

# NCERT SOLUTIONS

## CLASS-XI CHEMISTRY

### CHAPTER-7

### EQUILIBRIUM

Q.1. At a fixed temperature a liquid is in equilibrium with its vapour in a closed vessel. Suddenly, the volume of the vessel got increased.

I) What will be the final vapour pressure and what will happen when equilibrium is restored finally?

II) Write down, how initially the rates of evaporation and condensation got changed?

III) Write down the effect observed when there was a change in vapour pressure.

Ans.

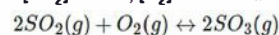
(I) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

(II) On increasing the volume of the container, the rates of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

(III) On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are now distributed over a large space

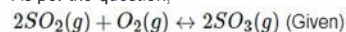
Q.2. Find out  $K_c$  for the given reaction in equilibrium state

:  $[SO_2] = 0.6 \text{ M}$ ,  $[O_2] = 0.82 \text{ M}$  and  $[SO_3] = 1.9 \text{ M}$  ?



Ans.

As per the question,



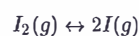
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \text{ (approximately)}$$

$$= \frac{(1.9)^2 M^2}{(0.6)^2 (0.82) M^3}$$

$$= 12.229 M^{-1}$$

Hence,  $K$  for the equilibrium is  $12.229 \text{ M}^{-1}$ .

Q.3. At a definite temperature and a total pressure of  $10^5 \text{ Pa}$ , iodine vapour contains 40% by volume of I atoms



Find  $K_p$  for the equilibrium.

Ans.

Partial pressure of Iodine atoms (I)

$$p_I = \frac{40}{100} \times p_{total}$$

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

$$= 4 \times 10^4 \text{ Pa}$$

Partial pressure of  $I_2$  molecules,

$$p_{I_2} = \frac{60}{100} \times p_{total}$$

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

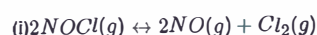
$$= 6 \times 10^4 \text{ Pa}$$

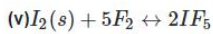
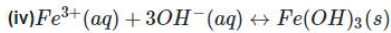
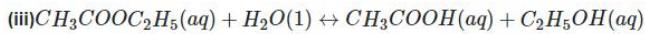
Now, for the given reaction,

$$K_p = \frac{(p_I)^2}{p_{I_2}} = \frac{(4 \times 10^4)^2 \text{ Pa}^2}{6 \times 10^4 \text{ Pa}}$$

$$= 2.67 \times 10^4 \text{ Pa}$$

Q.4. For the given reaction, find expression for the equilibrium constant





Ans.

$$K_C = \frac{[NO_2]^2 [Cl_2(g)]}{[NOCl(g)]^2}$$

$$(ii) K_C = \frac{[CuO(s)]^2 [NO_2(g)]^4 [O_2(g)]}{[Cu(NO_3)_2(g)]^2}$$

$$= [NO_2(g)]^4 [O_2(g)]$$

$$(iii) K_C = \frac{[CH_3COOH(aq)] [C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)] [H_2O(l)]}$$

$$= \frac{[CH_3COOH(aq)] [C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]}$$

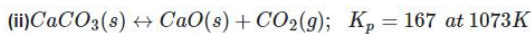
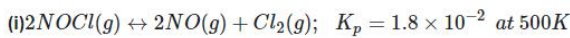
$$(iv) K_C = \frac{Fe(OH)_3(s)}{[Fe^{3+}(aq)] [OH^-(aq)]^3}$$

$$= \frac{1}{[Fe^{3+}(aq)] [OH^-(aq)]^3}$$

$$(v) K_C = \frac{[IF_5]^2}{[I_2(s)] [F_2]^5}$$

$$= \frac{[IF_5]^2}{[F_2]^5}$$

Q.5. Find the value of,  $K_c$  for each of the following equilibria from the given value of  $K_p$ :



Ans.

The relation between  $K_p$  and  $K_c$  is given as:

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

(a) Given,

$$R = 0.0831 \text{ barLmol}^{-1}\text{K}^{-1}$$

$$\Delta n = 3 - 2 = 1$$

$$T = 500 \text{ K}$$

$$K_p = 1.8 \times 10^{-2}$$

Now,

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

$$\Rightarrow 1.8 \times 10^{-2} = K_c (0.0831 \times 500)^1$$

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

$$= 4.33 \times 10^{-4} (\text{approximately})$$

(b) Here,

$$\Delta n = 2 - 1 = 1$$

$$R = 0.0831 \text{ barLmol}^{-1}\text{K}^{-1}$$

$$T = 1073 \text{ K}$$

$$K_p = 167$$

Now,

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

$$\Rightarrow 167 = K_c (0.0831 \times 1073)^{\Delta n}$$

$$\Rightarrow K_c = \frac{167}{0.0831 \times 1073}$$

$$= 1.87 (\text{approximately})$$

Q.6. For the following equilibrium,  $K_c = 6.3 \times 10^{14}$  at 1000K





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

Ans.

$$\begin{aligned} \text{For the reverse reaction, } K_c &= \frac{1}{K_c} \\ &= \frac{1}{6.3 \times 10^{14}} \\ &= 1.59 \times 10^{-15} \end{aligned}$$

Q.7. Explain why solids and pure liquids can be ignored while writing the equilibrium constant expression?

Ans.

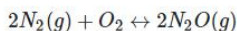
This is because molar concentration of a pure solid or liquid is independent of the amount present.

$$\begin{aligned} \text{Mole concentration} &= \frac{\text{Number of moles}}{\text{Volume}} \\ &= \frac{\text{Mass/molecular mass}}{\text{Volume}} \\ &= \frac{\text{Mass}}{\text{Volume} \times \text{Molecular mass}} \\ &= \frac{\text{Density}}{\text{Molecular mass}} \end{aligned}$$

Though density of solid and pure liquid is fixed and molar mass is also fixed .

∴ Molar concentration are constant.

Q.8. When oxygen and nitrogen react with each other, then the following reaction takes place:

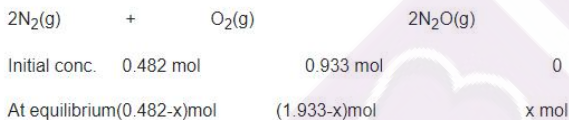


If a solution of 0.933 mol of oxygen and 0.482 mol of nitrogen is placed in a 10 L reaction vessel and allowed to form  $\text{N}_2\text{O}$  at a temperature for which  $K_c = 2.0 \times 10^{-37}$ , determine the composition of equilibrium solution.

Ans.

Let the concentration of  $\text{N}_2\text{O}$  at equilibrium be x.

The given reaction is:



$$[\text{N}_2] = \frac{0.482-x}{10}, [\text{O}_2] = \frac{0.933-x}{10}, [\text{N}_2\text{O}] = \frac{x}{10}$$

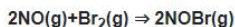
The value of equilibrium constant is extremely small. This means that only small amounts . Then,

$$[\text{N}_2] = \frac{0.482}{10} = 0.0482 \text{ mol L}^{-1} \text{ and } [\text{O}_2] = \frac{0.933}{10} = 0.0933 \text{ mol L}^{-1}$$

Now,

$$\begin{aligned} K_c &= \frac{[\text{N}_2\text{O}(\text{g})]^2}{[\text{N}_2(\text{g})][\text{O}_2(\text{g})]} & [\text{N}_2\text{O}] &= \frac{x}{10} = \frac{6.6 \times 10^{-20}}{10} \\ & \Rightarrow 2.0 \times 10^{-37} = \frac{(\frac{x}{10})^2}{(0.0482)^2(0.0933)} & &= 6.6 \times 10^{-21} \\ & \Rightarrow \frac{x^2}{100} = 2.0 \times 10^{-37} \times (0.0482)^2 \times (0.0933) \\ & \Rightarrow x^2 = 43.35 \times 10^{-40} \\ & \Rightarrow x = 6.6 \times 10^{-20} \end{aligned}$$

Q.9. Nitric oxide reacts with bromine and gives nitrosyl bromide as per reaction is given below:



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

Ans.

The given reaction is:



2mol      1mol                      2mol

Now, 2 mol of NOBr are formed from 2 mol of NO. Therefore, 0.0518 mol of NOBr are formed from 0.0518 mol of NO.

Again, 2 mol of NOBr are formed from 1 mol of Br.

Therefore, 0.0518 mol of NOBr are formed from  $\frac{0.0518}{2}$  mol of Br, or 0.0259 mol of NO.

