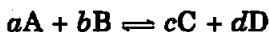


**FACTS THAT MATTER**

- **Equilibrium:** It can be established for both physical and chemical processes. The state of equilibrium rate of forward and backward reactions are equal.
- **Equilibrium constants:**  $K_c$  is expressed as the concentration of products divided by reactants each term raised to the stoichiometric-coefficients.

For reactions,



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

- **LeChateliers principle:** It states that the change in any factor such as temperature, pressure, concentration etc, will cause the equilibrium to shift in such a direction so as to reduce the effect of the change.
- **Electrolytes:** Substances that conduct electricity in aqueous solutions are called electrolytes.
- **Arrhenius Concept:** According to Arrhenius, acids give hydrogen ions while bases produce hydroxyl ions in their aqueous solution.
- **Bronsted-Lowry concept:** Bronsted-Lowry defined acids as proton donor and a base as a proton acceptor.
- **Conjugate base and Conjugate acid:** When a Bronsted-Lowry acid reacts with a base it produces its conjugate base and conjugate acid.
- **Conjugate pair of acid and base:** Conjugate pair of acid and base differs only by one proton.
- **Lewis acids:** Define acid as an electron pair acceptor and a base as an electron pair donor.

- **pH Scale:** Hydranium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of pure water is 7.
- **Buffer solution:** It is the solution whose pH does not change by addition of small amount of strong acid or base.  
**For example:**  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ .
- **Solubility product ( $K_{sp}$ ):** For a sparingly soluble salt. It is defined as the product of molar concentration of the ions raised to the power equal to the number of times each ion occurs in the equation for solubilities.



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

## TEXTBOOK QUESTIONS SOLVED

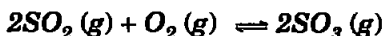
**Q1.** *A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.*

- What is the initial effect of the change on vapour pressure?*
- How do rates of evaporation and condensation change initially?*
- What happens when equilibrium is restored finally and what will be the final vapour pressure?*

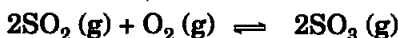
**Ans.** (a) On increasing the volume of the container suddenly, the vapour pressure would decrease.

- Rate of evaporation remains unaffected since temperature is fixed, but the rate of condensation would decrease. This because when the vapour pressure decreases, fewer molecules will be present per unit volume and the probability of their striking the liquid surface would decrease.
- When the equilibrium is restored finally, the rates of evaporation and condensation would become equal. The final vapour pressure will be the same as the initial vapour since temperature is fixed.

**Q2.** *What is  $K_c$  for the following equilibrium when the equilibrium concentration of each substance is:  $[\text{SO}_2] = 0.60 \text{ M}$ ,  $[\text{O}_2] = 0.82 \text{ M}$  and  $[\text{SO}_3\text{A}] = 1.90 \text{ M}$ ?*



**Ans.** For the reaction,



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

Given:  $[\text{SO}_2] = 0.60 \text{ M}$ ;  $[\text{O}_2] = 0.82 \text{ M}$

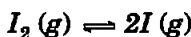
and  $[\text{SO}_3] = 1.90 \text{ M}$

Putting in the above expression

$$\begin{aligned} \therefore K_c &= \frac{(1.90 \text{ M})^2}{(0.60 \text{ M})^2(0.82 \text{ M})} = 12.229 \text{ M}^{-1} \\ &= 12.229 \text{ L mol}^{-1}. \end{aligned}$$

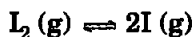
(Note: Ideally  $K_c$  should not have any units.)

**Q3.** At a certain temperature and total pressure of  $10^5 \text{ Pa}$ , iodine vapour contains 40% by volume of I atoms



Calculate  $K_p$  for the equilibrium.

**Ans.** For the reaction,



$$K_p = \frac{p_1^2}{p_{1_2}}$$

Given: Total pressure =  $10^5 \text{ Pa}$

Iodine vapour contains 40% by volume I atoms, i.e., contribution of I atoms towards total pressure is 40%.

$\therefore$  Partial pressure of I atoms =  $p_1$

$$= \frac{40}{100} \times 10^5 \text{ Pa} = 0.4 \times 10^5 \text{ Pa}$$

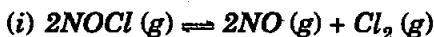
and partial pressure of  $\text{I}_2$  molecules =  $p_{1_2}$

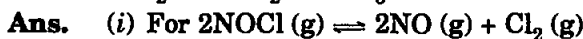
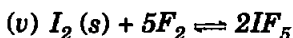
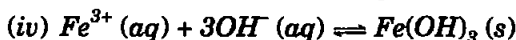
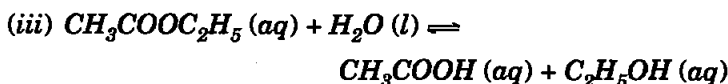
$$= \frac{60}{100} \times 10^5 \text{ Pa} = 0.6 \times 10^5 \text{ Pa}$$

Putting these values in the expression for  $K_p$ ,

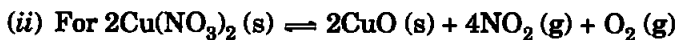
$$K_p = \frac{(0.4 \times 10^5)^2}{0.6 \times 10^5} = 2.67 \times 10^4.$$

**Q4.** Write the expression for the equilibrium constant,  $K_c$  for each of the following reactions:

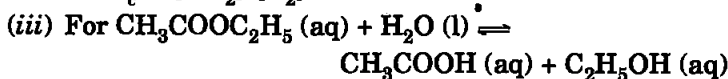




$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$$



$$K_c = [\text{NO}_2]^4 [\text{O}_2]$$

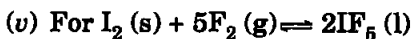


$$K_c = \frac{[\text{CH}_3\text{COOH}] [\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]}$$

Concentration of  $\text{H}_2\text{O}$  will appear in the expression for  $K_c$  since water is neither solvent nor present in the excess and its concentration is not constant.

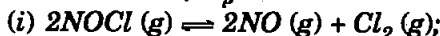


$$K_c = \frac{1}{[\text{Fe}^{3+}] [\text{OH}^-]^3}$$

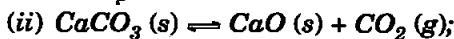


$$K_c = \frac{1}{[\text{F}_2]^5}$$

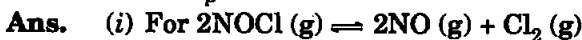
**Q5.** Find out the value of  $K_c$  for each of the following equilibria from the value of  $K_p$ :



$$K_p = 1.8 \times 10^{-2} \text{ at } 500 \text{ K}$$



$$K_p = 167 \text{ at } 1073 \text{ K}$$



$$\Delta n_g = (\text{No. of moles of gaseous products}) - (\text{No. of moles of gaseous reactants})$$

$$= (2 + 1) - 2 = 1$$

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

$$\text{or } K_c = \frac{K_p}{RT}$$

$$\text{Given: } K_p = 1.8 \times 10^{-2}; T = 500 \text{ K;} \\ R = 0.0831 \text{ bar L mol}^{-1} \text{ K}^{-1}$$

$$K_c = \frac{1.8 \times 10^{-2}}{0.0831 \times 500} = 4.33 \times 10^{-4}$$

(ii) For  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\Delta n_g = (1 + 0) - 0 = 1$$

$$K_c = \frac{K_p}{RT}$$

$$\text{Given: } K_p = 167; T = 1073 \text{ K;} \\ R = 0.0831 \text{ bar L mol}^{-1} \text{ K}^{-1}$$

$$\therefore K_c = \frac{167}{0.0831 \times 1073} = 1.87$$

**Q6.** For the following equilibrium,  $K_c = 6.3 \times 10^{14}$  at 1000 K



Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is  $K_c'$  for the reverse reaction?

**Ans.** For reverse reaction,  $K_c' = \frac{1}{K_c}$

$$\text{Given, } K_c = 6.3 \times 10^{14}$$

$$\therefore K_c' = \frac{1}{6.3 \times 10^{14}} = 1.59 \times 10^{-15}$$

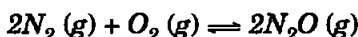
**Q7.** Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

**Ans.** Pure liquids and pure solids can be ignored while writing equilibrium constant expression because their molar concentration depends upon their density only since their concentration = Moles present in 1 L volume

$$= \frac{\text{Mass of 1 L substance}}{\text{Molar mass}} \\ = \frac{\text{Volume (1 L)} \times \text{Density}}{\text{Molar mass}}$$

Since density of any pure solid or liquid substance is constant at a given temperature, their concentration is also constant and is incorporated in the equilibrium constant. While writing the expression for equilibrium constant, their concentrations need not be written.

**Q8.** Reaction between  $N_2$  and  $O_2$  takes place as follows:



If a mixture of 0.482 mol  $N_2$  and 0.933 mol of  $O_2$  is placed in a 10 L reaction vessel and allowed to form  $N_2O$  at a temperature for which  $K_c = 2.0 \times 10^{-37}$ , determine the composition of equilibrium mixture.

**Ans.** Let  $x$  moles of  $O_2$  and  $2x$  moles of  $N_2$  react before the equilibrium is reached. The equilibrium concentrations can be calculated as:

	$2N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2N_2O(g)$
Initial moles	0.482		0.933		0
Eqm. moles	$(0.482 - 2x)$		$(0.933 - x)$		$2x$
Eqm. Concentrations	$\frac{(0.482 - 2x)}{10}$		$\frac{(0.933 - x)}{10}$		$\frac{2x}{10}$

Since  $K_c$  is very small ( $2.0 \times 10^{-37}$ ), the amounts of  $N_2$  and  $O_2$  reacted ( $2x$  and  $x$ ) are very small and can be neglected. Thus, equilibrium concentrations can be taken as:

$$[N_2] = \frac{0.482}{10} = 0.0482 \text{ mol L}^{-1}$$

$$[O_2] = \frac{0.933}{10} = 0.0933 \text{ mol L}^{-1}$$

$$[N_2O] = \frac{2x}{10} = 0.2x$$

Putting these in expression for  $K_c$ ,

$$K_c = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$2.0 \times 10^{-37} = \frac{(0.2x)^2}{(0.0482)^2(0.0933)}$$

$$0.04x^2 = (2.0 \times 10^{-37}) \times (0.0482)^2 \times (0.0933)$$

$$x^2 = \frac{(2.0 \times 10^{-37}) \times (0.0482)^2 \times (0.0933)}{0.04}$$

$$= 1.08 \times 10^{-39}$$

$$x = \sqrt{1.08 \times 10^{-39}} = 3.3 \times 10^{-20}$$

$$\therefore [N_2O] = 0.2x = 6.6 \times 10^{-21} \text{ mol L}^{-1}$$

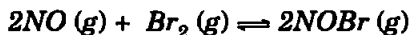
Thus, composition of equilibrium mixture is:

$$[\text{N}_2] = 0.0482 \text{ mol L}^{-1};$$

$$[\text{O}_2] = 0.0933 \text{ mol L}^{-1};$$

$$[\text{N}_2\text{O}] = 6.6 \times 10^{-21} \text{ mol L}^{-1}.$$

**Q9.** Nitric oxide reacts with  $\text{Br}_2$  and gives nitrosyl bromide as per reaction given below:



When 0.087 mol of NO and 0.0437 mol of  $\text{Br}_2$  are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and  $\text{Br}_2$ .

