.1 millimole of  $\text{H}_2\text{SO}_4$ . hence, solution will be neutral with  $\text{pH} = 7.0$

(c) 10 mL of 0.1 M  $\text{H}_2\text{SO}_4 = 1$  millimole

10 mL of 0.1 M KOH = 1 millimole



1 millimole of KOH will react with 0.5 millimole of  $\text{H}_2\text{SO}_4$

$\therefore$   $\text{H}_2\text{SO}_4$  left = 1 - 0.5 = 0.5 millimole

Volume of reaction mixture = 10 + 10 = 20 mL

$\therefore$  Molarity of  $\text{H}_2\text{SO}_4$  in the mixture solution

$$= \frac{0.5}{20} = 2.5 \times 10^{-2} \text{ M}$$

$$[\text{H}^+] = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2}$$

$$\text{pH} = -\log(5 \times 10^{-2}) = 2 - 0.699 = 1.3$$

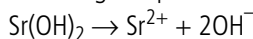
## Topic 5

1. Molar mass of  $\text{Sr}(\text{OH})_2 = 87.6 + 34 = 121.6 \text{ g mol}^{-1}$

Solubility of  $\text{Sr}(\text{OH})_2$  in moles  $\text{L}^{-1}$

$$= \frac{19.23 \text{ g L}^{-1}}{121.6 \text{ g mol}^{-1}} = 0.1581 \text{ M}$$

Assuming complete dissociation,



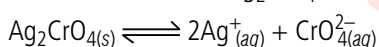
$$\therefore [\text{Sr}^{2+}] = 0.1581 \text{ M},$$

$$[\text{OH}^-] = 2 \times 0.1581 = 0.3162 \text{ M}$$

$$\text{pOH} = -\log(0.3162) = 0.5$$

$$\therefore \text{pH} = 14 - 0.5 = 13.5$$

2. Silver chromate,  $\text{Ag}_2\text{CrO}_4$

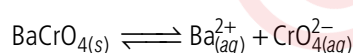


$$K_{sp} = 4s^3 = 1.1 \times 10^{-12} \therefore s = 6.50 \times 10^{-5} \text{ M}$$

$$\therefore [\text{Ag}^+] = 2 \times 6.50 \times 10^{-5} = 1.30 \times 10^{-4} \text{ M and}$$

$$[\text{CrO}_4^{2-}] = 6.50 \times 10^{-5} \text{ M}$$

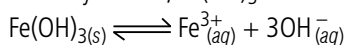
Barium chromate,  $\text{BaCrO}_4$



$$K_{sp} = s^2 = 1.2 \times 10^{-10} \therefore s = 1.09 \times 10^{-5} \text{ M}$$

$$[\text{Ba}^{2+}] = [\text{CrO}_4^{2-}] = 1.09 \times 10^{-5} \text{ M}$$

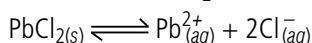
Ferric hydroxide,  $\text{Fe}(\text{OH})_3$



$$K_{sp} = 27s^4 = 1.0 \times 10^{-38} \therefore s = 1.38 \times 10^{-10} \text{ M}$$

$$[\text{Fe}^{3+}] = 1.38 \times 10^{-10} \text{ M and } [\text{OH}^-] = 3 \times 1.38 \times 10^{-10} \\ = 4.16 \times 10^{-10} \text{ M}$$

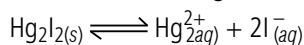
Lead chloride,  $\text{PbCl}_2$



$$K_{sp} = 4s^3 = 1.6 \times 10^{-5} \therefore s = 1.59 \times 10^{-2} \text{ M}$$

$$[\text{Pb}^{2+}] = 1.59 \times 10^{-2} \text{ M and } [\text{Cl}^-] = 2 \times 1.59 \times 10^{-2} \\ = 3.18 \times 10^{-2} \text{ M}$$

Mercurous iodide,  $\text{Hg}_2\text{I}_2$

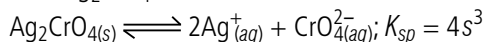


$$K_{sp} = 4s^3 = 4.5 \times 10^{-29} \text{ and } s = 2.24 \times 10^{-10} \text{ M}$$

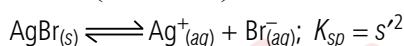
$$[\text{Hg}_2^{2+}] = 2.24 \times 10^{-10} \text{ M and } [\text{I}^-] = 2 \times 2.24 \times 10^{-10} \\ = 4.48 \times 10^{-10} \text{ M}$$

3.  $K_{sp}(\text{Ag}_2\text{CrO}_4) > K_{sp}(\text{AgBr})$

$\therefore$   $\text{Ag}_2\text{CrO}_4$  is more soluble.



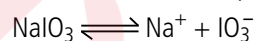
$$\therefore s = \left( \frac{1.1 \times 10^{-12}}{4} \right)^{1/3} = 6.50 \times 10^{-5} \text{ M}$$



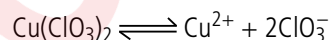
$$\therefore s' = (5 \times 10^{-13})^{1/2} = 7.07 \times 10^{-7} \text{ M}$$

$$\text{The ratio of the molarities} = \frac{s}{s'} = \frac{6.50 \times 10^{-5}}{7.07 \times 10^{-7}} \\ = 91.94$$

4. When equal volumes of sodium iodate and cupric chlorate are mixed, the molar concentrations of both the solutes would be reduced to half *i.e.*, 0.001 M



$$0.001 \text{ M} \qquad \qquad 0.001 \text{ M}$$

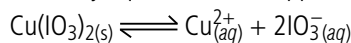


$$0.001 \text{ M} \qquad \qquad 0.001 \text{ M}$$

$\therefore$  After mixing,  $[\text{IO}_3^-] = [\text{NaIO}_3] = 0.001 \text{ M}$

$$[\text{Cu}^{2+}] = [\text{Cu}(\text{ClO}_3)_2] = 0.001 \text{ M}$$

Solubility equilibrium for copper iodate may be written as,



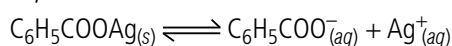
Ionic product of copper iodate

$$= [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (0.001)(0.001)^2 = 1 \times 10^{-9}$$

Since ionic product ( $1 \times 10^{-9}$ ) is less than

$K_{sp}$  ( $7.4 \times 10^{-8}$ ), therefore, no precipitation will take place.