The amount of NO and Br present initially is as follows:

$$[\text{NO}] = 0.087 \text{ mol} \quad [\text{Br}_2] = 0.0437 \text{ mol}$$

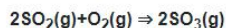
Therefore, the amount of NO present at equilibrium is:

$$[\text{NO}] = 0.087 - 0.0518 = 0.0352 \text{ mol}$$

And, the amount of Br present at equilibrium is:

$$[\text{Br}_2] = 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

**Q.10. 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.)**

For the given reaction,

$$\Delta n = 2 - 3 = -1$$

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

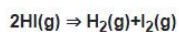
$$R = 0.0831 \text{ bar L bar K}^{-1} \text{ mol}^{-1}$$

$$K_p = 2.0 \times 10^{10} \text{ bar}^{-1}$$

We know that,

$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} \\ \Rightarrow 2.0 \times 10^{10} \text{ bar}^{-1} &= K_c (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K})^{-1} \\ \Rightarrow K_c &= \frac{2.0 \times 10^{10} \text{ bar}^{-1}}{(0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K})^{-1}} \\ &= (2.0 \times 10^{10} \text{ bar}^{-1}) (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K}) \\ &= 74.79 \times 10^{10} \text{ L mol}^{-1} \\ &= 7.48 \times 10^{11} \text{ L mol}^{-1} \\ &= 7.48 \times 10^{11} \text{ M}^{-1} \end{aligned}$$

**Q.11. A sample of  $\text{HI}(\text{g})$  is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of  $\text{HI}(\text{g})$  is 0.04 atm. What is  $K_p$  for the given equilibrium?**



**Ans.**

The initial concentration of HI is 0.2 atm. At equilibrium, it has a partial pressure of 0.04 atm.

Therefore, a decrease in the pressure of HI is  $0.2 - 0.04 = 0.16$ . The given reaction is:

2HI(g)	H <sub>2</sub> (g)	+	I <sub>2</sub> (g)	
Initial conc.	0.2 atm		0	0
At equilibrium	0.4 atm		0.16	2.15
2	2			
=0.08atm	=0.08atm			

Therefore,

$$\begin{aligned} K_p &= \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} \\ &= \frac{0.08 \times 0.08}{(0.04)^2} \\ &= \frac{0.0064}{0.0016} \\ &= 4.0 \end{aligned}$$

Hence, the value of  $K_p$  for the given equilibrium is 4.0.

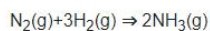
**Q.12.** A mixture of 1.57 mol of  $N_2$ , 1.92 mol of  $H_2$  and 8.13 mol of  $NH_3$  is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant,  $K_c$  for the reaction



Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

**Ans.**

The given reaction is:



The given concentration of various species is

$$[N_2] = \frac{1.57}{20} \text{ mol L}^{-1}$$

$$[H_2] = \frac{1.92}{20} \text{ mol L}^{-1}$$

$$[NH_3] = \frac{8.31}{20} \text{ mol L}^{-1}$$

Now, reaction quotient  $Q_c$  is:

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{8.31}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3} = 2.4 \times 10^3$$

Since,  $Q_c \neq K_c$ , the reaction mixture is not at equilibrium.

Again,  $Q_c > K_c$ . Hence, the reaction will proceed in the reverse direction.

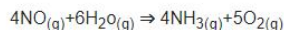
**Q.13.** The equilibrium constant expression for a gas reaction is,

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

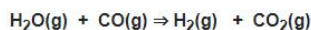
Write the balanced chemical equation corresponding to this expression.

**Ans.**

The balanced chemical equation corresponding to the given expression can be written as:



**Q.14.** One mole of  $H_2O$  and one mole of  $CO$  are taken in 10 L vessel and heated to 725 K. At equilibrium 60% of water (by mass) reacts with  $CO$  according to the equation,



Calculate the equilibrium constant for the reaction.

**Ans.**

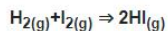
The given reaction is:

$H_2O(g) + CO(g)$	$H_2(g) + CO_2(g)$		
Initial conc.	1 M	1 M	0
10	10		0
At equilibrium	1-0.6 M	1-0.6 M	0.6 M
10	10	10	10
=0.04 M	=0.04M	=0.06 M	=0.06M

Therefore, the equilibrium constant for the reaction,

$$K_c = K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{0.06 \times 0.06}{0.04 \times 0.04} = \frac{0.0036}{0.0016} = 2.25 (\text{approximately})$$

**Q.15.** At 700 K. equilibrium constant for the reaction



is 54.8. If  $0.5 \text{ mol L}^{-1}$  of  $\text{HI}_{(g)}$  is present at equilibrium at 700 K, what are the concentration of  $\text{H}_{2(g)}$  and  $\text{I}_{2(g)}$  assuming that we initially started with  $\text{HI}_{(g)}$  and allowed it to reach equilibrium at 700 K?

Ans.

It is given that equilibrium constant  $K_c$  for the reaction



Therefore, at equilibrium, the equilibrium constant  $K_c$  for the reaction



$[\text{HI}] = 0.5 \text{ mol L}^{-1}$  will be  $1/54.8$ .

Let the concentrations of hydrogen and iodine at equilibrium be  $x \text{ mol L}^{-1}$

$[\text{H}_2] = [\text{I}_2] = x \text{ mol L}^{-1}$

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

$$\Rightarrow \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$$

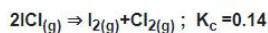
$$\Rightarrow x^2 = \frac{0.25}{54.8}$$

$$\Rightarrow x = 0.06754$$

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

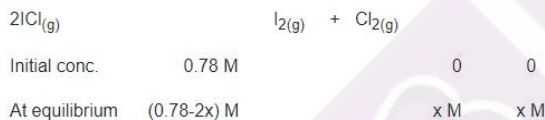
Hence, at equilibrium,  $[\text{H}_2] = [\text{I}_2] = 0.068 \text{ mol L}^{-1}$ .

Q.16. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of  $\text{ICI}$  was  $0.78 \text{ M}$ ?



Ans.

The given reaction is:



Now, we can write,  $\frac{[\text{I}_2][\text{Cl}_2]}{[\text{ICI}]^2} = K_c$

$$\Rightarrow \frac{x \times x}{(0.78 - 2x)^2} = 0.14$$

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

$$\Rightarrow \frac{x}{0.78 - 2x} = 0.374$$

$$\Rightarrow x = 0.292 - 0.748x$$

$$\Rightarrow 1.748x = 0.292$$

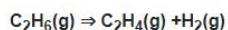
$$\Rightarrow x = 0.167$$

Hence, at equilibrium,

$[\text{H}_2] = [\text{I}_2] = 0.167 \text{ M}$

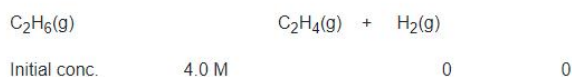
$[\text{HI}] = (0.78 - 2 \times 0.167) \text{ M}$   
 $= 0.446 \text{ M}$

Q.17.  $K_p = 0.04 \text{ atm}$  at 899 K for the equilibrium shown below. What is the equilibrium concentration of  $\text{C}_2\text{H}_6$  when it is placed in a flask at  $4.0 \text{ atm}$  pressure and allowed to come to equilibrium?



Ans.

Let  $p$  be the pressure exerted by ethene and hydrogen gas (each) at equilibrium. Now, according to the reaction,

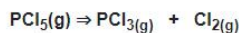




$$= 0.204(\text{approximately})$$

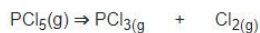
Since  $Q_c < K_c$ , equilibrium has not been reached.

**Q.19. 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  $0.5 \times 10^{-10} \text{ mol L}^{-1}$ . 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.**

Consider the conc. Of both  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium be  $x \text{ mol L}^{-1}$ . The given reaction is:



At equilibrium  $0.5 \times 10^{-10} \text{ mol L}^{-1}$        $x \text{ mol L}^{-1}$        $x \text{ mol L}^{-1}$

It is given that the value of equilibrium constant,  $K_c$  is  $8.3 \times 10^{-3} \text{ mol L}^{-3}$

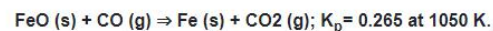
Now we can write the expression for equilibrium as:

$$\begin{aligned} \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} &= K_c \\ \Rightarrow \frac{x \times x}{0.5 \times 10^{-10}} &= 8.3 \times 10^{-3} \\ \Rightarrow x^2 &= 4.15 \times 10^{-4} \\ \Rightarrow x &= 2.04 \times 10^{-2} \\ &= 0.0204 \\ &= 0.02(\text{approximately}) \end{aligned}$$

Therefore, at equilibrium,

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.02 \text{ mol L}^{-1}$$

**Q.20. One of the reactions that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and  $\text{CO}_2$ .**



**What are the equilibrium partial pressures of CO and  $\text{CO}_2$  at 1050 K if the initial partial pressures are:  $p_{\text{CO}} = 1.4 \text{ atm}$  and  $p_{\text{CO}_2} = 0.80 \text{ atm}$ ?**

**Ans.**

For the given reaction,



$$\begin{aligned} Q_p &= \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \\ &= \frac{0.80}{1.4} \\ &= 0.571 \end{aligned}$$

Since  $Q_p > K_p$ , the reaction will proceed in the backward direction.

Therefore, we can say that the pressure of CO will increase while the pressure of  $\text{CO}_2$  will decrease.