**Ans.** The reaction is:

	$2\text{NO}(\text{g})$	$+ \text{Br}_2(\text{g})$	$\rightleftharpoons$	$2\text{NOBr}(\text{g})$
<i>Initial moles</i>	0.087	0.0437		0
<i>Eqm. moles</i>	$x$	$y$		0.0518

**Equilibrium amount of NO**

According to the reaction:

2 mol NOBr is formed from 2 mol NO

$\therefore$  0.0518 mol NOBr is formed from 0.0518 mol NO

$$\text{Initial moles of NO} = 0.087 \text{ mol}$$

$$\text{Moles of NO reacted} = 0.0518 \text{ mol}$$

$$\begin{aligned} \therefore \text{Equilibrium moles of NO} &= x \\ &= (0.087 - 0.0518) \text{ mol} \\ &= \mathbf{0.0352 \text{ mol}} \end{aligned}$$

**Equilibrium amount of  $\text{Br}_2$**

According to the reaction:

2 mol NOBr is formed from 1 mol  $\text{Br}_2$

$\therefore$  0.0518 mol NOBr is formed from

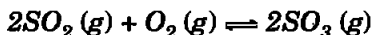
$$\frac{0.0518}{2} = 0.0259 \text{ mol Br}_2$$

$$\text{Initial moles of Br}_2 = 0.0437 \text{ mol}$$

$$\text{Moles of Br}_2 \text{ reacted} = 0.0259 \text{ mol}$$

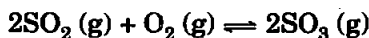
$$\begin{aligned} \therefore \text{Equilibrium moles of Br}_2 & \\ &= (0.0437 - 0.0259) \text{ mol} \\ &= \mathbf{0.0178 \text{ mol}}. \end{aligned}$$

**Q10.** At 450 K,  $K_p = 2.0 \times 10^{10}$ /bar for the given reaction at equilibrium.



What is  $K_c$  at this temperature?

**Ans.** The reaction is:



$$\begin{aligned}\Delta n_g &= n_g(\text{Products}) - n_g(\text{Reactants}) \\ &= 2 - (2 + 1) = -1\end{aligned}$$

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

$$K_c = K_p (RT)^{-\Delta n_g} = K_p (RT)^{-(-1)} = K_p (RT)$$

Given:  $K_p = 2.0 \times 10^{10}$ /bar

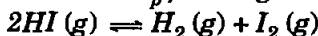
$$T = 450 \text{ K}$$

$$R = 0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

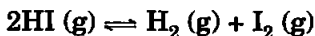
Putting the values in above relation,

$$\begin{aligned}K_c &= (2.0 \times 10^{10} \text{ bar}^{-1}) \\ &\quad (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1})(450 \text{ K}) \\ &= 7.48 \times 10^{11} \text{ L mol}^{-1}.\end{aligned}$$

**Q11.** A sample of HI (g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is  $K_p$  for the given equilibrium?



**Ans.** The reaction is:



Initial pressure	0.2 atm	0	0
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Eqm. partial pressures	0.04 atm	x	x
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Decrease in pressure of HI due to reaction

$$= (0.2 - 0.04) \text{ atm} = 0.16 \text{ atm}$$

Since 2 moles of HI produce 1 mol each of  $\text{H}_2$  and  $\text{I}_2$

the partial pressures of  $\text{H}_2$  and  $\text{I}_2 = \frac{1}{2} \times$  decrease in pressure of HI

$$= \frac{1}{2} \times 0.16 = 0.08 \text{ atm}$$

$\therefore$  At equilibrium

$$p_{\text{H}_2} = 0.08 \text{ atm}, p_{\text{I}_2} = 0.08 \text{ atm}$$

$$p_{\text{HI}} = 0.04 \text{ atm}$$

$$K_p = \frac{p_{\text{H}_2} \times p_{\text{I}_2}}{p_{\text{HI}}^2} = \frac{(0.08) \times (0.08)}{(0.04)^2} = 4.0.$$



**Q12.** A mixture of 1.57 mol of  $N_2$ , 1.92 mol of  $H_2$  and 8.13 mol of  $NH_3$  is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant,  $K_c$  for the reaction  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  is  $1.7 \times 10^2$ . Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

**Ans.** The reaction is:

	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$		
Moles present /	1.57	1.92	8.13
mol			
Concentrations /	$\frac{1.57}{20}$	$\frac{1.92}{20}$	$\frac{8.13}{20}$
mol $L^{-1}$			

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

Given that:  $K_c = 1.7 \times 10^2$

Since  $Q_c \neq K_c$  the reaction mixture is not at equilibrium. Also, since  $Q_c > K_c$  the net reaction would occur in backward direction.

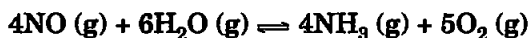
**Q13.** The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

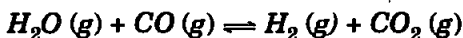
**Ans.** Since  $K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$

The products are 4 mol  $NH_3$  and 5 mol  $O_2$  and the reactants are 4 mol  $NO$  and 6 mol  $H_2O$  and the balanced equation for the reaction is:



(water must be present in gaseous state, if it were present in the liquid state, as per convention, its concentration term would not have been present in the expression for  $K_c$ ).

- Q14.** One mole of  $\text{H}_2\text{O}$  and one mole of  $\text{CO}$  are taken in 10L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with  $\text{CO}$  according to the equation,



Calculate the equilibrium constant for the reaction.

- Ans.** Given that at equilibrium 40% of water by mass reacts with  $\text{CO}$ . Since number of moles is directly proportional to mass, the 40% of water would have reacted by moles. Thus, number of moles of water reaction = 40% of 1 mol = 0.4 mol. With this information, the number of moles and concentrations of all the substances at equilibrium can be calculated as:

	$\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$			
Initial moles	1 mol	1 mol	0	0
Eqm. moles / mol	(1 - 0.4)	(1 - 0.4)	0.4 mol	0.4 mol
Equilibrium concentrations / mol L <sup>-1</sup>	$\left(\frac{0.6}{10}\right)$	$\left(\frac{0.6}{10}\right)$	$\left(\frac{0.4}{10}\right)$	$\left(\frac{0.4}{10}\right)$
	0.06	0.06	0.04	0.04

$$K_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{(0.04)(0.04)}{(0.06)(0.06)} = 0.44.$$

- Q15.** At 700 K, equilibrium constant for the reaction:



is 54.8. If 0.5 mol L<sup>-1</sup> of  $\text{HI}(\text{g})$  is present at equilibrium at 700 K, what are the concentration of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  assuming that we initially started with  $\text{HI}(\text{g})$  and allowed it to reach equilibrium at 700 K?

- Ans.** For the reaction:

	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$		
Equilibrium concentrations / mol L <sup>-1</sup>	x	x	0.5

Since the reaction is started by taking HI only,  $H_2$  and  $I_2$  would be formed in equal amounts and their equilibrium concentrations would be equal. The equilibrium constant,  $K_c$  (54.8) for the reaction is:

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

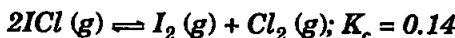
$$54.8 = \frac{(0.5)^2}{x \times x} = \frac{0.5^2}{x^2}$$

$$\therefore x^2 = \frac{0.5^2}{54.8} = 0.0046$$

$$x = 0.068 \text{ mol L}^{-1}$$

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

**Q16.** What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?



**Ans.** The reaction is:

	$2ICl(g)$	$\rightleftharpoons$	$I_2(g)$	$+$	$Cl_2(g)$
<i>Initial concentrations /</i>	0.78		0		0
<i>mol L<sup>-1</sup>,</i>					
<i>Equilibrium</i>	$(0.78 - x)$		$\frac{x}{2}$		$\frac{x}{2}$
<i>concentrations / mol L<sup>-1</sup></i>					

If  $x \text{ mol L}^{-1}$  of ICl react when equilibrium is reached, the concentration of  $I_2$  and  $Cl_2$  would be one-half of it according

the equation, i.e.,  $\frac{x}{2} \text{ mol L}^{-1}$  each.

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2} = \frac{\left(\frac{x}{2}\right)\left(\frac{x}{2}\right)}{(0.78 - x)^2} = 0.14$$

$$0.14 = \left(\frac{x}{2(0.78 - x)}\right)^2$$

$$\text{or } \frac{x}{1.56 - 2x} = \sqrt{0.14} = 0.374$$

$$x = 0.374(1.56 - 2x) = 0.583 - 0.748x$$

$$\text{or } 1.748x = 0.583$$

$$x = \frac{0.583}{1.748} = 0.334$$

The equilibrium concentrations are:

$$[I_2] = [Cl_2] = \frac{x}{2} = \frac{0.334}{2} = 0.167 \text{ mol L}^{-1}$$

$$\text{and } [ICl] = 0.78 - 0.334 = 0.446 \text{ mol L}^{-1}.$$

- Q17.**  $K_p = 0.04 \text{ atm}$  at  $899 \text{ K}$  for the equilibrium shown below. What is the equilibrium concentration of  $C_2H_6$  when it is placed in a flask at  $4.0 \text{ atm}$  pressure and allowed to come to equilibrium?



**Ans.** The reaction is:

	$C_2H_6(g)$	$\rightleftharpoons$	$C_2H_4(g)$	$+$	$H_2(g)$
<i>Initial pressure / atm</i>	4.0		0		0
<i>Equilibrium partial pressures / atm</i>	$(4.0 - x)$		$x$		$x$

$$K_p = \frac{P_{C_2H_4} \times P_{H_2}}{P_{C_2H_6}}$$

$$0.04 = \frac{(x) \times (x)}{(4.0 - x)}$$

$$0.04(4.0 - x) = x^2$$

$$0.16 - 0.04x = x^2$$

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

$$x = \frac{-0.04 \pm \sqrt{0.04^2 - 4(-0.16)}}{2}$$

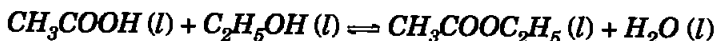
Taking only positive sign,

$$x = \frac{-0.04 + \sqrt{0.0016 + 0.64}}{2}$$

$$= \frac{-0.04 + \sqrt{0.6416}}{2} = \frac{-0.04 + 0.801}{2} = 0.38$$

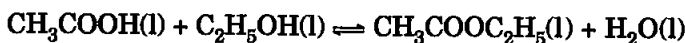
$$P_{C_2H_6} \text{ at equilibrium} = 4.0 - 0.38 = 3.62 \text{ atm.}$$

**Q18.** Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:



- (i) Write the concentration ratio (reaction quotient),  $Q_c$ , for this reaction (note: water is not in excess and is not a solvent in this reaction).
- (ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- (iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

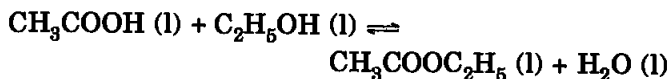
**Ans.** For the reaction:



$$(i) \quad Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Concentration of water will come in this expression since it is neither solvent nor present in excess and hence would not be constant.

(ii)

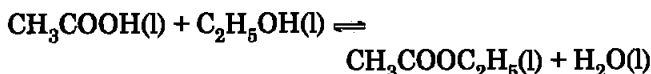


<i>Initial moles</i>	1.00	0.18	0	0
<i>Eqn. moles</i>	(1.00 – 0.171)	(0.18 – 0.171)	0.171	0.171
	0.829	0.009		
<i>Equilibrium</i>	$\frac{0.829}{V}$	$\frac{0.009}{V}$	$\frac{0.171}{V}$	$\frac{0.171}{V}$
	<i>Concentrations/mol L<sup>-1</sup></i>			

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$= \frac{\left(\frac{0.171}{V}\right)\left(\frac{0.171}{V}\right)}{\left(\frac{0.829}{V}\right)\left(\frac{0.009}{V}\right)} = \frac{(0.171)^2}{0.829 \times 0.009} = 3.92.$$

(iii)



<i>Initial moles</i>	1.0	0.5	0	0
<i>Final moles</i>	(1.0 - 0.214)	(0.5 - 0.214)	0.214	0.214
	0.786	0.286		
<i>Final Concentrations</i>	$\frac{0.786}{V}$	$\frac{0.286}{V}$	$\frac{0.214}{V}$	$\frac{0.214}{V}$

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

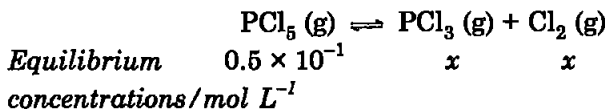
$$= \frac{\left(\frac{0.214}{V}\right)\left(\frac{0.214}{V}\right)}{\left(\frac{0.786}{V}\right)\left(\frac{0.286}{V}\right)} = \frac{0.214^2}{0.786 \times 0.286} = 0.204$$

Since  $Q_c \neq K_c$  equilibrium has not been reached.

**Q19.** A sample of pure  $\text{PCl}_5$  was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of  $\text{PCl}_5$  was found to be  $0.5 \times 10^{-1} \text{ mol L}^{-1}$ . If value of  $K_c$  is  $8.3 \times 10^{-3}$ , what are the concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium?