5. Suppose  $s$  is the molar solubility of silver benzoate in water, then

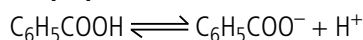


$$K_{sp} = s^2 \therefore s = \sqrt{2.5 \times 10^{-13}} = 5.0 \times 10^{-7} \text{ M}$$

Given,  $\text{pH} = 3.19$

$$\text{i.e., } [\text{H}^+] = 6.46 \times 10^{-4} \text{ M}$$

$\text{C}_6\text{H}_5\text{COO}^-$  ions now combine with  $\text{H}^+$  ions to form  $\text{C}_6\text{H}_5\text{COOH}$ , but  $[\text{H}^+]$  remains almost constant because it is buffer solution.



$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} \Rightarrow \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{[\text{H}^+]}{K_a} \\ = \frac{6.457 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let solubility in buffer solution is  $x$  mol/L. Then as most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionized), we have

$$x = [\text{Ag}^+] = [\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COOH}] = [\text{C}_6\text{H}_5\text{COO}^-] + 10[\text{C}_6\text{H}_5\text{COO}^-]$$

$$= 11[\text{C}_6\text{H}_5\text{COO}^-]$$

$$\therefore [\text{C}_6\text{H}_5\text{COO}^-] = \frac{x}{11}$$

$$K_{sp} = [\text{C}_6\text{H}_5\text{COO}^-][\text{Ag}^+]$$

$$\text{or } 2.5 \times 10^{-3} = \frac{x}{11} \times x$$

$$\Rightarrow x^2 = 2.75 \times 10^{-12} \Rightarrow x = 1.66 \times 10^{-6}$$

$$\therefore \frac{x}{5} = \frac{1.66 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.32$$

Silver benzoate is 3.32 times more soluble in buffer of pH 3.19 than in pure water.

6. Let the concentration of each of  $\text{FeSO}_4$  and  $\text{Na}_2\text{S}$  be  $x$  mol  $\text{L}^{-1}$ . Then after mixing equal volumes :

$$[\text{FeSO}_4] = \frac{x}{2} \text{ M}, [\text{Na}_2\text{S}] = \frac{x}{2} \text{ M}$$

$$\text{or } [\text{Fe}^{2+}] = \frac{x}{2} \text{ M and } [\text{S}^{2-}] = \frac{x}{2} \text{ M}$$

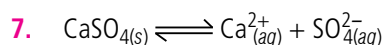
$$\text{FeS} \rightleftharpoons \text{Fe}^{2+} + \text{S}^{2-}, K_{sp} = [\text{Fe}^{2+}][\text{S}^{2-}]$$

$$6.3 \times 10^{-18} = \frac{x}{2} \times \frac{x}{2}$$

$$\text{or } x^2 = 4 \times 6.3 \times 10^{-18} = 25.2 \times 10^{-18}$$

$$\text{or } x = 5.02 \times 10^{-9} \text{ mol L}^{-1}$$

Maximum concentration of  $\text{FeSO}_4$  and  $\text{Na}_2\text{S}$  which will not precipitate iron sulphide =  $5.02 \times 10^{-9} \text{ mol L}^{-1}$



If  $s$  is the solubility of  $\text{CaSO}_4$  in  $\text{mol L}^{-1}$ , then

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = s^2$$

$$\text{or, } s = \sqrt{K_{sp}} = \sqrt{9.1 \times 10^{-6}} = 3.02 \times 10^{-3} \text{ mol L}^{-1}$$

$$= 3.02 \times 10^{-3} \times 136 \text{ g L}^{-1} = 0.411 \text{ g L}^{-1}$$

(Molar mass of  $\text{CaSO}_4 = 136 \text{ g mol}^{-1}$ ).

Thus, for dissolving 0.411 g, water required = 1 L

$$\therefore \text{For dissolving 1 g, water required} = \frac{1}{0.411} = 2.43 \text{ L}$$

8. Precipitation will take place in the solution for which ionic product is greater than solubility product. As 10 mL of solution containing  $\text{S}^{2-}$  ion is mixed with 5 mL of metal salt solution, after mixing

$$[\text{S}^{2-}] = 1.0 \times 10^{-19} \times \frac{10}{15} = 6.67 \times 10^{-20}$$

$$[\text{Fe}^{2+}] = [\text{Mn}^{2+}] = [\text{Zn}^{2+}] = [\text{Cd}^{2+}] = \frac{5}{15} \times 0.04 = 1.33 \times 10^{-2} \text{ M}$$

Hence the ionic product  $[M^{2+}][\text{S}^{2-}]$

$$= 1.33 \times 10^{-2} \times 6.67 \times 10^{-20} = 8.87 \times 10^{-22}$$

Therefore, in  $\text{ZnS}$  ( $K_{sp} = 1.6 \times 10^{-24}$ )

and  $\text{CdS}$  ( $K_{sp} = 8.0 \times 10^{-27}$ ), ionic product exceeds solubility product. Hence, precipitation will take place.