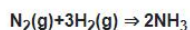
Now, let the increase in pressure of CO = decrease in pressure of  $\text{CO}_2$  be  $p$ . Then, we can write,

$$\begin{aligned} K_p &= \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \\ \Rightarrow 0.265 &= \frac{0.80 - p}{1.4 + p} \\ \Rightarrow 0.371 + 0.265p &= 0.80 - p \\ \Rightarrow 1.265p &= 0.429 \\ \Rightarrow p &= 0.339 \text{ atm} \end{aligned}$$

Therefore, equilibrium partial of  $\text{CO}_2$ ,  $p_{\text{CO}_2} = 0.80 - 0.339 = 0.461 \text{ atm}$

And, equilibrium partial pressure of CO,  $p_{\text{CO}} = 1.4 + 0.339 = 1.739 \text{ atm}$

**Q.21. A reaction is given:**

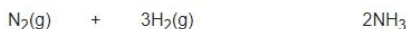




For the above equation, Equilibrium constant = 0.061 at 500 K

At a specific time, from the analysis we can conclude that composition of the reaction mixture is, 2.0 mol L<sup>-1</sup> H<sub>2</sub>, 3.0 mol L<sup>-1</sup> N<sub>2</sub> and 0.5 mol L<sup>-1</sup> NH<sub>3</sub>. Find out whether the reaction is at equilibrium or not? Find in which direction the reaction proceeds to reach equilibrium.

Ans.



At a particular time: 3.0 mol L<sup>-1</sup>      2.0 mol L<sup>-1</sup>      0.5 mol L<sup>-1</sup>

So,

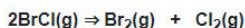
$$\begin{aligned} Q_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\ &= \frac{(0.5)^2}{(3.0)(2.0)^3} \\ &= 0.0104 \end{aligned}$$

It is given that  $K_c = 0.061$

$\therefore Q_c \neq K_c$ , the reaction is not at equilibrium.

$\therefore Q_c < K_c$ , the reaction proceeds in the forward direction to reach at equilibrium.

**Q.22. Bromine monochloride (BrCl) decays into bromine and chlorine and reaches the equilibrium:**



For which  $K_c = 42$  at 600 K.

If initially pure BrCl is present at a concentration of  $5.5 \times 10^{-5} \text{ mol L}^{-1}$ , what is its molar concentration in the mixture at equilibrium?

Ans.)

Let the amount of bromine and chlorine formed at equilibrium be x. The given reaction is:



Initial conc.  $5.5 \times 10^{-5}$       0      0

At equilibrium  $5.5 \times 10^{-5} - 2x$       x      x

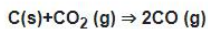
Now, we can write,

$$\begin{aligned} \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} &= K_c \\ \Rightarrow \frac{x \times x}{(5.5 \times 10^{-5} - 2x)^2} &= 42 \\ \Rightarrow \frac{x}{5.5 \times 10^{-5} - 2x} &= 6.48 \\ \Rightarrow x &= 35.64 \times 10^{-5} - 12.96x \\ \Rightarrow 13.96x &= 35.64 \times 10^{-5} \\ \Rightarrow x &= \frac{35.64}{13.96} \times 10^{-5} = 2.55 \times 10^{-5} \end{aligned}$$

So, at equilibrium

$$\begin{aligned} [\text{BrCl}] &= 5.5 \times 10^{-5} - (2 \times 2.55 \times 10^{-5}) \\ &= 5.5 \times 10^{-5} - 5.1 \times 10^{-5} \\ &= 0.4 \times 10^{-5} \\ &= 4.0 \times 10^{-6} \text{ mol L}^{-1} \end{aligned}$$

**Q.23. Find out  $K_c$  for the given reaction at temperature 1127K where the pressure is 1 atm. A solution of CO and CO<sub>2</sub> is in equilibrium with carbon(solid). It has 93.55% CO by mass.**



Ans.)

Let us assume that the solution is of 100g in total.

Given, mass of CO = 93.55 g

Now, the mass of CO<sub>2</sub> = (100 - 93.55) = 6.45 g

Now, number of moles of CO,  $n_{\text{CO}} = \frac{93.5}{28} = 3.34 \text{ mol}$

$\therefore n_{\text{CO}_2} = \frac{6.45}{44} = 0.147 \text{ mol}$

$$\text{Number of moles of } CO_2, n_{CO_2} = \frac{w}{M} = 0.140 \text{ mol}$$

Partial pressure of CO,

$$P_{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2}} \times p_{total} = \frac{3.34}{3.34 + 0.146} \times 1 = 0.958 \text{ atm}$$

$$\text{Partial pressure of } CO_2, P_{CO_2} = \frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \times p_{total} = \frac{0.146}{3.34 + 0.146} \times 1 = 0.042 \text{ atm}$$

$$\begin{aligned} \text{Therefore, } K_p &= \frac{[CO]^2}{[CO_2]} \\ &= \frac{(0.938)^2}{0.062} \\ &= 14.19 \end{aligned}$$

For the given reaction,

$$\Delta n = 2 - 1 = 1$$

We know that,

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

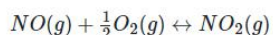
$$\Rightarrow 14.19 = K_c(0.082 \times 1127)^1$$

$$\begin{aligned} \Rightarrow K_c &= \frac{14.19}{0.082 \times 1127} \\ &= 0.154 (\text{approximately}) \end{aligned}$$

#### Q.24. Find out

(I) The equilibrium constant for the formation of  $NO_2$  from  $NO$  and  $O_2$  at 298 K and

(II)  $\Delta G^\circ$



Where;

$$\Delta_f G^\circ (NO_2) = 52.0 \text{ kJ/mol}$$

$$\Delta_f G^\circ (NO) = 87.0 \text{ kJ/mol}$$

$$\Delta_f G^\circ (O_2) = 0 \text{ kJ/mol}$$

Ans.)

(I) We know that,

$$\Delta G^\circ = RT \log K_c$$

$$\Delta G^\circ = 2.303 RT \log K_c$$

$$K_c = \frac{-35.0 \times 10^{-3}}{-2.303 \times 8.314 \times 298}$$

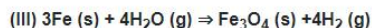
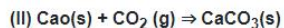
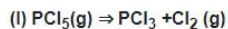
$$= 6.134$$

$$\therefore K_c = \text{antilog}(6.134)$$

$$= 1.36 \times 10^6$$

Therefore, the equilibrium constant for the given reaction  $K_c$  is  $1.36 \times 10^6$

Q.25. When each of the following equilibria is subjected to a decrease in pressure by increasing the volume, does the number of moles of reaction products increase, decrease or remain same?



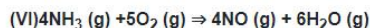
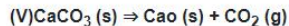
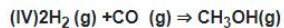
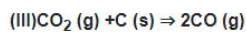
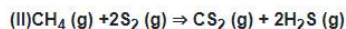
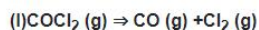
Ans.

(I) The number of moles of reaction products will increase. According to Le Chatelier's principle, if pressure is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more. In the given reaction, the number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward direction. As a result, the number of moles of reaction products will increase.

(II) The number of moles of reaction products will decrease.

(III) The number of moles of reaction products remains the same.

Q.26. 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.)

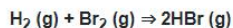
When pressure is increased:

The reactions given in (i), (iii), (iv), (v), and (vi) will get affected.

Since, the number of moles of gaseous reactants is more than that of gaseous products; the reaction given in (iv) will proceed in the forward direction

Since, the number of moles of gaseous reactants is less than that of gaseous products, the reactions given in (i), (iii), (v), and (vi) will shift in the backward direction

**Q.27. 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.

Given,  $K_p$  for the reaction i.e.,  $\text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2\text{HBr}(g)$  is  $1.6 \times 10^5$ .

Therefore, for the reaction  $2\text{HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g)$  the equilibrium constant will be,

$$\begin{aligned} K'_p &= \frac{1}{K_p} \\ &= \frac{1}{1.6 \times 10^5} \\ &= 6.25 \times 10^{-6} \end{aligned}$$

Now, let p be the pressure of both  $\text{H}_2$  and  $\text{Br}_2$  at equilibrium.

2HBr (g)		H <sub>2</sub> (g)	+	Br <sub>2</sub> (g)	
Initial conc.	10			0	0
At equilibrium	10-2p			p	p

Now, we can write,

$$\begin{aligned} \frac{P_{\text{HBr}}^2 \times P_2}{P_{\text{HBr}}^2} &= K'_p \\ \frac{p \times p}{(10-2p)^2} &= 6.25 \times 10^{-6} \\ \frac{p}{10-2p} &= 2.5 \times 10^{-3} \end{aligned}$$

$$p = 2.5 \times 10^{-2} - (5.0 \times 10^{-3})p$$

$$p + (5.0 \times 10^{-3})p = 2.5 \times 10^{-2}$$

$$(1005 \times 10^{-3}) = 2.5 \times 10^{-2}$$

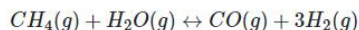
$$p = 2.49 \times 10^{-2} \text{ bar} = 2.5 \times 10^{-2} \text{ bar (approximately)}$$

Therefore, at equilibrium,

$$[\text{H}_2] = [\text{Br}_2] = 2.49 \times 10^{-2} \text{ bar}$$

$$\begin{aligned} [\text{HBr}] &= 10 - 2 \times (2.49 \times 10^{-2}) \text{ bar} \\ &= 9.95 \text{ bar} = 10 \text{ bar (approximately)} \end{aligned}$$

**Q.28. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:**



(I) Write an expression for  $K_p$  for the above reaction.