**Ans.** For the reaction:



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$8.3 \times 10^{-3} = \frac{(x)(x)}{0.5 \times 10^{-1}} = \frac{x^2}{0.05}$$

$$x^2 = 0.05 \times 8.3 \times 10^{-3}$$

$$x = \sqrt{0.415 \times 10^{-3}} = 0.020$$

$$\therefore [\text{PCl}_3] = [\text{Cl}_2] = 0.020 \text{ mol L}^{-1}$$

**Q20.** One of the reaction that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and  $\text{CO}_2$ .



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = \frac{0.25}{3 \times 8.0} = 0.0104$$

Given,  $K_c = 0.061$ .

Since  $Q_c < K_c$ , the reaction is not at equilibrium and would proceed in *forward direction* to reach equilibrium.

**Q22.** Bromine monochloride,  $\text{BrCl}$  decomposes into bromine and chlorine and reaches the equilibrium:



for which  $K_c = 32$  at 500 K. If initially pure  $\text{BrCl}$  is present at a concentration of  $3.3 \times 10^{-3} \text{ mol L}^{-1}$ , what is its molar concentration in the mixture at equilibrium?

**Ans.** For the reaction:

	$2\text{BrCl}(\text{g})$	$\rightleftharpoons$	$\text{Br}_2(\text{g})$	$+$	$\text{Cl}_2(\text{g})$
Initial concentrations / mol $\text{L}^{-1}$	$3.3 \times 10^{-3}$		0		0
Equilibrium concentrations / mol $\text{L}^{-1}$	$(3.3 \times 10^{-3} - 2x)$		$x$		$x$

$$K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} = \frac{(x)(x)}{(3.3 \times 10^{-3} - 2x)^2} = 32 \text{ (given)}$$

$$\text{or} \quad \left( \frac{x}{3.3 \times 10^{-3} - 2x} \right)^2 = 32$$

$$\frac{x}{3.3 \times 10^{-3} - 2x} = \sqrt{32} = 5.66$$

$$x = 5.66(3.3 \times 10^{-3} - 2x)$$

$$= 18.68 \times 10^{-3} - 11.32x$$

$$12.32x = 18.68 \times 10^{-3}$$

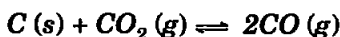
$$x = \frac{18.68 \times 10^{-3}}{12.32} = 0.0015 \text{ mol L}^{-1}$$

$\therefore [\text{BrCl}_2]$  at equilibrium

$$= 3.3 \times 10^{-3} - 2 \times 0.0015 = 0.0033 - 0.0030$$

$$= 0.0003 = 3 \times 10^{-4} \text{ mol L}^{-1}.$$

**Q23.** At 1127 K and 1 atm pressure, a gaseous mixture of  $\text{CO}$  and  $\text{CO}_2$  in equilibrium with solid carbon has 90.55%  $\text{CO}$  by mass



Calculate  $K_c$  for this reaction at the above temperature.



**Ans.** Let the total mass of gaseous mixture at equilibrium be 100 g.

$$\therefore \text{Mass of CO} = 90.55 \text{ g}$$

$$\text{Mass of CO}_2 = 100 - 90.55 = 9.45 \text{ g}$$

$$\text{Moles of CO (molar mass} = 12 + 16 = 28 \text{ g mol}^{-1}\text{)}$$

$$= \frac{90.55 \text{ g}}{28 \text{ g mol}^{-1}} = 3.23 \text{ mol}$$

$$\text{Moles of CO}_2 \text{ (molar mass} = 12 + 32 = 44 \text{ g mol}^{-1}\text{)}$$

$$= \frac{9.45 \text{ g}}{44 \text{ g mol}^{-1}} = 0.22 \text{ mol}$$

Let the volume of reaction mixture be  $V$  litre

$$pV = nRT$$

$$V = \frac{nRT}{p}$$

$$n = 3.23 + 0.22 = 3.45 \text{ mol}$$

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

$$T = 1127 \text{ K}$$

$$p = 1 \text{ atm}$$

$$\therefore V = \frac{(3.45 \text{ mol})(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(1127 \text{ K})}{1 \text{ atm}}$$

$$= 319.2 \text{ L}$$

Equilibrium concentrations are:

$$[\text{CO}] = \frac{3.23}{319.2} \text{ mol L}^{-1}; [\text{CO}_2] = \frac{0.22}{319.2} \text{ mol L}^{-1}$$

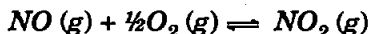
For the reaction:



$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{\left(\frac{3.23}{319.2}\right)^2}{\left(\frac{0.22}{319.2}\right)} = \frac{3.23^2}{0.22 \times 319.2}$$

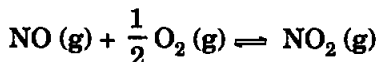
$$= 0.149 \approx 0.15.$$

**Q24.** Calculate (a)  $\Delta G^0$  and (b) the equilibrium constant for the formation of  $\text{NO}_2$  from  $\text{NO}$  and  $\text{O}_2$  at 298 K



$$\begin{aligned} \text{where } \Delta_f G^0(\text{NO}_2) &= 52.0 \text{ kJ/mol} \\ \Delta_f G^0(\text{NO}) &= 87.0 \text{ kJ/mol} \\ \Delta_f G^0(\text{O}_2) &= 0 \text{ kJ/mol} \end{aligned}$$

**Ans.** For the reaction:



$$(a) \Delta_r G^0 = \Delta_f G^0(\text{NO}_2) - \Delta_f G^0(\text{NO}) - \frac{1}{2} \Delta_f G^0(\text{O}_2)$$

$$\text{Given: } \Delta_f G^0(\text{NO}_2) = 52.0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^0(\text{NO}) = 87.0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^0(\text{O}_2) = 0 \text{ kJ mol}^{-1}$$

$$\therefore \Delta_r G^0 = 52.0 - 87.0 - 0 = -35 \text{ kJ mol}^{-1}$$

$$(b) \Delta_r G^0 = -RT \ln K_p = -2.303 RT \log K_p$$

$$\log K_p = -\frac{\Delta_r G^0}{2.303 RT}$$

$$\Delta_r G^0 = -35 \text{ kJ mol}^{-1}$$

$$= -35 \times 10^3 \text{ J mol}^{-1}$$

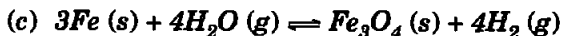
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\therefore \log K_p = \frac{-35 \times 10^3 \text{ J mol}^{-1}}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 6.1341$$

$$K_p = \text{antilog } 6.1341 = 1.362 \times 10^6.$$

**Q25.** Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?



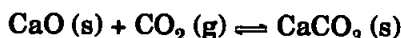
**Ans.** (a) For the reaction:



$$\Delta n_g = (1 + 1) - 1 = +1$$

Since  $\Delta n_g = +$ , on decreasing pressure, the moles of products would increase.

(b) For the reaction:



$$\Delta n_g = 0 - (0 + 1) = -1$$

Since  $\Delta n_g = -ve$ , on decreasing the pressure, the moles of products would *decrease*.

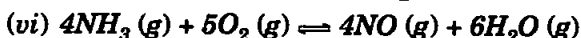
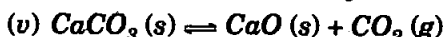
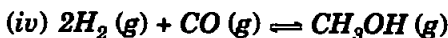
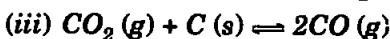
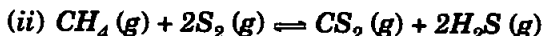
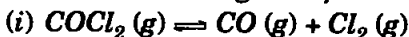
(c) For the reaction:



$$\Delta n_g = 4 - 4 = 0$$

Since  $\Delta n_g = 0$ , there will be no effect of decrease in pressure and the moles of products *would remain unchanged*.

**Q26.** Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

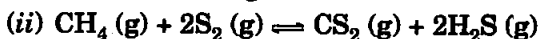


**Ans.** (i) For the reaction:



$$\Delta n_g = (1 + 1) - 1 = +1$$

Since  $\Delta n_g = +ve$ , increasing the pressure would cause the reaction to go in the *backward direction*.



$$\Delta n_g = (1 + 2) - (1 + 2) = 0$$

Since  $\Delta n_g = 0$ , there will be *no effect* of increasing pressure.



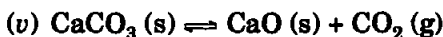
$$\Delta n_g = 2 - 1 = +1$$

Since  $\Delta n_g = +ve$ , the reaction would occur in the *backward direction* on increasing the pressure.



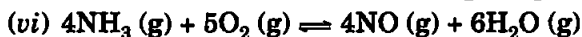
$$\Delta n_g = 1 - (2 + 1) = -2$$

Since  $\Delta n_g = -ve$ , the reaction would occur in the *forward direction* on increasing the pressure.



$$\Delta n_g = 1 - 0 = +1$$

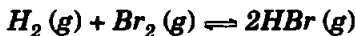
Since  $\Delta n_g = +ve$ , the reaction would occur in the *backward direction* on increasing the pressure.



$$\Delta n_g = (4 + 6) - (4 + 5) = +1$$

Since  $\Delta n_g = +ve$ , the reaction would occur in the *backward direction* on increasing the pressure.

**Q27.** The equilibrium constant for the following reaction is  $1.6 \times 10^5$  at 1024 K



Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

**Ans.**

	$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$		
Initial pressure /	0	0	10
bar			
Equilibrium	x	x	(10 - 2x)
partial pressures / bar			

$$K_p = \frac{p_{\text{HBr}}^2}{p_{\text{H}_2} \times p_{\text{Br}_2}} = \frac{(10 - 2x)^2}{(x)(x)}$$

$$= \left( \frac{10 - 2x}{x} \right)^2 = 1.6 \times 10^5$$

$$\frac{10 - 2x}{x} = \sqrt{1.6 \times 10^5} = 400$$

$$10 - 2x = 400x$$

$$402x = 10$$

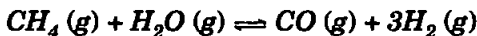
$$x = \frac{10}{402} = 0.025 \text{ bar}$$

Equilibrium partial pressures

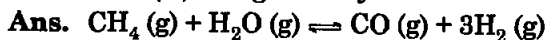
$$p_{\text{H}_2} = p_{\text{Br}_2} = 0.025 \text{ bar} = 2.5 \times 10^{-2} \text{ bar}$$

$$p_{\text{HBr}} = 10 - 2 \times 0.025 = 10 - 0.05 = 10 \text{ bar.}$$

**Q28.** Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:



- (a) Write an expression for  $K_p$  for the above reaction.
- (b) How will the values of  $K_p$  and composition of equilibrium mixture be affected by
- increasing the pressure
  - increasing the temperature
  - using a catalyst?



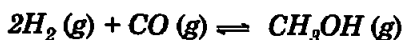
$$(a) \quad K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}^3}{P_{\text{CH}_4} \times P_{\text{H}_2\text{O}}}$$

- (b) (i)  $\Delta n_g = (3 + 1) - (1 + 1) = +2$ . Since it is positive, the equilibrium will shift in *backward direction*, on increasing the pressure. No change in value of  $K_p$ .
- (ii) Since the reaction is *endothermic*, on increasing the temperature, equilibrium will shift in *forward direction* and  $K_p$  will increase.
- (iii) No effect on composition or value of  $K_p$ .

**Q29.** Describe the effect of :

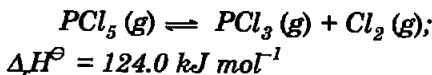
- addition of  $\text{H}_2$
- addition of  $\text{CH}_3\text{OH}$
- removal of  $\text{CO}$
- removal of  $\text{CH}_3\text{OH}$

on the equilibrium of the reaction:



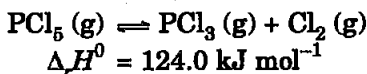
- Addition of  $\text{H}_2$  will shift the equilibrium in *forward direction*.
- Addition of  $\text{CH}_3\text{OH}$  will shift the equilibrium in *backward direction*.
- Removal of  $\text{CO}$  will shift the equilibrium in *backward direction*.
- Removal of  $\text{CH}_3\text{OH}$  will shift the equilibrium in *forward direction*.

**Q30.** At 473 K, equilibrium constant  $K_c$  for decomposition of phosphorus pentachloride,  $\text{PCl}_5$  is  $8.3 \times 10^{-3}$ . If decomposition is depicted as,



- (a) Write an expression for  $K_c$  for the reaction.  
 (b) What is the value of  $K_c$  for the reverse reaction at the same temperature?  
 (c) What would be the effect on  $K_c$  if (i) more  $\text{PCl}_5$  is added (ii) pressure is increased (iii) the temperature is increased?

**Ans.** For the reaction,



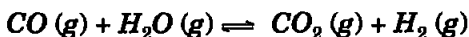
$$(a) \quad K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

(b) For the reverse reaction

$$K_c' = \frac{1}{K_c} = \frac{1}{8.3 \times 10^{-3}} = 120.48$$

- (c) (i) If more  $\text{PCl}_5$  is added, there will not be any effect on  $K_c$ .  
 (ii) If pressure is increased, there will not be any effect on  $K_c$ .  
 (iii) If temperature is increased, since the reaction is endothermic, the equilibrium will shift in the forward direction and the value of  $K_c$  will increase.

**Q31.** Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and  $\text{H}_2$ . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,



If a reaction vessel at  $400^\circ\text{C}$  is charged with an equimolar mixture of CO and steam such that  $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 4.0$  bar, what will be the partial pressure of  $\text{H}_2$  at equilibrium?  $K_p = 10.1$  at  $400^\circ\text{C}$ .

**Ans.** For the reaction,

	$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$			
Initial partial pressures / bar	4.0	4.0	0	0
Equilibrium partial pressures / bar	$(4.0 - x)$	$(4.0 - x)$	$x$	$x$

$$K_p = \frac{P_{\text{CO}_2} \times P_{\text{H}_2}}{P_{\text{CO}} \times P_{\text{H}_2\text{O}}} = \frac{(x)(x)}{(4.0-x)(4.0-x)}$$

$$= \left( \frac{x}{4.0-x} \right)^2 = 10.1$$

$$\therefore \left( \frac{x}{4.0-x} \right) = \sqrt{10.1} = 3.18$$

$$x = 3.18(4.0-x) = 12.72 - 3.18x$$

$$4.18x = 12.72$$

$$x = \frac{12.72}{4.18} = 3.04$$

$P_{\text{H}_2}$  at equilibrium =  $x = 3.04$  bar.

There seems to be printing error and  $K_p$  should be 0.1. If so

$$\left( \frac{x}{4.0-x} \right) = \sqrt{0.1} = 0.316$$

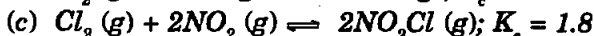
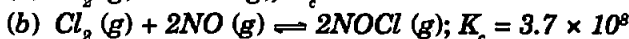
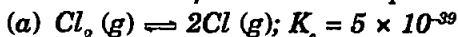
$$x = 0.316(4.0-x) = 1.264 - 0.316x$$

$$1.316x = 1.264$$

$$\text{or } x = \frac{1.264}{1.316} = 0.96$$

$\therefore P_{\text{H}_2}$  at equilibrium =  $x = 0.96$  bar.

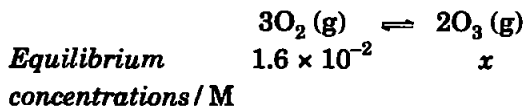
**Q32.** Predict which of the following reaction will have appreciable concentration of reactants and products:



**Ans.**  $K_c$  for reaction (c) is moderate, neither very small nor very large. Therefore, in this reaction, reactants and products both will have appreciable concentration at equilibrium.

**Q33.** The value of  $K_c$  for the reaction  $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$  is  $2.0 \times 10^{50}$  at  $25^\circ\text{C}$ . If the equilibrium concentration of  $\text{O}_2$  in air at  $25^\circ\text{C}$  is  $1.6 \times 10^{-2}$ , what is the concentration of  $\text{O}_3$ ?

**Ans.** For the reaction,



$$K_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$$

$$2.0 \times 10^{-50} = \frac{x^2}{(1.6 \times 10^{-2})^3}$$

$$x^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3 = 8.192 \times 10^{-56}$$

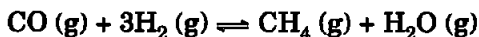
$$\text{or } x = 2.86 \times 10^{-28} \text{ M}$$

**Q34.** *The reaction,*



*is at equilibrium at 1300 K in a 1L flask. It also contains 0.30 mol of CO, 0.10 mol of H<sub>2</sub> and 0.02 mol of H<sub>2</sub>O and an unknown amount of CH<sub>4</sub> in the flask. Determine the concentration of CH<sub>4</sub> in the mixture. The equilibrium constant, K<sub>c</sub> for the reaction at the given temperature is 3.90.*

**Ans.** For the reaction,



<i>Equilibrium</i>	0.30	0.1	<i>x</i>	0.02
<i>concentrations / M</i>				

Since volume of vessel is 1 L, number of moles is equal to the molar concentrations.

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

$$3.90 = \frac{x \times (0.02)}{(0.30)(0.1)^3}$$

$$x = \frac{3.90 \times 0.30 \times 0.001}{0.02} = 0.0585 \text{ M}$$

$$\therefore [\text{CH}_4] = 5.85 \times 10^{-2} \text{ M.}$$

**Q35.** *What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO<sub>2</sub>, CN<sup>-</sup>, HClO<sub>4</sub>, F<sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and S<sup>2-</sup>.*

**Ans.** **Conjugate acid-base pair:** The acid-base pair that differs only by one H<sup>+</sup> ion (proton) is called conjugate acid-base pair.

Species	Conjugate acid/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>



$F^-$	$HF$
$OH^-$	$H_2O$
$CO_3^{2-}$	$HCO_3^-$
$S^{2-}$	$HS^-$

**Q36.** Which of the followings are Lewis acids?  $H_2O$ ,  $BF_3$ ,  $H^+$  and  $NH_4^+$ .

**Ans.** Lewis acids:  $BF_3$ ,  $H^+$ ,  $NH_4^+$  (electron-pair acceptors).

**Q37.** What will be the conjugate bases for the Brönsted acids:  $HF$ ,  $H_2SO_4$  and  $HCO_3^-$ ?

<b>Ans. Brönsted Acid</b>	<b>Conjugate Base</b>
$HF$	$F^-$
$H_2SO_4$	$HSO_4^-$
$HCO_3^-$	$CO_3^{2-}$

**Q38.** Write the conjugate acids for the following Brönsted bases:  $NH_2^-$ ,  $NH_3$  and  $HCOO^-$ .

<b>Ans. Bronsted Base</b>	<b>Conjugate Acid</b>
$NH_2^-$	$NH_3$
$NH_3$	$NH_4^+$
$HCOO^-$	$HCOOH$

**Q39.** The species:  $H_2O$ ,  $HCO_3^-$ ,  $HSO_4^-$  and  $NH_3$  can act both as Brönsted acids and bases. For each case, give the corresponding conjugate acid and base.

<b>Ans. Specie</b>	<b>Conjugate Acid</b>	<b>Conjugate Base</b>
$H_2O$	$H_3O^+$	$OH^-$
$HCO_3^-$	$H_2CO_3$	$CO_3^{2-}$
$HSO_4^-$	$H_2SO_4$	$SO_4^{2-}$
$NH_3$	$NH_4^+$	$NH_2^-$

**Q40.** Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a)  $OH^-$  (b)  $F^-$  (c)  $H^+$  (d)  $BCl_3$ .

**Ans.** (a)  $OH^-$ : It is a Lewis base as it can donate an electron pair  $:OH^-$

(b)  $F^-$ : It is a Lewis base as it can donate any of its four electron pairs:  $:\ddot{F}:^-$

(c)  $H^+$ : It is a Lewis acid as it can accept a lone pair of electrons in its vacant 1s orbital from bases like  $OH^-$  and  $F^-$ .

(d)  $\text{BCl}_3$ : It is a Lewis acid as it can accept a lone pair of electrons in L shell of B to complete its octet from Lewis bases like  $\ddot{\text{N}}\text{H}_3$  or amine molecules  $\text{RNH}_2$ .

**Q41.** The concentration of hydrogen ion in a sample of soft drink is  $3.8 \times 10^{-3} \text{ M}$ . What is its pH?

**Ans.**  $[\text{H}^+] = 3.8 \times 10^{-3} \text{ M}$   
 $\text{pH} = -\log [\text{H}^+]/\text{M} = -\log 3.8 \times 10^{-3} = 2.42$ .

**Q42.** The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

**Ans.**  $\text{pH} = 3.76$   
 $\therefore [\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog} -3.76$   
 $= 1.74 \times 10^{-4} \text{ M}$ .

**Q43.** The ionisation constant of HF, HCOOH and HCN at 298 K are  $6.8 \times 10^{-4}$ ,  $1.8 \times 10^{-4}$  and  $4.8 \times 10^{-9}$  respectively. Calculate the ionisation constants of the corresponding conjugate base.

**Ans.** The ionisation constants of conjugate acid-base pair are related as:

$$K_a \times K_b = K_w \quad \text{or} \quad K_b = \frac{K_w}{K_a}$$

(i) **HF**

$$K_b \text{ for } \text{F}^- = \frac{K_w}{K_a} = \frac{10^{-14}}{6.8 \times 10^{-4}}$$

$$= 1.47 \times 10^{-11} \approx 1.5 \times 10^{-11}$$

(ii) **HCOOH**

$$K_b \text{ for } \text{HCOO}^- = \frac{K_w}{K_a}$$

$$= \frac{10^{-14}}{1.8 \times 10^{-4}}$$

$$= 5.56 \times 10^{-11} \approx 5.6 \times 10^{-11}$$

(iii) **HCN**

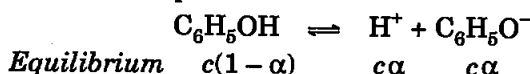
$$K_b \text{ for } \text{CN}^- = \frac{K_w}{K_a} = \frac{10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

**Q44.** The ionisation constant of phenol is  $1.0 \times 10^{-10}$ . What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionisation if the solution is also 0.01 M in sodium phenolate?

**Ans.** Since phenol is an extremely weak acid with  $K_a = 1.0 \times 10^{-10}$ , its degree of dissociation is very small and Ostwald's dilution law can be used to calculate.

$$\alpha = \sqrt{\frac{K_a}{c}}$$

From dissociation of phenol



concentrations/ion

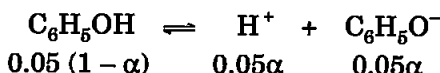
Concentration of phenolate ion,  $[\text{C}_6\text{H}_5\text{O}^-] = c\alpha$

$$= c \sqrt{\frac{K_a}{c}} = \sqrt{c \times K_a}$$

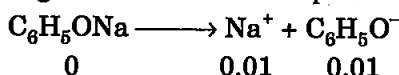
Given:  $c = 0.05 \text{ M}$  and  $K_a = 1.0 \times 10^{-10}$

$$\therefore [\text{C}_6\text{H}_5\text{O}^-] = \sqrt{0.05 \times 1.0 \times 10^{-10}} = 2.2 \times 10^{-6} \text{ M.}$$

In presence of 0.01 M sodium phenolate, the equilibria and equilibrium concentrations are



( $\alpha$  is new degree of dissociation in presence of common ion)



$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]}$$

Since  $\alpha$  is very small as such and still smaller due to common ion effect

$$1 - \alpha \approx 1 \quad \therefore [\text{C}_6\text{H}_5\text{OH}] = 0.05 \text{ M}$$

$$\text{and} \quad [\text{C}_6\text{H}_5\text{O}^-] = 0.01 + 0.05\alpha \approx 0.01$$

$$1.0 \times 10^{-10} = \frac{0.05\alpha \times 0.01}{0.05} = 0.01\alpha = 10^{-2} \alpha$$

$$\alpha = \frac{1.0 \times 10^{-10}}{10^{-2}} = 1.0 \times 10^{-8}.$$

**Q45.** The first ionisation constant of  $\text{H}_2\text{S}$  is  $9.1 \times 10^{-8}$ . Calculate the concentration of  $\text{HS}^-$  ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ , calculate the concentration of  $\text{S}^{2-}$  under both conditions.