(II) How will the values of  $K_p$  and composition of equilibrium mixture be affected by

(i) Increasing the pressure

(ii) Increasing the temperature

(iii) Using a catalyst?

Ans.)

(I) For the given reaction,

$$K_p = \frac{P_{CO} \times P_{H_2}^2}{P_{CH_4} \times P_{H_2O}}$$

(II) (i) According to Le Chatelier's principle, the equilibrium will shift in the backward direction.

(ii) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.

(iii) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increases the rate of a reaction. Thus, equilibrium will be attained quickly.

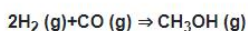
**Q.29. Describe the effect of:**

I) Removal of CO

II) Addition of  $H_2$

III) Removal of  $CH_3OH$  on the equilibrium of the reaction:

IV) Addition of  $CH_3OH$



Ans.)

(I) On removing CO, the equilibrium will shift in the backward direction.

(II) According to Le Chatelier's principle, on addition of  $H_2$ , the equilibrium of the given reaction will shift in the forward direction.

(III) On removing  $CH_3OH$ , the equilibrium will shift in the forward direction.

(IV) On addition of  $CH_3OH$ , the equilibrium will shift in the backward direction.

**Q.30. At 473 K, equilibrium constant  $K_c$  for decomposition of phosphorus pentachloride,  $PCl_5$  is  $8.3 \times 10^{-3}$ . If decomposition is depicted as,**



$$\Delta_r H^\circ = 124.0 \text{ kJmol}^{-1}$$

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  $PCl_5$  is added

(ii) pressure is increased?

(iii) The temperature is increased?

Ans.)

$$(a) K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$$

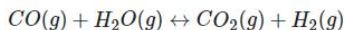
(b) Value of  $K_c$  for the reverse reaction at the same temperature is:

$$\begin{aligned} K_c' &= \frac{1}{K_c} \\ &= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2 \\ &= 120.48 \end{aligned}$$

(c)(i)  $K_c$  would remain the same because in this case, the temperature remains the same.

(ii)  $K_c$  is constant at constant temperature. Thus, in this case,  $K_c$  would not change. (iii) In an endothermic reaction, the value of  $K_c$  increases with an increase in temperature. Since the given reaction is an endothermic reaction, the value of  $K_c$  will increase if the temperature is increased.

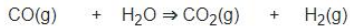
**Q.31.** Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H<sub>2</sub>. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,



If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that  $P_{CO} = P_{H_2O} = 4.0$  bar, what will be the partial pressure of H<sub>2</sub> at equilibrium?  $K_p = 10.1$  at 400°C

**Ans.)**

Let the partial pressure of both carbon dioxide and hydrogen gas be p. The given reaction is:



Initial conc.      4.0 bar      4.0 bar                      0                      0

At equilibrium    4.0-p            4.0-p                      p                      p

Given  $K_p = 10.1$

$$\frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}} = K_p$$

$$\Rightarrow \frac{p \times p}{(4.0-p)(4.0-p)} = 10.1$$

$$\Rightarrow \frac{p}{4.0-p} = 3.178$$

$$\Rightarrow p = 12.712 - 3.178p$$

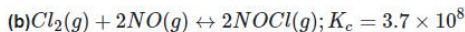
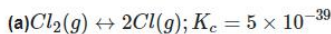
$$4.178p = 12.712$$

$$p = \frac{12.712}{4.178}$$

$$p = 3.04$$

So, partial pressure of H<sub>2</sub> is 3.04 bar at equilibrium.

**Q.32.** Predict which of the following reaction will have appreciable concentration of reactants and products:



**Ans.)**

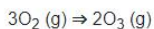
If the value of  $K_c$  lies between  $10^{-3}$  and  $10^3$ , a reaction has appreciable concentration of reactants and products.

Thus, the reaction given in (c) will have appreciable concentration of reactants and products.

**Q.33.** The value of  $K_c$  for the reaction  $3O_2(g) \rightleftharpoons 2O_3(g)$  is  $2.0 \times 10^{-50}$  at 25°C. If the equilibrium concentration of O<sub>2</sub> in air at 25°C is  $1.6 \times 10^{-2}$ , what is the concentration of O<sub>3</sub>?

**Ans.)**

Given,



$$\text{Then, } K_c = \frac{[O_3(g)]^2}{[O_2(g)]^3}$$

Given that  $K_c = 2.0 \times 10^{-50}$  and  $[O_2(g)] = 1.6 \times 10^{-2}$

Then,

$$2.0 \times 10^{-50} = \frac{[O_3(g)]^2}{[1.6 \times 10^{-2}]^3}$$

$$\Rightarrow [O_3(g)]^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3$$

$$\Rightarrow [O_3(g)]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow [O_3(g)]^2 = 2.86 \times 10^{-28} M$$

So, the conc. of O<sub>3</sub> is  $2.86 \times 10^{-28} M$ .

**Q.34.** The reaction,  $CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$  at 1300K is at equilibrium in a 1L container. It has 0.30 mol of CO, 0.10 mol of H<sub>2</sub> and 0.02 mol of H<sub>2</sub>O and y amount of CH<sub>4</sub> in the container. Find the concentration of CH<sub>4</sub> in the mixture.

The equilibrium constant,  $K_c$  is 3.90 at the given temp.

**Ans.)**

Let the concentration of  $CH_4$  at equilibrium be  $y$ .



At equilibrium,

$$\text{For } CO_2 - \frac{0.3}{1} = 0.3M$$

$$\text{For } H_2 - \frac{0.1}{1} = 0.1M$$

$$\text{For } H_2O - \frac{0.02}{1} = 0.02M$$

$$K_c = 3.90$$

Therefore,

$$\frac{[CH_4][H_2O]}{[CO_2][H_2]^3} = K_c \frac{y \times 0.02}{0.3 \times (0.1)^3} = 3.9 y = \frac{3.9 \times 0.3 \times (0.1)^3}{0.02} y = \frac{0.00117}{0.02} y = 0.0585M$$
$$y = 5.85 \times 10^{-2}M$$

Therefore, the concentration of  $CH_4$  at equilibrium is  $5.85 \times 10^{-2}M$

**Q.35. What is conjugate acid-base pair? Find the conjugate acid/base of the given species:**

(i)  $HNO_2$

(ii)  $CN^-$

(iii)  $HClO_4$

(iv)  $F^-$

(v)  $OH^-$

(vi)  $CO_3^{2-}$

(vii)  $S^-$

**Ans.)**

A conjugate acid-base pair is a pair that has a difference of only one proton.

The conjugate acid-base pair of the following are as follows:

(i)  $HNO_2 - NO_2^-$  (Base)

(ii)  $CN^- - HCN$  (Acid)

(iii)  $HClO_4 - ClO_4^-$  (Base)

(iv)  $F^- - HF$  (Acid)

(v)  $OH^- - H_2O$  (Acid)/  $O^{2-}$  (Base)

(vi)  $CO_3^{2-} - HCO_3^-$  (Acid)

(vii)  $S^- - HS^-$  (Acid)

**Q.36. From the compounds given below which are Lewis acids?**

(i)  $H_2O$

(ii)  $BF_3$

(iii)  $H^+$

(iv)  $NH_4^+$

**Ans.)**

Lewis acids are the acids which can accept a pair of electrons.

(i)  $H_2O$  - Not Lewis acid

(ii)  $BF_3$  - Lewis acid

(iii)  $H^+$  - Lewis acid

(iv)  $NH_4^+$  - Lewis acid

Q.37. From the compounds given below which will be the conjugate base for the Bronsted acids?

(i) HF

(ii)  $H_2SO_4$

(iii)  $HCO_3$

Ans.)

The following shows the conjugate bases for the Bronsted acids:

(i)  $HF - F^-$

(ii)  $H_2SO_4 - HSO_4^-$

(iii)  $HCO_3 - CO_3^{2-}$

Q.38. For the Brönsted bases given below find their conjugate acids.

1.  $NH_3$

2.  $HCOO^-$

3.  $NH_2^-$

Ans.)

	Brönsted base	Conjugate acid
1	$NH_3$	$NH_4^+$
2	$HCOO^-$	HCOOH
3	$NH_2^-$	$NH_3$

Q.39. The species given below can act as both Brönsted bases as well as Brönsted acids. For each of them give their conjugate acid and base.

1.  $HCO_3^-$

2.  $HSO_4^-$

3.  $NH_3$

4.  $H_2O$

Ans.)

	Species	Conjugate base	Conjugate acid
1	$HCO_3^-$	$CO_3^{2-}$	$H_2CO_3$
2	$HSO_4^-$	$SO_4^{2-}$	$H_2SO_4$
3	$NH_3$	$NH_2^-$	$NH_4^+$
4	$H_2O$	$OH^-$	$H_3O^+$

Q.40. Classify the species given below into bases and acids and also show that these species act as base/acid:

1.  $BCl_3$

2.  $H^+$

3.  $OH^-$

4.  $F^-$

Ans.)