**Ans.**  $\text{HS}^-$  ions are produced in the first step of ionisation of  $\text{H}_2\text{S}$ . Very few of them ionise in the second step to produce  $\text{S}^{2-}$  ions which do not change its concentration significantly. Considering the first ionisation:

(i) **Concentration of  $\text{HS}^-$**



Since  $\text{H}_2\text{S}$  is very weak electrolyte ( $K_1 \approx 10^{-8}$ ) using Ostwald's dilution law

$$\alpha = \sqrt{\frac{K_1}{c}}$$

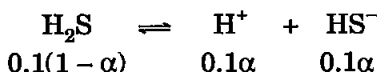
and  $[\text{HS}^-] = c\alpha = \sqrt{cK_1}$

Given that  $c = 0.1 \text{ M}$  and  $K_1 = 9.1 \times 10^{-8}$

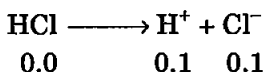
$$\therefore [\text{HS}^-] = \sqrt{0.1 \times 9.1 \times 10^{-8}} = \sqrt{9.1 \times 10^{-9}} \\ = 9.54 \times 10^{-5} \text{ M}$$

**In presence of 0.1 M HCl**

The two ionisation processes and equilibrium molar concentrations are:



( $\alpha$  is the degree of dissociation in presence of 0.1 M HCl)



(HCl is completely dissociated)

$$K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$[\text{HS}^-] = K_1 \frac{[\text{H}_2\text{S}]}{[\text{H}^+]}$$

Given:  $K_1 = 9.1 \times 10^{-8}$ ;

$$[\text{H}_2\text{S}] = 0.1(1 - \alpha) \approx 0.1 \text{ M}$$

[since  $(1 - \alpha) \approx 1$ ]

$$[\text{H}^+] = 0.1 + 0.1\alpha$$

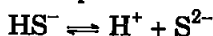
$$= 0.1(1 + \alpha) \approx 0.1 \text{ M}$$

since  $1 + \alpha \approx 1$  as  $\alpha$  is very small.

$$\begin{aligned}\therefore [\text{HS}^-] &= \frac{9.1 \times 10^{-8} \times 0.1}{0.1} \\ &= 9.1 \times 10^{-8} \text{ M}\end{aligned}$$

(ii) **Concentration of  $\text{S}^{2-}$**

$\text{S}^{2-}$  ions are produced in the second ionisation



$$\text{and } K_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \text{ or } [\text{S}^{2-}] = K_2 \frac{[\text{HS}^-]}{[\text{H}^+]}$$

Contribution of second ionisation in concentrations of  $\text{H}^+$  and  $\text{HS}^-$  (produced in 1<sup>st</sup> ionisation) is negligible and they are produced in equal concentrations in the first ionisations, i.e.,

$$[\text{H}^+] = [\text{HS}^-]$$

$$\therefore [\text{S}^{2-}] = K_2 = 1.2 \times 10^{-13} \text{ M}$$

**In presence of 0.1 M HCl**

As seen earlier, in presence of 0.1 M HCl

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

$$\text{and } [\text{HS}^-] = 9.1 \times 10^{-8} \text{ M}$$

Putting in the expression for  $[\text{S}^{2-}]$

$$\begin{aligned}\therefore [\text{S}^{2-}] &= \frac{1.2 \times 10^{-13} \times 9.1 \times 10^{-8}}{0.1} \\ &= 1.09 \times 10^{-19} \text{ M}\end{aligned}$$

**Q46.** The ionisation constant of acetic acid is  $1.74 \times 10^{-5}$ . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

**Ans.** Acetic acid being a weak acid, Ostwald's dilution law is applicable.

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.74 \times 10^{-5}}{0.05}} = 0.0186$$

$$\begin{aligned}[\text{Ac}^-] &= \sqrt{cK_a} = \sqrt{0.05 \times 1.74 \times 10^{-5}} \\ &= 9.3 \times 10^{-4} \text{ M} = 0.00093 \text{ M}\end{aligned}$$

$$[\text{H}^+] = [\text{Ac}^-] = 9.3 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 9.3 \times 10^{-4} = 3.03.$$

**Q47.** It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionisation constant of the acid and its  $pK_a$ .

**Ans.** Given: pH = 4.15,  $c = 0.01$  M

$$\text{pH} = -\log [\text{H}^+] = 4.15$$

$$[\text{H}^+] = \text{antilog}(-4.15) = 7.08 \times 10^{-5} \text{ M}$$

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

$$= \sqrt{cK_a} = \sqrt{0.01 K_a}$$

**Concentration of anion:**

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

**Ionisation constant of the acid:**

$$[\text{H}^+] = \sqrt{0.01 K_a} = 7.08 \times 10^{-5}$$

$$0.01 K_a = (7.08 \times 10^{-5})^2$$

$$K_a = \frac{(7.08 \times 10^{-5})^2}{0.01} = 5.01 \times 10^{-7}$$

**$pK_a$ :**

$$pK_a = -\log K_a$$

$$= -\log 5.01 \times 10^{-7} = 6.3.$$

**Q48.** Assuming complete dissociation, calculate the pH of the following solutions:

(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr

(d) 0.002 M KOH

**Ans.** (a) **pH of 0.003 M HCl**

$$[\text{H}^+] = 0.003 \text{ M}; \text{pH} = -\log(0.003) = 2.52$$

(b) **pH of 0.005 M NaOH**

$$[\text{OH}^-] = 0.005 \text{ M}; \text{pOH} = -\log(0.005) = 2.30$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.30 = 11.70$$

(c) **pH of 0.002 M HBr**

$$[\text{H}^+] = 0.002 \text{ M}; \text{pH} = -\log(0.002) = 2.70$$

(d) **pH of 0.002 M KOH**

$$[\text{OH}^-] = 0.002 \text{ M}; \text{pOH} = -\log(0.002) = 2.70$$

$$\text{pH} = pK_w - \text{pOH} = 14 - 2.70 = 11.30$$

**Q49.** Calculate the pH of the following solutions:

(a) 2 g of TlOH dissolved in water to give 2 litre of solution.

(b) 0.3 g of  $\text{Ca}(\text{OH})_2$  dissolved in water to give 500 mL of solution.

- (c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.
- (d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

**Ans. (a) 2 g TlOH in 2 L of solution**

$$\text{Mass per litre} = 1 \text{ g L}^{-1}$$

Molar mass of TlOH

$$= 204.4 + 16 + 1 = 221.4 \text{ g mol}^{-1}$$

$$[\text{TlOH}] = \frac{1}{221.4} = 4.52 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 4.52 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log 4.52 \times 10^{-3} \text{ M} = 2.35$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 2.35 = 11.65.$$

(b) 0.3 g Ca(OH)<sub>2</sub> dissolved in 500 mL of solution

$$\text{Mass per litre} = 0.6 \text{ g L}^{-1},$$

Molar mass of Ca(OH)<sub>2</sub>

$$= 40 + 34 = 74 \text{ g mol}^{-1}$$

$$[\text{Ca(OH)}_2] = \frac{0.6}{74} = 8.11 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 2[\text{Ca(OH)}_2] = 2 \times 8.11 \times 10^{-3} \text{ M}$$

$$= 16.22 \times 10^{-3} \text{ M}$$

∴ One mole Ca(OH)<sub>2</sub> would give two moles of OH<sup>-</sup> ions.

$$\text{pOH} = -\log[\text{OH}^-] = -\log 16.22 \times 10^{-3} = 1.79$$

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

(c) 0.3 g NaOH dissolved in 200 mL of water

$$\text{Mass per litre} = \frac{0.3 \times 1000}{200} = 1.5 \text{ g L}^{-1}$$

Molar mass of NaOH = 23 + 16 + 1 = 40 g mol<sup>-1</sup>

$$\therefore [\text{NaOH}] = [\text{OH}^-] = \frac{1.5}{40} = 0.0375 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.0375 = 1.43$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 1.43 = 12.57.$$

(d) 1 mL of 13.6 M HCl is diluted with water to 1 L volume

Molarity of the final solution is given by,

$$M_1V_1 = M_2V_2$$

$$M_2 = \frac{M_1 V_1}{V_2}$$

$$M_1 = 13.6 \text{ M,}$$

$$V_1 = 1 \text{ mL; } V_2 = 1 \text{ L} = 1000 \text{ mL}$$

$$\therefore M_2 = \frac{13.6 \times 1}{1000} = 1.36 \times 10^{-2} \text{ M}$$

$$\therefore [\text{HCl}] = [\text{H}^+] = 1.36 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 1.36 \times 10^{-2} = 1.87.$$

**Q50.** The degree of ionisation of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the  $\text{p}K_a$  of bromoacetic acid.

**Ans.** For acids,

$$[\text{H}^+] = c\alpha$$

Given that  $c = 0.1 \text{ M}$  and  $\alpha = 0.132$

$$[\text{H}^+] = 0.1 \times 0.132 = 0.0132 \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 0.0132 = 1.88$$

$$K_a = \frac{c\alpha^2}{1 - \alpha} = \frac{0.1 \times 0.132^2}{1 - 0.132} = \frac{0.00174}{0.868}$$

$$= 0.002 = 2 \times 10^{-3}$$

$$\text{p}K_a = -\log K_a = -\log 0.002 = 2.70.$$

**Q51.** The pH of 0.005 M codeine ( $\text{C}_{18}\text{H}_{21}\text{NO}_3$ ) solution is 9.95. Calculate its ionisation constant and  $\text{p}K_b$ .

**Ans.** pH of 0.005 M codeine solution = 9.95

$$\text{pOH} = \text{p}K_w - \text{pH} = 14.0 - 9.95 = 4.05$$

$$[\text{OH}^-] = \text{antilog}(-4.05) = 8.91 \times 10^{-5} \text{ M}$$

$$\text{Since } [\text{OH}^-] = c\alpha; \alpha = \frac{[\text{OH}^-]}{c} = \frac{8.91 \times 10^{-5}}{0.005} = 0.0178$$

$$K_b = \frac{c\alpha^2}{1 - \alpha} = \frac{0.005 \times 0.0178^2}{1 - 0.0178} = 1.6 \times 10^{-6}$$

$$\text{p}K_b = -\log K_b = \log 1.6 \times 10^{-6} = 5.8.$$

**Q52.** What is the pH of 0.001 M aniline solution? The ionisation constant of aniline can be taken from Table 7.7. Calculate the degree of ionisation of aniline in the solution. Also calculate the ionisation constant of the conjugate acid of aniline.

**Ans.** From the Table 7.7,  $K_b$  for aniline =  $4.27 \times 10^{-10}$



Since it is very small, Ostwald's dilution law can be used for calculation, ( $c = 0.001 \text{ M}$ )

$$\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{4.27 \times 10^{-10}}{0.001}} = 6.53 \times 10^{-4}$$

$$\text{and } [\text{OH}^-] = c\alpha = \sqrt{cK_b}$$

$$= \sqrt{0.001 \times 4.27 \times 10^{-10}}$$

$$= \sqrt{4.27 \times 10^{-13}} = 6.53 \times 10^{-7}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 6.53 \times 10^{-7} = 6.19$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 6.19 = 7.81$$

$$K_b = c\alpha^2 = 0.001 \times (6.53 \times 10^{-4})^2 = 4.26 \times 10^{-10}$$

$$\begin{aligned} K_a \text{ of conjugate acid} &= \frac{K_w}{K_b} = \frac{10^{-14}}{4.26 \times 10^{-10}} \\ &= 2.35 \times 10^{-5}. \end{aligned}$$

**Q53.** Calculate the degree of ionisation of 0.05 M acetic acid if its  $\text{p}K_a$  value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M in HCl?

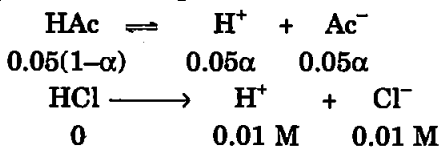
**Ans.** Given:  $c = 0.05 \text{ M}$ ;  $\text{p}K_a = 4.74 = -\log K_a$

$$K_a = \text{antilog}(-4.74) = 1.82 \times 10^{-5}$$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = 0.019 = 1.9 \times 10^{-2}.$$

**In presence of 0.01 M HCl**

Equilibria and equilibrium concentrations are



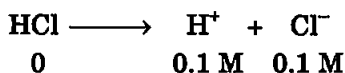
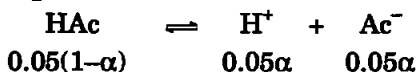
$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$[\text{H}^+] = 0.01 + 0.05\alpha \approx 0.01$$

$$[\text{HAc}] = 0.05(1 - \alpha) \approx 0.05$$

$$\therefore 1.82 \times 10^{-5} = \frac{0.01 \times 0.05\alpha}{0.05}$$

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

**In presence of 0.1 M HCl**

$$[\text{H}^+] = 0.1 + 0.05\alpha \approx 0.1 \text{ M}$$

$$[\text{HAc}] = 0.05(1 - \alpha) \approx 0.05 \text{ M}$$

$$K_a = 1.82 \times 10^{-5}$$

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$1.82 \times 10^{-5} = \frac{0.1 \times 0.05\alpha}{0.05}$$

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

**Q54.** The ionisation constant of dimethylamine is  $5.4 \times 10^{-4}$ . Calculate its degree of ionisation in its 0.02 M solution. What percentage of dimethylamine is ionised if the solution is also 0.1 M in NaOH?

**Ans.** Given  $K_b = 5.4 \times 10^{-4}$ . Since it is not very small, Ostwald's dilution law cannot be applied. Using the exact relation

$$K_b = \frac{c\alpha^2}{(1-\alpha)}$$

$$c\alpha^2 = K_b(1-\alpha) = K_b - K_b\alpha$$

$$\text{or } c\alpha^2 + K_b\alpha - K_b = 0$$

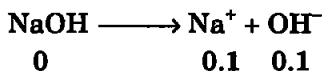
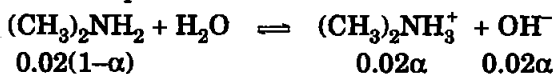
$$\text{and } \alpha = \frac{-K_b + \sqrt{K_b^2 + 4cK_b}}{2c}$$

$$= \frac{-5.4 \times 10^{-4} + \sqrt{(5.4 \times 10^{-4})^2 + 4 \times 0.02 \times 5.4 \times 10^{-4}}}{2 \times 0.02}$$

$$= 0.1535.$$

**In presence of 0.1 M NaOH**

The equilibria and equilibrium concentrations are:



$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_3^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}_2]}$$

$$[(\text{CH}_3)_2\text{NH}_3^+] = K_b \frac{[(\text{CH}_3)_2\text{NH}_2]}{[\text{OH}^-]}$$

$$[(\text{CH}_3)_2\text{NH}_2] = 0.02(1 - \alpha) \approx 0.02\text{M},$$

$$[\text{OH}^-] = 0.1 + 0.02\alpha \approx 0.1\text{M}$$

$$0.02\alpha = \frac{5.4 \times 10^{-4} \times 0.02}{0.1}$$

$$\alpha = \frac{5.4 \times 10^{-4} \times 0.02}{0.1 \times 0.02} = 5.4 \times 10^{-3} = 0.0054$$

or  $\alpha = 0.54\%$ .

**Q55.** Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a) Human muscle-fluid, 6.83

(b) Human stomach fluid, 1.2

(c) Human blood, 7.38

(d) Human saliva, 6.4.

**Ans.** (a) **Human muscle-fluid**

$$\text{pH} = -\log [\text{H}^+] = 6.83$$

$$\log [\text{H}^+] = -6.83$$

$$[\text{H}^+] = \text{antilog}(-6.83) = 1.5 \times 10^{-7} \text{ M.}$$

(b) **Human stomach fluid**

$$\text{pH} = 1.2$$

$$[\text{H}^+] = \text{antilog}(-1.2) = 0.064 \text{ M.}$$

(c) **Human blood**

$$\text{pH} = 7.38$$

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

(d) **Human saliva**

$$\text{pH} = 6.4$$

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

**Q56.** The pH of milk, black coffee, tomato juice, lemon juice and white egg are 6.8, 5.0, 4.2, 2.2 and 7.8, respectively. Calculate corresponding hydrogen ion concentration in each.

**Ans.** (i) **Milk:** pH = 6.8

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

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

(ii) **Black coffee:** pH = 5.0

$$[\text{H}^+] = \text{antilog}(-5.0) = 1 \times 10^{-5} \text{ M.}$$

(iii) **Tomato juice:** pH = 4.2

$$[\text{H}^+] = \text{antilog}(-4.2) = 6.3 \times 10^{-5} \text{ M.}$$

(iv) **Lemon juice:** pH = 2.2;

$$[\text{H}^+] = \text{antilog}(-2.2) = 6.31 \times 10^{-3} \text{ M.}$$

(v) **White egg:** pH = 7.8

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

**Q57.** If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

**Ans.** Mass of KOH dissolved in 200 mL solution = 0.561 g  
 $\therefore$  Strength = Mass of KOH dissolved in 1000 mL

$$\text{solution} = \frac{0.561 \times 1000}{200} \text{ g L}^{-1}$$

$$\text{Molar mass of KOH} = 39 + 16 + 1 = 56 \text{ g mol}^{-1}$$

$$\text{Molarity of KOH solution} = \frac{\text{Strength}}{\text{Molar mass}}$$

$$= \frac{0.561 \times 1000}{200 \times 56} = 0.05 \text{ M.}$$

Since KOH is strong electrolyte, it ionises completely as



$$\text{Initial concentration} \quad 0.05 \text{ M} \quad 0 \quad 0$$

$$\text{Final concentrations} \quad 0 \quad 0.05 \text{ M} \quad 0.05 \text{ M}$$

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

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13} \text{ M}$$

$$\text{pH} = -\log 2 \times 10^{-13} = 12.70.$$

**Q58.** The solubility of  $\text{Sr}(\text{OH})_2$  at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

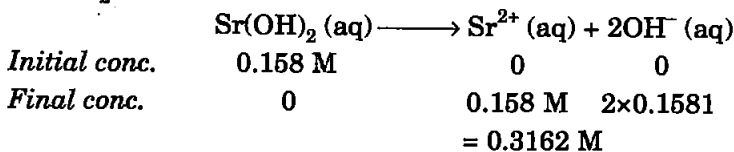
**Ans.** Mass of  $\text{Sr}(\text{OH})_2$  dissolved per litre = 19.23 g L<sup>-1</sup>

$$\begin{aligned} \text{Molar mass of Sr}(\text{OH})_2 &= 87.6 + 2(16 + 1) \\ &= 121.6 \text{ g mol}^{-1} \end{aligned}$$

$\therefore$  Molarity of the saturated solution

$$= \frac{19.23 \text{ g L}^{-1}}{121.6 \text{ g mol}^{-1}} = 0.158 \text{ M}$$

$\text{Sr}(\text{OH})_2$  ionises as



$$\therefore [\text{Sr}^{2+}] = 0.1581 \text{ M}; [\text{OH}^-] = 0.3162 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.3162 = 0.50$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14.0 - 0.50 = 13.50.$$

**Q59.** The ionisation constant of propanoic acid is  $1.32 \times 10^{-5}$ . Calculate the degree of ionisation of the acid in its 0.05 M solution and also its pH. What will be its degree of ionisation if the solution is 0.01 M in HCl also?

**Ans.** Given:  $K_a = 1.32 \times 10^{-5}$ ;  $c = 0.05 \text{ M}$

Since  $K_a$  is small, propanoic acid is weak acid and Ostwald's dilution law can be used

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.32 \times 10^{-5}}{0.05}} = 0.0163$$

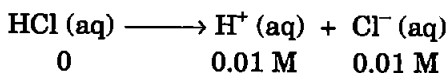
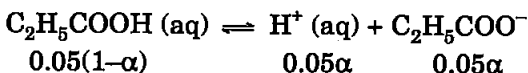
$$= 1.63 \times 10^{-2}$$

$$[\text{H}^+] = c\alpha = 0.05 \times 0.0163 = 8.15 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 8.15 \times 10^{-4} = 3.09.$$

**In presence of 0.01 M HCl**

The ionisation equilibria and equilibrium concentrations are:



$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]}$$

$$K_a = 1.32 \times 10^{-5};$$

$$[\text{H}^+] = (0.01 + 0.05\alpha)$$

$$\approx 0.01$$

( $\because \alpha$  is very small)

$$[\text{C}_2\text{H}_5\text{COOH}] = 0.05(1 - \alpha)$$

$$\approx 0.05 \text{ M}$$

$$[\text{C}_2\text{H}_5\text{COO}^-] = 0.05\alpha$$

$$\therefore 1.32 \times 10^{-5} = \frac{(0.01) \times (0.05\alpha)}{0.05} = 0.01\alpha$$

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

**Q60.** The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionisation constant of the acid and its degree of ionisation in the solution.

**Ans.** Given: pH = 2.34 and concentration of acid,  $c = 0.1$  M

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

Ionisation equilibrium and equilibrium concentrations are:



$$0.1(1 - \alpha) \qquad 0.1\alpha \qquad 0.1\alpha$$

$$\therefore [\text{H}^+] = 0.1\alpha = 4.57 \times 10^{-3}$$

$$\alpha = \frac{4.57 \times 10^{-3}}{0.1} = 4.57 \times 10^{-2} = 0.0457$$

Since  $\alpha$  is small

$$K_a = c\alpha^2 = 0.1 \times (4.57 \times 10^{-2})^2$$

$$= 2.09 \times 10^{-4}$$

**Q61.** The ionisation constant of nitrous acid is  $4.5 \times 10^{-4}$ . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

**Ans.** Since nitrous acid is a weak acid, its anion  $\text{NO}_2^-$  would hydrolyse and pH of the solution is given by relation.

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$$

(See competition booster for details.)

$$K_w = 1 \times 10^{-14}; K_a = 4.5 \times 10^{-4};$$

$$c = 0.04 \text{ M}$$

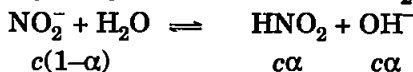
$$\text{pH} = \frac{1}{2} [(-\log 10^{-14}) + (-\log 4.5 \times 10^{-4}) + (\log 0.04)]$$

$$= \frac{1}{2} [14 + 3.35 - 1.40] = \frac{1}{2} \times 15.95 = 7.98$$

$$\text{Also, } K_h = \frac{K_w}{K_a} \quad (K_h = \text{hydrolysis constant})$$

(See competition booster for details.)

**For hydrolysis of the anion ( $\text{NO}_2^-$ )**



$$K_{eqm} = K_h = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{(c\alpha) \times (c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Since  $\alpha$  is small  $1 - \alpha \approx 1$

$$K_h = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{1 \times 10^{-14}}{(4.5 \times 10^{-4})(0.04)}}$$

$$= 2.36 \times 10^{-5}$$

**Q62.** A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionisation constant of pyridine.

**Ans.** Given: pH = 3.44; concentration  $c = 0.02$  M

$$\therefore [\text{H}^+] = \text{antilog}(-3.44)$$

$$= 3.63 \times 10^{-4} \text{ M}$$

Pyridinium hydrochloride is a weak acid and the

$$[\text{H}^+] = c\alpha$$

$$\alpha = \frac{[\text{H}^+]}{c} = \frac{3.63 \times 10^{-4}}{0.02} = 0.0182$$

Since it is weak acid, Ostwald's dilution law is applicable and

$$K_a = c\alpha^2 = 0.02 \times (0.0182)^2 = 6.63 \times 10^{-6}$$

Pyridine is conjugate base of pyridinium hydrochloride and its dissociation constant is related to that of the latter as:

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{6.63 \times 10^{-6}} = 1.5 \times 10^{-9}$$

**Q63.** Predict if the solutions of the following salts are neutral, acidic or basic:

$\text{NaCl}$ ,  $\text{KBr}$ ,  $\text{NaCN}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_2$  and  $\text{KF}$

**Ans. Neutral solutions:** (Salts of a strong acid and a strong base)

$\text{NaCl}$  and  $\text{KBr}$

**Basic solutions:** (Salts of a weak acid and a strong base)

$\text{NaCN}$ ,  $\text{NaNO}_2$  and  $\text{KF}$

**Acidic solutions:** (Salts of a strong acid and a weak base)  
 $\text{NH}_4\text{NO}_3$

**Q64.** The ionisation constant of chloroacetic acid is  $1.35 \times 10^{-3}$ . What will be the pH of 0.1 M acid and its 0.1 M sodium salt solution?