1.  $BCl_3$ :

It is a Lewis acid as it has tendency to accept a pair of electrons.

2.  $H^+$

It is a Lewis acid as it has tendency to accept a pair of electrons.

3.  $OH^-$

It is a Lewis base as it has tendency to lose a pair of electrons.



It is a Lewis base as it has tendency to lose its lone pair of electrons.

**Q.41. A sample soft drink is taken, whose hydrogen ion concentration is  $2.5 \times 10^{-4} M$ . Find out pH.**

**Ans.)**

$$\begin{aligned} pH &= -\log[H^+] \\ &= -\log(2.5 \times 10^{-4}) \\ &= -\log 2.5 - \log 10^{-4} \\ &= -\log 2.5 + 4 \\ &= -0.398 + 4 \\ &= 3.602 \end{aligned}$$

**Q.42. A sample of white vinegar is taken, whose pH is 2.36. Find out the hydrogen ion concentration in the sample.**

**Ans.)**

$$\begin{aligned} pH &= -\log[H^+] \\ \Rightarrow \log[H^+] &= -pH \\ \Rightarrow [H^+] &= \text{antilog}(-pH) \\ &= \text{antilog}(-2.36) \\ &= 0.004365 \\ &= 4.37 \times 10^{-3} \end{aligned}$$

$\therefore 4.37 \times 10^{-3}$  is the concentration of white vinegar sample.

**Q.43. Ionization constant for the following acids are given:**

**HF =  $5.7 \times 10^{-5}$  at 298K**

**HCOOH =  $1.7 \times 10^{-3}$  at 298K**

**HCN =  $3.7 \times 10^{-8}$  at 298K**

**Find out the conjugate bases for the above acids.**

**Ans.)**

For  $F^-$ ,  $K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{(5.7 \times 10^{-5})} = 1.75 \times 10^{-9}$

For  $HCOO^-$ ,  $K_b = \frac{10^{-14}}{(1.7 \times 10^{-3})} = 5.88 \times 10^{-11}$

For  $CN^-$ ,  $K_b = \frac{10^{-14}}{(3.7 \times 10^{-8})} = 2.70 \times 10^{-6}$

**Q.44. Phenol has ionization constant of  $1.0 \times 10^{-8}$ . In a 0.06M of phenol solution calculate the presence of phenolate ion. Find out the degree of ionization if 0.02M of sodium phenolate is given.**

**Ans.)**



Initial                      0.06M

After dissociation    0.06-x                      x                      x

$$\therefore K_a = \frac{x \cdot x}{0.06-x} = 1.0 \times 10^{-8}$$

$$\Rightarrow \frac{x^2}{0.06} = 1.0 \times 10^{-8}$$

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

$$\Rightarrow x = 2.4 \times 10^{-5} M$$

In presence of 0.02 sodium phenolate ( $C_6H_5Na$ ), suppose y is the amount of phenol dissociated, then at equilibrium

$$[C_6H_5OH] = 0.06 - y \approx 0.06,$$

$$[C_6H_5O^-] = 0.02 + y \approx 0.02M,$$

$$[H^+] = y M$$



$$\therefore K_a = \frac{(y)(y)}{0.06} = 1.0 \times 10^{-6}$$

$$\Rightarrow y = \frac{1.0 \times 0.06}{(0.02)} \times 10^{-8}$$

$$\Rightarrow y = 6 \times 10^{-8}$$

$$\therefore \text{degree of ionization} = \alpha = \frac{y}{c} = \frac{6 \times 10^{-8}}{6 \times 10^{-2}} (\text{Here } c = 0.06 = 6 \times 10^{-2}) = 10^{-6}$$

$$\text{So, } \alpha = 10^{-6}$$

**Q.45** Given,  $9.1 \times 10^{-8}$  is the initial (first) ionization constant of the gas  $\text{H}_2\text{S}$ . Find out concentration of the ion  $\text{HS}^-$  in 0.1M solution of  $\text{H}_2\text{S}$ . Find the changes in concentration if the concentration is 0.1M in HCl. Find the concentration of  $\text{S}^{2-}$  under both conditions, if  $1.2 \times 10^{-13}$  is the second dissociation constant of  $\text{H}_2\text{S}$ .

Ans.)

To calculate  $[\text{HS}^-]$



Initial 0.1 M

After dissociation 0.1-x x x

$$\approx 0.1 K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8}$$

$$\Rightarrow x^2 = 9.1 \times 10^{-9}$$

$$\Rightarrow x = 9.54 \times 10^{-5}$$

In the presence of 0.1 M HCl, suppose  $\text{H}_2\text{S}$  dissociated is y. Then at equilibrium,  $[\text{H}_2\text{S}] = 0.1 - y \approx 0.1$ ,

$$[\text{H}^+] = 0.1 + y \approx 0.1,$$

$$[\text{HS}^-] = y \text{ M}$$

$$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8}$$

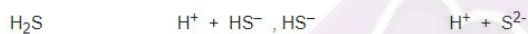
$$y = \frac{9.1 \times 0.1}{0.1} \times 10^{-8}$$

$$y = 9.1 \times 10^{-8}$$

$K_{a2}$

$K_{a1}$

To calculate  $[\text{S}^{2-}]$



For the overall reaction,



$$K_a = K_{a1} \times K_{a2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20} \quad K_a = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

In the absence of 0.1M HCl,

$$[H^+] = 2[S^{2-}]$$

Hence, if  $[S^{2-}] = x$ ,  $[H^+] = 2x$

$$\therefore \frac{(2x)^2}{0.1} = 1.092 \times 10^{-20}$$

$$\Rightarrow 4x^3 = 1.092 \times 10^{-21}$$

$$\Rightarrow x^3 = \frac{1.092}{4} \times 10^{-21} = 273 \times 10^{-24}$$

$$\Rightarrow \log x^3 = \log 273 - \log 10^{-24} = 2.4362 - 24$$

$$\Rightarrow 3 \log x = 2.4362 - 24$$

$$\Rightarrow \log x = \frac{2.4362}{3} - \frac{24}{3}$$

$$\Rightarrow x = 0.8127 - 8 = -7.1873$$

$$\Rightarrow x = \text{Antilog } -7.1873 = 6.497 \times 10^{-8} = 6.5 \times 10^{-8}$$

**In presence of 0.1M HCl,**

Suppose  $[S^{2-}] = y$ , then

$$[H_2S] = 0.1 - y \approx 0.1M,$$

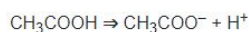
$$[H^+] = 0.1 + y \approx 0.1M$$

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20}$$

$$y = 1.09 \times 10^{-19} M$$

**Q.46. Given, the ionization constant of acetic acid is  $1.74 \times 10^{-5}$ . Find the degree of dissociation of acetic acid in its 0.05 M solution. Find the concentration of acetate ion in the solution and its pH.**

**Ans.)**



$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

$$\Rightarrow [H^+] = \sqrt{K_a [CH_3COOH]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4} M$$

$$[CH_3COO^-] = [H^+] = 9.33 \times 10^{-4} M$$

$$pH = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$$

**Q.47. It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its  $pK_a$ .**

**Ans.)**



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

$$\log[H^+] = -4.15$$

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

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

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}} = 5.0 \times 10^{-7}$$

$$pK_a = -\log K_a = -\log(5.0 \times 10^{-7}) = 7 - 0.699 = 6.301$$

**Q.48. Consider complete dissociation, find out the pH of the following :**

(I) 0.004 M HCl

(II) 0.003 M NaOH

(III) 0.002 M HBr

(IV) 0.002 M KOH

**Ans.)**



$$\therefore [H^+] = [HCl] = 4 \times 10^{-3} M$$

$$pH = -\log(4 \times 10^{-3}) = 2.398$$



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

$$[H^+] = \frac{10^{-14}}{(3 \times 10^{-3})} = 3 \times 10^{-12} M$$

$$pH = -\log(3 \times 10^{-12}) = 11.52$$



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

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



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

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

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

**Q.49. Find out the pH of the following solution:**

(I) 2g of TIOH dissolved in water to give 2 litre of the solution

(II) 0.3g of Ca(OH)<sub>2</sub> dissolved in water to give 500mL of the solution

(III) 0.3g of NaOH dissolved in water to give 200mL of the solution

(IV) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of the solution

**Ans.)**

$$(I) \text{Molar conc. of TIOH} = \frac{2g}{(204+16+1)g \text{ mol}^{-1}} \times \frac{1}{2L} = 4.52 \times 10^{-3} M$$