**Ans.** (i) **0.1 M chloroacetic acid solution**

Since the acid is weak. Ostwald's dilution law can be

used and  $\alpha = \sqrt{\frac{K_a}{c}}$  and

$$[\text{H}^+] = c\alpha = \sqrt{cK_a} = \sqrt{0.1 \times 1.35 \times 10^{-3}} = 0.0117 \text{ M}$$

$$\text{pH} = -\log 0.0117 = 1.93.$$

(ii) **0.1 M Sodium chloroacetate solution**

It is salt of weak acid and strong base; its anion will hydrolyse in the solution and solution would become basic. The pH is given by the relation

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

$$pK_w = -\log K_w = -\log 1 \times 10^{-14} = 14$$

$$pK_a = -\log K_a = -\log 1.35 \times 10^{-3} = 2.87$$

$$\log c = \log 0.1 = -1$$

$$\text{pH} = \frac{1}{2}[14 + 2.87 - 1] = 7.9.$$

(iii) **Mixture solution which is 0.1 M acid and 0.1 M its sodium salt**

This solution would act as an acid buffer whose pH is given by the relation

$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

(See competition booster for details.)

Since  $[\text{Salt}] = [\text{Acid}] = 0.1 \text{ M}$  each

$$\text{pH} = pK_a = -\log K_a = -\log 1.35 \times 10^{-3}$$

$$= 2.87.$$

**Q65.** Ionic product of water at 310 K is  $2.7 \times 10^{-14}$ . What is the pH of neutral water at this temperature?

**Ans.** Given:  $K_w = 2.7 \times 10^{-14}$   
 $K_w = [\text{H}^+][\text{OH}^-]$



Since in pure water  $[H^+] = [OH^-]$

$$\therefore K_w = [H^+]^2 = [OH^-]^2$$

$$\text{or } [H^+] = \sqrt{K_w}$$

$$\text{pH} = -\log [H^+] = -\log \sqrt{K_w} = -\frac{1}{2} \log K_w$$

$$= -\frac{1}{2} \log (2.7 \times 10^{-14}) = 6.78.$$

**Q66.** Calculate the pH of the resultant mixtures:

(a) 10 mL of 0.2 M  $\text{Ca(OH)}_2$  + 25 mL of 0.1 M HCl

(b) 10 mL of 0.01 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.01 M  $\text{Ca(OH)}_2$

(c) 10 mL of 0.1 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.1 M KOH

**Ans.** (a) Mixture of 10 mL of 0.2 M  $\text{Ca(OH)}_2$  + 25 mL of 0.1 M HCl

10 mL of 0.2 M  $\text{Ca(OH)}_2$  contains

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

25 mL of 0.1 M HCl contains

$$25 \times 0.1 = 2.5 \text{ m mol HCl}$$

According to reaction



2 mol HCl neutralise 1 mol  $\text{Ca(OH)}_2$

$$\therefore 2.5 \text{ mmol HCl would neutralise} = \frac{2.5}{2}$$

$$= 1.25 \text{ m mol } \text{Ca(OH)}_2$$

Unreacted  $\text{Ca(OH)}_2 = 2.0 - 1.25 = 0.75 \text{ mmol}$

Volume of mixture solution = 10 + 25 = 35 mL

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

$$= 0.02 \text{ M}$$

Since 1 formula unit of  $\text{Ca(OH)}_2$  gives  $2\text{OH}^-$ , concentration of  $\text{OH}^-$  is

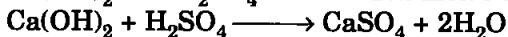
$$[\text{OH}^-] = 2 \times 0.02 = 0.04 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.04 = 1.40$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.40 = 12.60.$$

(b) Mixture of 10 mL of 0.01 M  $\text{H}_2\text{SO}_4$  and 10 mL of 0.01 M  $\text{Ca(OH)}_2$

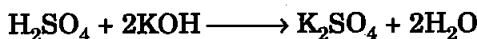
$\text{Ca(OH)}_2$  and  $\text{H}_2\text{SO}_4$  react in 1:1 molar ratio



10 mL of 0.01 M  $\text{H}_2\text{SO}_4$  contains  $10 \times 0.01 = 0.1$  mmol  $\text{H}_2\text{SO}_4$  and 10 mL of 0.01M  $\text{Ca}(\text{OH})_2$  contains  $10 \times 0.01 = 0.1$  mmol  $\text{Ca}(\text{OH})_2$ . Since the amounts of two are equal, they would neutralise each other completely and the resulting solution will be neutral and its  $\text{pH} = 7.0$ .

(c) **Mixture of 10 mL of 0.1 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.1 M KOH**

$\text{H}_2\text{SO}_4$  and KOH react in 1:2 molar ratio as



10 mL of 0.1 M  $\text{H}_2\text{SO}_4$  contains  $10 \times 0.1$   
 $= 1$  mmol  $\text{H}_2\text{SO}_4$

10 mL of 0.1 M KOH contains  $10 \times 0.1$   
 $= 1$  mmol KOH

1 mmol KOH would neutralise 0.5 mmol  $\text{H}_2\text{SO}_4$

Unreacted  $\text{H}_2\text{SO}_4 = 1 - 0.5 = 0.5$  mmol

Volume of mixture solution =  $10 + 10 = 20$  mL

Concentration of  $\text{H}_2\text{SO}_4 = \frac{0.5}{20} = 0.025$  M

Since 1 mol  $\text{H}_2\text{SO}_4$  gives 2 mol  $\text{H}^+$ ,

$$[\text{H}^+] = 2[\text{H}_2\text{SO}_4] = 2 \times 0.025 = 0.05 \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 0.05 = 1.301.$$

**Q67.** Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants given in Table 7.9. Determine also the molarities of individual ions.

**Ans.** (i) **Silver chromate,  $\text{Ag}_2\text{CrO}_4$**

$$s = \left( \frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}}$$

For  $\text{Ag}_2\text{CrO}_4$ ,

$$x = 2, y = 1 \text{ and } x + y = 3;$$

$$K_{sp} = 1.1 \times 10^{-12}$$

$$\therefore s = \left( \frac{1.1 \times 10^{-12}}{2^2 \times 1^1} \right)^{\frac{1}{3}} = \left( \frac{1.1 \times 10^{-12}}{4} \right)^{\frac{1}{3}}$$

$$= (0.275 \times 10^{-12})^{\frac{1}{3}} = 6.5 \times 10^{-5} \text{ M}$$

$$[\text{Ag}^+] = 2[\text{Ag}_2\text{CrO}_4] = 2 \times s = 2 \times 6.5 \times 10^{-5}$$

$$= 1.3 \times 10^{-4} \text{ M}$$

$$[\text{CrO}_4^{2-}] = [\text{Ag}_2\text{CrO}_4] = s = 6.5 \times 10^{-5} \text{ M.}$$

**(ii) Barium chromate, BaCrO<sub>4</sub>**For BaCrO<sub>4</sub>,

$$x = 1, y = 1, x + y = 2, K_{sp} = 1.2 \times 10^{-10}$$

$$s = \left( \frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}} = (1.2 \times 10^{-10})^{\frac{1}{2}} = 1.1 \times 10^{-5} \text{ M}$$

From the formula,

$$[\text{Ba}^{2+}] = [\text{CrO}_4^{2-}] = s = 1.1 \times 10^{-5} \text{ M.}$$

**(iii) Ferric hydroxide, Fe(OH)<sub>3</sub>**For Fe(OH)<sub>3</sub>,

$$x = 1, y = 3, x + y = 4, K_{sp} = 1.0 \times 10^{-38}$$

$$s = \left( \frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}} = \left( \frac{1.0 \times 10^{-38}}{1^1 3^3} \right)^{\frac{1}{4}}$$

$$= \left( \frac{1.0 \times 10^{-38}}{27} \right)^{\frac{1}{4}} = 1.39 \times 10^{-10} \text{ M}$$

$$[\text{Fe}^{3+}] = [\text{Fe(OH)}_3] = s = 1.39 \times 10^{-10} \text{ M}$$

$$[\text{OH}^-] = 3[\text{Fe(OH)}_3] = 3s = 3 \times 1.39 \times 10^{-10}$$

$$= 4.17 \times 10^{-10} \text{ M.}$$

**(iv) Lead chloride, PbCl<sub>2</sub>**For PbCl<sub>2</sub>,

$$x = 1, y = 2, x + y = 3, K_{sp} = 1.6 \times 10^{-5}$$

$$s = \left( \frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}} = \left( \frac{1.6 \times 10^{-5}}{1^1 2^2} \right)^{\frac{1}{3}}$$

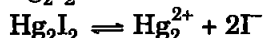
$$= \left( \frac{1.6 \times 10^{-5}}{4} \right)^{\frac{1}{3}} = 0.16 \text{ M}$$

$$[\text{Pb}^{2+}] = [\text{PbCl}_2] = s = 0.16 \text{ M}$$

$$[\text{Cl}^-] = 2[\text{PbCl}_2] = 2s = 0.32 \text{ M.}$$

(v) **Mercurous iodide,  $\text{Hg}_2\text{I}_2$**

$\text{Hg}_2\text{I}_2$  ionises as:



$$\therefore x = 1, y = 2, x + y = 3, K_{sp} = 4.5 \times 10^{-29}$$

$$s = \left( \frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}} = \left( \frac{4.5 \times 10^{-29}}{1^1 \cdot 2^2} \right)^{\frac{1}{3}}$$

$$= \left( \frac{4.5 \times 10^{-29}}{4} \right)^{\frac{1}{3}} = 2.24 \times 10^{-10} \text{ M}$$

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

$$[\text{I}^-] = 2[\text{Hg}_2\text{I}_2] = 2s = 4.48 \times 10^{-10} \text{ M.}$$

**Q68.** The solubility product constant of  $\text{Ag}_2\text{CrO}_4$  and  $\text{AgBr}$  are  $1.1 \times 10^{-12}$  and  $5.0 \times 10^{-13}$  respectively. Calculate the ratio of the molarities of their saturated solutions.

**Ans.** (i)  **$\text{Ag}_2\text{CrO}_4$**

$$x = 2, y = 1, x + y = 3, K_{sp} = 1.1 \times 10^{-12}$$

$$s = \left( \frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}} = \left( \frac{1.1 \times 10^{-12}}{2^2 \cdot 1^1} \right)^{\frac{1}{3}}$$

$$= \left( \frac{1.1 \times 10^{-12}}{4} \right)^{\frac{1}{3}} = 6.5 \times 10^{-5} \text{ M.}$$

(ii)  **$\text{AgBr}$**

$$x = 1, y = 1, x + y = 2, K_{sp} = 5.0 \times 10^{-13}$$

$$s = \left( \frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}} = \left( \frac{5.0 \times 10^{-13}}{1^1 \cdot 1^1} \right)^{\frac{1}{2}}$$

$$= (5.0 \times 10^{-13})^{1/2} = 7.1 \times 10^{-7} \text{ M}$$

Comparing the solubilities,  $\text{Ag}_2\text{CrO}_4$  is more soluble

$$\text{Ratio of their molarities} = \frac{6.5 \times 10^{-5} \text{ M}}{7.1 \times 10^{-7} \text{ M}} = 91.5.$$

**Q69.** Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate  $K_{sp} = 7.4 \times 10^{-8}$ ).

**Ans.** Since equal volumes of two solutions are mixed, the molarities will become one-half, *i.e.*,

$$[\text{CuCrO}_4] = 0.001 \text{ M}$$

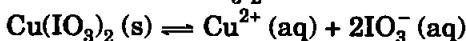
$$[\text{NaIO}_3] = 0.001 \text{ M} = 10^{-3} \text{ M}$$

$$[\text{Cu}^{2+}] = [\text{CuCrO}_4] = 0.001 \text{ M}$$

$$[\text{IO}_3^-] = [\text{NaIO}_3]$$

$$= 0.001 \text{ M} = 10^{-3} \text{ M}$$

For cupric iodate,  $\text{Cu}(\text{IO}_3)_2$



$$Q_{sp} = [\text{Cu}^{2+}] [\text{IO}_3^-]^2 = (10^{-3})(10^{-3})^2 = 1 \times 10^{-9}$$

$$\text{Since } K_{sp} = 7.4 \times 10^{-8}$$

$$Q_{sp} < K_{sp}$$

No precipitation would occur.