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

$$[H^+] = \frac{10^{-14}}{(4.52 \times 10^{-3})} = 2.21 \times 10^{-12} M$$

$$\therefore pH = -\log(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$$

$$(II) \text{Molar conc. of Ca(OH)}_2 = \frac{0.3g}{(40+34)g \text{ mol}^{-1}} \times \frac{1}{0.5L} = 8.11 \times 10^{-3} M$$

$$[OH^-] = 2[Ca(OH)_2] = 2 \times (8.11 \times 10^{-3}) M = 16.22 \times 10^{-3} M$$

$$pOH = -\log(16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$$

$$pH = 14 - 1.79 = 12.21$$

$$(III) \text{Molar conc. of NaOH} = \frac{0.3g}{(40+34)g \text{ mol}^{-1}} \times \frac{1}{0.2L} = 3.75 \times 10^{-2} M$$

$$[OH^-] = 3.75 \times 10^{-2} M$$

$$pOH = -\log(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$

$$pH = 14 - 1.43 = 12.57$$

$$(IV) M_1 V_1 = M_2 V_2$$

$$\therefore 13.6 M \times 1 mL = M_2 \times 1000 mL$$

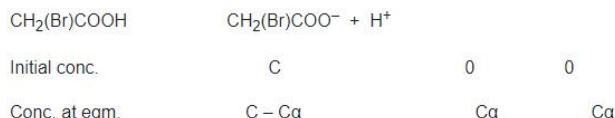
$$\therefore M_2 = 1.36 \times 10^{-2} M$$

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

$$pH = -\log(1.36 \times 10^{-2}) = 2 - 0.1335 \approx 1.87$$

**Q.50. The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK<sub>a</sub> of bromoacetic acid.**

**Ans.)**



$$K_a = \frac{C\alpha C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$

$$[H^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} M$$

$$pH = -\log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$$

**Q.51. The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK<sub>a</sub> of bromoacetic acid.**

**Ans.)**

$\text{CH}_2(\text{Br})\text{COOH}$	$\text{CH}_2(\text{Br})\text{COO}^- + \text{H}^+$		
Initial conc.	C	0	0
Conc. at eqm.	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$

$$[\text{H}^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} \text{ M}$$

$$pH = -\log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$$

**Q.52. What is the pH of 0.001 M aniline solution? The ionization constant of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.**

**Ans.)**

$$K_b = 4.27 \times 10^{-10}$$

$$c = 0.001 \text{ M}$$

$$pH = ?$$

$$\alpha = ?$$

$$K_b = c\alpha^2$$

$$4.27 \times 10^{-10} = 0.001 \times \alpha^2$$

$$4270 \times 10^{-10} = \alpha^2$$

$$65.34 \times 10^{-5} = \alpha = 6.53 \times 10^{-4}$$

$$\text{Then, } [\text{anion}] = c\alpha = 0.001 \times 65.34 \times 10^{-5} = 0.065 \times 10^{-5}$$

$$pOH = -\log(0.065 \times 10^{-5})$$

$$= 6.187$$

$$pH = 7.813$$

Now,

$$K_a \times K_b = K_w$$

$$K_a = \frac{10^{-14}}{4.27 \times 10^{-10}}$$

$$= 2.34 \times 10^{-5}$$

$\therefore 2.34 \times 10^{-5}$  is the ionization constant.

**Q.53. Calculate the degree of ionization of 0.05M acetic acid if its  $pK_a$  value is 4.74. How is the degree of dissociation affected when its solution also contains**

**(i) 0.01 M**

**(ii) 0.1 M in HCl?**

**Ans.)**

$$c = 0.05 \text{ M}$$

$$pK_a = 4.74$$

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

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

$$K_a = c\alpha^2$$

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

$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{5 \times 10^{-2}}} = 1.908 \times 10^{-2}$$

When HCl is added to the solution, the concentration of  $\text{H}^+$  ions will increase. Therefore, the equilibrium will shift in the backward direction i.e., dissociation of acetic acid will decrease.

Case 1: When 0.01 M HCl is taken.

Let  $x$  be the amount of acetic acid dissociated after the addition of HCl.

$\text{CH}_3\text{COOH}$	$\text{H}^+ + \text{CH}_3\text{COO}^-$		
Initial conc.	0.05M	0	0
After dissociation	$0.05 - x$	$0.01 + x$	$x$

As the dissociation of a very small amount of acetic acid will take place, the values i.e.,  $0.05 - x$  and  $0.01 + x$  can be taken as 0.05 and 0.01 respectively.

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

$$\therefore = \frac{(0.01)x}{0.05}$$

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

$$x = 1.82 \times 10^{-3} \times 0.05M$$

Now,

$$\begin{aligned}\alpha &= \frac{\text{Amount of acid dissociation}}{\text{Amount of acid taken}} \\ &= \frac{1.82 \times 10^{-3} \times 0.05}{0.05} \\ &= 1.82 \times 10^{-3}\end{aligned}$$

Case 2: When 0.1 M HCl is taken.

Let the amount of acetic acid dissociated in this case be X. As we have done in the first case, the concentrations of various species involved in the reaction are:

$$[CH_3COOH] = 0.05 - X; 0.05 M$$

$$[CH_3COO^-] = X$$

$$[H^+] = 0.1 + X; 0.1 M$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\therefore K_a = \frac{(0.1)X}{0.05}$$

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

$$x = 1.82 \times 10^{-4} \times 0.05M$$

Now,

$$\begin{aligned}\alpha &= \frac{\text{Amount of acid dissociation}}{\text{Amount of acid taken}} \\ &= \frac{1.82 \times 10^{-4} \times 0.05}{0.05} \\ &= 1.82 \times 10^{-4}\end{aligned}$$

**Q.54. The ionization constant of dimethylamine is  $5.4 \times 10^{-4}$ . Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?**

**Ans.)**

$$K_b = 5.4 \times 10^{-4}$$

$$c = 0.02M$$

$$\text{Then, } \alpha = \sqrt{\frac{K_b}{c}}$$

$$= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 0.1643$$

Now, if 0.1 M of NaOH is added to the solution, then NaOH (being a strong base) undergoes complete ionization.



$$0.1M \quad 0.1M$$

And,



$$(0.02-x) \quad \quad \quad x \quad \quad \quad x$$

$$; 0.02M \quad \quad \quad ; 0.1M$$

Then,  $[(CH_3)_2NH_2^+] = x$

$$[OH^-] = x + 0.1; 0.1$$

$$\Rightarrow K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

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

$$x = 0.0054$$

It means that in the presence of 0.1 M NaOH, 0.54% of dimethylamine will get dissociated.

**Q.55. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:**

(I) Human saliva, 6.4

(II) Human stomach fluid, 1.2

(III) Human muscle-fluid, 6.83

(IV) Human blood, 7.38

**Ans.)**

(I) Human saliva, 6.4:

$$\text{pH} = 6.4$$

$$6.4 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 3.98 \times 10^{-7}$$

(II) Human stomach fluid, 1.2:

$$\text{pH} = 1.2$$

$$1.2 = -\log [\text{H}^+]$$

$$\therefore [\text{H}^+] = 0.063$$

(III) Human muscle fluid 6.83:

$$\text{pH} = 6.83$$

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

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

$$[\text{H}^+] = 1.48 \times 10^{-7} \text{ M}$$

(IV) Human blood, 7.38:

$$\text{pH} = 7.38 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 4.17 \times 10^{-8} \text{ M}$$

**Q.56. The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.**

**Ans.)**

The hydrogen ion concentration in the given substances can be calculated by using the given relation:  $\text{pH} = -\log [\text{H}^+]$

(I) pH of milk = 6.8

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

$$6.8 = -\log [\text{H}^+] \log$$

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

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

$$= 1.5 \times 10^{-7} \text{ M}$$

(II) pH of black coffee = 5.0

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

$$5.0 = -\log [\text{H}^+] \log$$

$$[\text{H}^+] = -5.0$$

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

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

(III) pH of tomato = 4.2

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

$$4.2 = -\log [\text{H}^+] \log$$

$$[\text{H}^+] = -4.2$$

$$[\text{H}^+] = \text{antilog}(-4.2)$$

$$= 6.31 \times 10^{-5} \text{ M}$$

(IV) pH of lemon juice = 2.2

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

$$2.2 = -\log [\text{H}^+] \log$$

$$[H^+] = -2.2$$

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

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

(V) pH of egg white = 7.8

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

$$7.8 = -\log [H^+] \log$$

$$[H^+] = -7.8$$

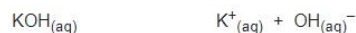
$$[H^+] = \text{antilog}(-7.8)$$

$$= 1.58 \times 10^{-8} M$$

**Q.57. 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.)**

$$\begin{aligned} [KOH]_{\text{aq}} &= \frac{0.561 \text{ g/L}}{\frac{1}{5}} \\ &= 2.805 \text{ g/L} \\ &= 2.805 \times \frac{1}{56.11} M \\ &= 0.05 M \end{aligned}$$



$$[OH^-] = 0.05 M = [K^+]$$

$$[H^+][H^-] = K_w$$

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$= \frac{10^{-14}}{0.05} = 2 \times 10^{-13} M$$

$$\therefore \text{pH} = 12.70$$

**Q.58. The solubility of  $Sr(OH)_2$  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.)**

Solubility of  $Sr(OH)_2 = 19.23 \text{ g/L}$

Then, concentration of  $Sr(OH)_2$

$$\begin{aligned} &= \frac{19.23}{121.63} M \\ &= 0.1581 M \end{aligned}$$



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

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

Now,

$$K_w = [OH^-][H^+]$$

$$\frac{10^{-14}}{0.3126} = [H^+]$$

$$\Rightarrow [H^+] = 3.2 \times 10^{-14}$$

$$\therefore \text{pH} = 13.495; 13.50$$

**Q.59. The ionization constant of propanoic acid is  $1.32 \times 10^{-5}$ . Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?**

**Ans.)**

Let the degree of ionization of propanoic acid be  $\alpha$ .