**Q70.** The ionisation constant of benzoic acid is  $6.46 \times 10^{-5}$  and  $K_{sp}$  for silver benzoate is  $2.5 \times 10^{-13}$ . How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

**Ans.** (i) **Solubility of silver benzoate in water**

For silver benzoate,  $\text{C}_6\text{H}_5\text{COOAg}$ ,  $x = 1$ ,  $y = 1$

$$x + y = 2 \text{ and } K_{sp} = 2.5 \times 10^{-13}$$

$$s = \left( \frac{K_{sp}}{x^x \cdot y^y} \right) = \left( \frac{2.5 \times 10^{-13}}{1^1 \cdot 1^1} \right)^{\frac{1}{2}}$$

$$= (2.5 \times 10^{-13})^{\frac{1}{2}} = 5 \times 10^{-7} \text{ M.}$$

(ii) **Solubility of silver benzoate in a buffer of pH 3.19**

pH of buffer = 3.19

$$[\text{H}^+] = \text{antilog}(-3.19) = 6.46 \times 10^{-4}$$

$$K_a \text{ of benzoic acid} = 6.46 \times 10^{-5}$$

Solubility of silver benzoate in buffer of pH 3.19 is

$$s = \left\{ \frac{K_{sp}([\text{H}^+] + K_a)}{K_a} \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{2.5 \times 10^{-13}(6.46 \times 10^{-4} + 6.46 \times 10^{-5})}{6.46 \times 10^{-5}} \right\}^{\frac{1}{2}}$$

$$\begin{aligned}
 &= \left\{ \frac{2.5 \times 10^{-13} \times 7.11 \times 10^{-4}}{6.46 \times 10^{-5}} \right\}^{\frac{1}{2}} \\
 &= (2.75 \times 10^{-12})^{1/2} \\
 &= 1.658 \times 10^{-6} \text{ M.}
 \end{aligned}$$

Solubility is more in acidic buffer than in water.

The ratio of solubilities

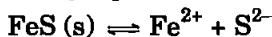
$$= \frac{1.658 \times 10^{-6}}{5 \times 10^{-7}} = \mathbf{3.316 \text{ times.}}$$

**Q71.** What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide,  $K_{sp} = 6.3 \times 10^{-18}$ ).

**Ans.** For iron sulphide,  $\text{FeS}$ ,  $x = 1$ ,  $y = 1$ ,  $x + y = 2$  and  $K_{sp} = 6.3 \times 10^{-18}$

$$\begin{aligned}
 \text{Solubility } s &= \left( \frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}} = \left( \frac{6.3 \times 10^{-18}}{1^1 \cdot 1^1} \right)^{\frac{1}{2}} \\
 &= (6.3 \times 10^{-18})^{1/2} = 2.51 \times 10^{-9} \text{ M}
 \end{aligned}$$

Solubility equilibrium of  $\text{FeS}$  is



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

When the solutions of ferrous sulphate and sodium sulphide are mixed

$$Q_{sp} = [\text{Fe}^{2+}][\text{S}^{2-}]$$

Precipitation would occur only if  $Q_{sp} > K_{sp}$ .

The maximum value of  $Q_{sp}$  when precipitation would not occur is when  $Q_p = K_p$ .

Since solutions are equimolar, the maximum concentration upto which no precipitation occurs can be calculated as given below:

$$Q = K_{sp} = [\text{Fe}^{2+}][\text{S}^{2-}] = [\text{Fe}^{2+}]^2 \text{ or } [\text{S}^{2-}]^2$$

$$\begin{aligned}
 \therefore [\text{Fe}^{2+}] &= [\text{S}^{2-}] = \sqrt{K_{sp}} = \sqrt{6.3 \times 10^{-18}} \\
 &= \mathbf{2.51 \times 10^{-9} \text{ M.}}
 \end{aligned}$$

**Q72.** What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K? (For calcium sulphate,  $K_{sp}$  is  $9.1 \times 10^{-6}$ ).

**Ans.** For Calcium sulphate,  $\text{CaSO}_4$ ,

$$x = 1, y = 1, x + y = 2, K_{sp} = 9.1 \times 10^{-6}$$

$$\begin{aligned}\text{Solubility} = s &= (K_{sp})^{1/2} = \sqrt{9.1 \times 10^{-6}} \\ &= 3.02 \times 10^{-3} \text{ M}\end{aligned}$$

Mass of  $\text{CaSO}_4$  to be dissolved = 1 g

Molar mass of  $\text{CaSO}_4 = 40 + 32 + 64 = 136 \text{ g mol}^{-1}$

$$\therefore \text{Moles of } \text{CaSO}_4 \text{ to be dissolved} = \frac{1}{136} \text{ mol}$$

When a solute is dissolved in minimum volume of solvent, the solution prepared would be its saturated solution and its molarity would be equal to its solubility. Thus,

Molarity = Solubility,

$$s = \frac{\text{Moles of solute}}{\text{Volume of solution (in litres)}}$$

Assuming that volume of solution obtained is the same as that of the solvent water used

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of water (in litres)}}$$

$\therefore$  Minimum volume of water required

$$\begin{aligned}&= \frac{\text{Moles of solute}}{\text{Molarity}} = \frac{1}{136} \times \frac{1}{3.02 \times 10^{-3}} \\ &= 2.435 \text{ L.}\end{aligned}$$

**Q73.** The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is  $1.0 \times 10^{-19} \text{ M}$ . If 10 mL of this is added to 5 mL of 0.04 M solution of the following:  $\text{FeSO}_4$ ,  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2$ . In which of these solutions precipitation will take place?

**Ans.** In solution of any salt, the concentration of metal ion  $\text{M}^{2+}$  is same as that of salt, i.e.,

$$[\text{M}^{2+}] = 0.04 \text{ M}$$

Since 5 mL of this solution are mixed with 10 mL of 0.1 M HCl saturated with  $\text{H}_2\text{S}$ , the total volume becomes 15 mL.

$\therefore$  Concentration of  $\text{M}^{2+}$  in final solution

$$[M^{2+}] = \frac{0.04 \times 5}{15} = \frac{4 \times 10^{-2}}{3} \text{ M}$$

Concentration of  $S^{2-}$  ions in 0.1 M HCl  
 $= 1.0 \times 10^{-19} \text{ M}$

10 mL of this solution is mixed with 5 mL of salt solution and final volume becomes 15 mL.

$\therefore$  Concentration of  $S^{2-}$  in final solution  $[S^{2-}]$   
 $= \frac{10 \times 1.0 \times 10^{-19}}{15} = \frac{2 \times 10^{-19}}{3} \text{ M}$

Since all the metals are bivalent the formula of their sulphides is MS

and  $Q_{sp} = [M^{2+}][S^{2-}]$   
 $= \left( \frac{4 \times 10^{-2}}{3} \right) \left( \frac{2 \times 10^{-19}}{3} \right)$   
 $Q_{sp} = 8.8 \times 10^{-22}$

$K_{sp}$  of sulphides of given metals are

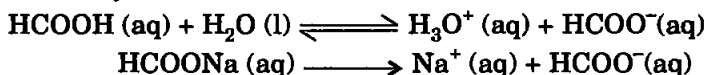
Sulphide	$K_{sp}$
FeS	$6.3 \times 10^{-18}$
MnS	$2.5 \times 10^{-13}$
ZnS	$1.6 \times 10^{-24}$
CdS	$8.0 \times 10^{-27}$

Comparing the  $Q_{sp}$  ( $8.8 \times 10^{-22}$ ) with these,  $Q_{sp} > K_{sp}$  only in case of ZnS and CdS. Thus, precipitation would occur in  $ZnCl_2$  and  $CdCl_2$  solutions.

## TEXTBOOK PROBLEMS SOLVED

**Problem 1.** A certain buffer is made by mixing sodium formate and formic acid in water. With the help of equations explain how this buffer neutralizes addition of a small amount of an acid or a base.

**Solution.** The buffer mixture contains formic acid and sodium acetate. They ionize as shown below:



Sodium formate being a strong electrolyte is completely dissociated. Due to common ion effect it suppresses the ionization of formic acid which is a weak acid.



**Buffer action of this buffer**

(i) **Addition of a small amount of an acid (e.g. HCl)**, furnishes  $\text{H}^+$  ions which are removed from the solution by combining with excess of  $\text{HCOO}^-$  (formate) ions present in the buffer to form undissociated formic acid ( $\text{HCOOH}$ ).

(ii) **Addition of a small amount of a base (e.g. NaOH)**, furnishes some  $\text{OH}^-$  ions which are neutralized by  $\text{H}_3\text{O}^+$  ions present in the buffer. Thus the buffer neutralizes the addition of a small amount of an acid or a base.

**Problem 2.** A basic buffer is made by mixing ammonium hydroxide and ammonium nitrate in water. Explain how this buffer resists change in its pH on addition of a small amount on an acid or a base.

**Solution.** Buffer action of ammonium hydroxide–ammonium nitrate buffer. Their dissociation furnishes  $\text{NH}_4^+$   $\text{OH}^-$  and  $\text{NO}_3^-$  ions in the solution.

(i) **Addition of a small amount of an acid (e.g. HCl)** furnishes some  $\text{H}^+$  ions which are neutralized by  $\text{OH}^-$  ions present in the buffer to form  $\text{H}_2\text{O}$ .

(ii) **Addition of a small amount of a base (e.g. NaOH)** furnishes some  $\text{OH}^-$  which are removed from the solution by combination with  $\text{NH}_4^+$  ions to form undissociated  $\text{NH}_4\text{OH}$ .

Thus the buffer resists the change in pH on addition of a small amount of an acid on a base.

**Problem 3.** What would be the pH of a solution obtained by mixing 10 g of acetic acid and 15 g of sodium acetate and making the volume equal to 1 L. Dissociation constant of acetic acid at  $25^\circ\text{C}$  is  $1.75 \times 10^{-5}$ .

**Solution.** Mass of acetic acid dissolved = 10 g

Molar mass of acetic acid ( $\text{CH}_3\text{COOH}$ ) =  $60 \text{ g mol}^{-1}$

$$\therefore \text{Moles of acetic acid dissolved in 1L solution} = \frac{10}{60} = \frac{1}{6} \text{ mol}$$

$$[\text{Acid}] = \frac{1}{6} \text{ mol L}^{-1}.$$

Mass of sodium acetate dissolved = 15 g

Molar mass of sodium acetate ( $\text{CH}_3\text{COONa}$ ) =  $82 \text{ g mol}^{-1}$

$$\therefore \text{Moles of sodium acetate dissolved in 1L solution} = \frac{15}{82} \text{ mol}$$

$$[\text{Salt}] = \frac{15}{82} \text{ mol L}^{-1}$$

**Given:**  $K_a = 1.75 \times 10^{-5}$

For an acidic buffer according to the Henderson-Hasselbalch equation

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log (1.75 \times 10^{-5}) + \log \left( \frac{15/82}{1/6} \right) \\ &= -\log (1.75 \times 10^{-5}) + \log \frac{15 \times 6}{82} = 4.798 \end{aligned}$$

or  $\text{pH} = 4.80$

**Problem 4.** A buffer solution contains 0.40 mol of ammonium hydroxide and 0.50 mol of ammonium chloride to make a buffer solution of 1 L. Calculate the pH of the resulting buffer solution. Dissociation constant of ammonium hydroxide at 25 °C is  $1.81 \times 10^{-5}$ .

**Solution.** Number of moles of ammonium hydroxide dissolved in 1L solution = 0.4

$$\therefore [\text{Base}] = 0.4 \text{ mol L}^{-1}$$

Number of moles of ammonium chloride dissolved in 1 L solution = 0.5 mol

$$\therefore [\text{Salt}] = 0.5 \text{ mol L}^{-1}$$

Given:  $K_b = 1.81 \times 10^{-5}$

Henderson-Hasselbalch equation for a basic buffer is

$$\begin{aligned} \text{pOH} &= \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ &= -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ &= -\log (1.81 \times 10^{-5}) + \log \frac{0.5}{0.4} = 4.839 \end{aligned}$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.839 = 9.161$$



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