Then, representing propanoic acid as HA, we have:

...



$$(0.05 - 0.05\alpha) \approx 0.05 \qquad 0.05\alpha \qquad 0.05\alpha$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \alpha = \sqrt{\frac{K_a}{0.05}} = 1.63 \times 10^{-2}$$

$$= \frac{(0.05\alpha)(0.05\alpha)}{0.05} = 0.05\alpha^2$$

$$\text{Then, } [H_3O^+] = 0.05\alpha = 0.05 \times 1.63 \times 10^{-2} = K_b \cdot 15 \times 10^{-4} M$$

$$\therefore pH = 3.09$$

In the presence of 0.1M of HCl, let  $\alpha'$  be the degree of ionization.

$$\text{Then, } [H_3O^+] = 0.01$$

$$[A^-] = 0.05 \alpha'$$

$$[HA] = 0.05$$

$$K_a = \frac{0.01 \times 0.05 \alpha'}{0.05}$$

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

$$\alpha' = 1.32 \times 10^{-3}$$

**Q.60. The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.**

**Ans.)**

$$c = 0.1 M$$

$$pH = 2.34$$

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

$$-\log [H^+] = 2.34$$

$$[H^+] = 4.5 \times 10^{-3}$$

Also,

$$[H^+] = c\alpha$$

$$4.5 \times 10^{-3} = 0.1 \times \alpha$$

$$\frac{4.5 \times 10^{-3}}{0.1} = \alpha$$

$$\alpha = 4.5 \times 10^{-3} = 0.045$$

Then,

$$K_a = c\alpha^2$$

$$= 0.1 \times (4.5 \times 10^{-3})^2$$

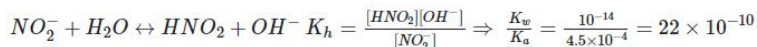
$$= 202.5 \times 10^{-6}$$

$$= 2.02 \times 10^{-4}$$

**Q.61. for nitrous acid  $K_a = 4.5 \times 10^{-4}$ . Calculate degree of hydrolysis and pH for 0.04M of sodium nitrite.**

**Ans.)**

Sodium nitrite is a salt of NaOH (strong base) and HNO<sub>2</sub> (weak acid).



Let, y mole of salt has undergone hydrolysis, then the concentration of various species present in the solution will be:

$$[NO_2^-] = 0.04 - y; 0.04 [HNO_2] = y [OH^-] = y K_h = \frac{y^2}{0.04} = 0.22 \times 10^{-10} \quad y^2 = 0.0088 \times 10^{-10}$$

$$y = 0.093 \times 10^{-5}; \therefore [OH^-] = 0.093 \times 10^{-5} M \quad [H_3O^+] = \frac{10^{-14}}{0.093 \times 10^{-5}} = 10.75 \times 10^{-9} M$$

$$\text{Thus, } pH = -\log(10.75 \times 10^{-9})$$

$$= 7.96$$

Thus, the degree of hydrolysis is

$$= \frac{y}{0.04} = \frac{0.093 \times 10^{-5}}{0.04} = 2.325 \times 10^{-5}$$



**Q.62.** 0.02M solution of pyridinium hydrochloride ( $C_5H_6ClN$ ) is having pH = 3.44. Determine the ionization constant of  $C_5H_5N$  (pyridine).

**Ans.)**

$$pH = 3.44$$

As we know,

$$pH = \log[H^+] \therefore [H^+] = 3.63 \times 10^{-4}$$

$$\text{Now, } K_h = \frac{3.63 \times 10^{-4}}{0.02}; \text{ (Given that concentration} = 0.02M)$$

$$\Rightarrow K_h = 6.6 \times 10^{-6}$$

As we know that,

$$K_h = \frac{K_w}{K_a} \quad K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6 \times 10^{-6}}$$

$$= 1.51 \times 10^{-9}$$

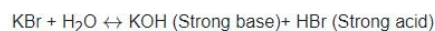
**Q.63.** Few salts are given below;

1. KBr
2.  $NH_4NO_3$
3. KF
4.  $NaNO_2$
5. NaCN
6. NaCl

**Determine the nature of solution of these salts i.e. Is it acidic or basic or neutral?**

**Ans.)**

1. KBr



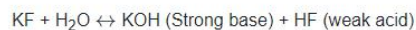
Thus, it is a neutral solution.

2.  $NH_4NO_3$



Thus, it is an acidic solution.

3. KF



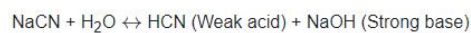
Thus, it is a basic solution.

4.  $NaNO_2$



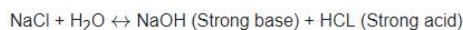
Thus, it is a basic solution.

5. NaCN



Thus, it is a basic solution.

6. NaCl



Thus, it is a neutral solution.

**Q.64. Find the pH of 0.1M acid and its 0.1M NaCl solution. The  $K_a$  for chloroacetic acid is  $1.35 \times 10^{-3}$ .**

**Ans.)**

The  $K_a$  for chloroacetic acid ( $\text{ClCH}_2\text{COOH}$ ) is  $1.35 \times 10^{-3}$ .

$$\Rightarrow K_a = c\alpha^2 \therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.35 \times 10^{-3}}{0.1}}; \text{ (given concentration} = 0.1\text{M)}$$

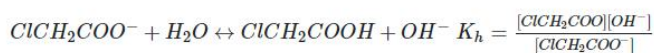
$$\alpha = \sqrt{1.35 \times 10^{-2}}$$

$$= 0.116$$

$$\therefore [H^+] = c\alpha = 0.1 * 0.116 = 0.0116$$

$$\text{pH} = -\log[H^+] = 1.94$$

$\text{ClCH}_2\text{COONa}$  is a salt of strong base i.e.  $\text{NaOH}$ , and weak acid i.e.  $\text{ClCH}_2\text{COOH}$



$$\text{Now, } K_h = \frac{K_w}{K_a}$$

$$K_h = \frac{10^{-14}}{1.35 \times 10^{-3}} = 0.740 \times 10^{-11}$$

$$\text{Also, } K_h = \frac{y^2}{0.1}$$

$$\Rightarrow 0.740 \times 10^{-11} = \frac{y^2}{0.1} \Rightarrow 0.0740 \times 10^{-11} = y^2 \quad y = 0.86 \times 10^{-6} \quad [\text{OH}^-] = 0.86 \times 10^{-6}$$

$$\therefore [H^+] = \frac{K_w}{0.86 \times 10^{-6}} = \frac{10^{-14}}{0.86 \times 10^{-6}} \quad [H^+] = 1.162 \times 10^{-3}$$

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

$$= 7.94$$

**Q.65. Determine the pH of neutral water at 310K temperature. Ionic product of  $\text{H}_2\text{O}$  is  $2.7 \times 10^{-14}$ .**

**Ans.)**

Ionic Product,

$$K_w = [H^+][OH^-]$$

Assuming,  $[H^+] = y$

$$\text{As, } [H^+] = [OH^-], K_w = y^2.$$

$$K_w \text{ at } 310\text{K is } 2.7 \times 10^{-14}.$$

$$\therefore 2.7 \times 10^{-14} = y^2$$

$$y = 1.64 \times 10^{-7}$$

$$[H^+] = 1.64 \times 10^{-7}$$

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

$$= -\log[1.64 \times 10^{-7}]$$

$$= 6.78$$

Thus, the pH of neutral water at 310K temperature is 6.78.

**Q.66. Find out the pH of resultant mixture;**

i) n10 ml of 0.02M  $\text{H}_2\text{SO}_4$  + 10 ml of 0.02M  $\text{Ca(OH)}_2$

ii) 10 ml of 0.1M  $\text{H}_2\text{SO}_4$  + 10 ml of 0.1M  $\text{KOH}$

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

**Ans.)**

i) Moles of  $\text{OH}^-$

$$= \frac{2 \times 10 + 0.02}{1000} = 0.0004 \text{ mol}$$

Moles of  $H_3O^+$

$$= \frac{2 \times 10 + 0.02}{1000} = 0.0004 \text{ mol}$$

ii) Moles of  $OH^-$

$$= \frac{2 \times 10 + 0.1}{1000} = 0.002 \text{ mol}$$

Moles of  $H_3O^+$

$$= \frac{2 \times 10 + 0.1}{1000} = 0.001 \text{ mol}$$

Here, the  $H_3O^+$  is in excess is 0.01 mol

$$\text{So, } [H_3O^+] = \frac{0.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = 0.5$$

Thus,  $\text{pH} = -\log(0.05)$

$$= 1.3$$

As the solution is neutral  $\text{pH} = 7$ .

iii) Moles of  $OH^-$

$$= \frac{2 \times 10 + 0.2}{1000} = 0.004 \text{ mol}$$

Moles of  $H_3O^+$

$$= \frac{25 \times 0.1}{1000} = 0.0025 \text{ mol}$$

Here, the  $OH^-$  is in excess is 0.0015 mol

$$\text{So, } [OH^-] = \frac{0.0015}{35 \times 10^{-3}} = 0.0428$$

Thus,  $\text{pH} = -\log(OH)$

$$= 1.36$$

$$\text{pH} = 14 - 1.36 = 12.63$$

As the solution is neutral  $\text{pH} = 12.63$ .

**Q.67. Calculate the solubilities of**

**a) barium chromate**

**b) ferric hydroxide**

**c) lead chloride**

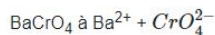
**d) mercurous iodide**

**e) silver chromate**

**At 300K from their solubility product constant. Also calculate the molarities of the individual ions.**

**Ans.)**

a) Barium Chromate



$$\text{Now, } K_{\text{sp}} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}]$$

Assuming the solubility of  $\text{BaCrO}_4$  is 'x'.

Thus,

$$[\text{Ba}^{2+}] = x \text{ and } [\text{CrO}_4^{2-}] = x$$

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

$$1.2 \times 10^{-10} = x^2$$

$$x = 1.09 \times 10^{-10} \text{ M}$$

$$\text{Molarity of } \text{Ba}^{2+} = \text{Molarity of } \text{CrO}_4^{2-} = x = 1.09 \times 10^{-10} \text{ M}$$

b) Ferric Hydroxide



$$\text{Now, } K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

Assuming the solubility of  $\text{Fe(OH)}_3$  is 'x'.

Thus,

$$[\text{Fe}^{3+}] = x \text{ and } [\text{OH}^-] = 3x$$

$$K_{sp} = x(3x)^3$$

$$= x \cdot 27x^3$$

$$K_{sp} = 27x^4$$

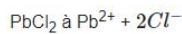
$$1.0 \times 10^{-38} = 27x^4$$

$$x = 0.00037 \times 10^{-36} \text{ M}$$

$$\text{Molarity of } \text{Fe}^{3+} = x = 1.39 \times 10^{-10} \text{ M}$$

$$\text{Molarity of } \text{OH}^- = 3x = 4.17 \times 10^{-10} \text{ M}$$

c) Lead Chloride



$$\text{Now, } K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

Assuming the solubility of  $\text{PbCl}_2$  is 'x'.

Thus,

$$[\text{Pb}^{2+}] = x \text{ and } [\text{Cl}^-] = 2x$$

$$K_{sp} = x(2x)^2$$

$$= x \cdot 4x^2$$

$$K_{sp} = 4x^3$$

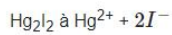
$$1.6 \times 10^{-5} = 4x^3$$

$$x = 1.58 \times 10^{-2} \text{ M}$$

$$\text{Molarity of } \text{Pb}^{2+} = x = 1.58 \times 10^{-2} \text{ M}$$

$$\text{Molarity of } \text{Cl}^- = 2x = 3.16 \times 10^{-2} \text{ M}$$

d) Mercurous iodide



$$\text{Now, } K_{sp} = [\text{Hg}_2^{2+}][\text{I}^-]^2$$

Assuming the solubility of  $\text{Hg}_2\text{I}_2$  is 'x'.

Thus,

$$[\text{Hg}_2^{2+}] = x \text{ and } [\text{I}^-] = 2x$$

$$K_{sp} = x(2x)^2$$

$$= x \cdot 4x^2$$

$$K_{sp} = 4x^3$$

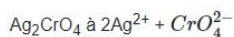
$$4.5 \times 10^{-29} = 4x^3$$

$$x = 2.24 \times 10^{-10} \text{ M}$$

$$\text{Molarity of } \text{Hg}_2^{2+} = x = 2.24 \times 10^{-10} \text{ M}$$

$$\text{Molarity of } \text{I}^- = 2x = 4.48 \times 10^{-10} \text{ M}$$

e) Silver Chromate



$$\text{Now, } K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

Assuming the solubility of  $\text{Ag}_2\text{CrO}_4$  is 'x'.

Thus,

$$[\text{Ag}^{2+}] = 2x \text{ and } \text{CrO}_4^{2-} = x$$

$$K_{sp} = (2x)^2 \cdot x$$

$$1.1 \times 10^{-12} = 4x^3$$

$$x = 0.65 \times 10^{-4} M$$

$$\text{Molarity of } \text{Ag}^{2+} = 2x = 1.3 \times 10^{-4} M$$

$$\text{Molarity of } \text{CrO}_4^{2-} = x = 0.65 \times 10^{-4} M$$

**Q-68. Determine the ratio of molarities to their saturated solutions for the following:**

**$\text{Ag}_2\text{CrO}_4$  and  $\text{AgBr}$**

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.

**Ans.)**



$$\text{Now, } K_{sp} = [\text{Ag}^{2+}]^2 [\text{CrO}_4^{2-}]$$

Assuming the solubility of  $\text{Ag}_2\text{CrO}_4$  is 'x'.

Thus,

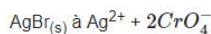
$$[\text{Ag}^{2+}] = 2x \text{ and } \text{CrO}_4^{2-} = x$$

$$K_{sp} = (2x)^2 \cdot x$$

$$1.1 \times 10^{-12} = 4x^3$$

$$x = 0.65 \times 10^{-4} M$$

Assuming the solubility of  $\text{AgBr}$  is y.



$$K_{sp} = (y)^2$$

$$5.0 \times 10^{-13} = y^2$$

$$y = 7.07 \times 10^{-7} M$$

The ratio of molarities to their saturated solution is:

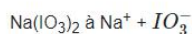
$$\frac{x}{y} = \frac{0.65 \times 10^{-4} M}{7.07 \times 10^{-7} M} = 91.9$$

**Q.69. Cupric chlorate and sodium iodate having equal volume of 0.002M. Will the precipitation of copper iodate will occur or not?**

**Ans.)**

Cupric chlorate and sodium iodate having equal volume are mixed together, then molar concentration of cupric chlorate and sodium iodate will reduce to half.

So, molar concentration of cupric chlorate and sodium iodate in mixture is 0.001M.



$$0.0001M \qquad \qquad \qquad 0.001M$$



$$0.001M \qquad \qquad \qquad 0.001M$$

**The Solubility for  $\text{Cu}(\text{IO}_3)_2 \Rightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{IO}_3^- (\text{aq})$**

Now, the ionic product of the copper iodate is:

$$= [\text{Cu}^{2+}] [\text{IO}_3^-]^2$$

$$= (0.001)(0.001)^2$$

$$= 1.0 \times 10^{-9} M$$

As the value of  $K_{sp}$  is more than Ionic product.

Thus, the precipitation will not occur.

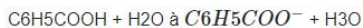
**Q.70. For benzoic acid the ionization constant is  $6.46 \times 10^{-5} M$  and for silver benzoate  $K_{sp}$  is**

$2.5 \times 10^{-5} M$ . Give relation between the solubility of silver benzoate in buffer of pH = 3.19 and its solubility in water.

Ans.)

Here, pH = 3.19

$$[H_3O^+] = 6.46 \times 10^{-5} M$$



$$K_a \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} = K_a \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{[H_3O^+]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Assuming the solubility of silver benzoate ( $C_6H_5COOAg$ ) is  $y$  mol/L.

Now,  $[Ag^+] = y$

$$[C_6H_5COOH] = [C_6H_5COO^-] = y$$

$$10[C_6H_5COO^-] + [C_6H_5COO^-] = y$$

$$[C_6H_5COO^-] = y/11$$

$$K_{sp}[Ag^+][C_6H_5COO^-] = y$$

$$2.5 \times 10^{-13} = y \frac{y}{11}$$

$$y = 1.66 \times 10^{-6} \text{ mol/L}$$

Hence, solubility of  $C_6H_5COOAg$  in buffer of pH = 3.19 is  $1.66 \times 10^{-6}$  mol/L.

For, water:

Assuming the solubility of silver benzoate ( $C_6H_5COOAg$ ) is  $x$  mol/L.

Now,  $[Ag^+] = x$  M

$$K_{sp} = [Ag^+][C_6H_5COO^-]$$

$$K_{sp} = (x)^2$$

$$y = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ mol/L}$$

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

Thus, the solubility of silver benzoate in water is 3.32 times the solubility of silver benzoate in pH = 3.19.

**Q.71. Calculate the maximum concentration of equimolar solutions of  $FeSO_4$  and  $Na_2SO_4$  so that when they are mixed in equal volume there is no precipitation of  $FeS$ ? ( $K_{sp}$  for  $FeS$  is  $6.3 \times 10^{-18}$ )**

Ans.)

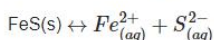
Assuming the maximum concentration of each solution is  $y$  mol/L

On mixing the solutions the volume of the concentration of each solution is reduced to half.

After mixing the maximum concentration of each solution is  $y/2$  mol/L.

$$\text{Thus, } [FeSO_4] = [Na_2S] = y/2 \text{ M}$$

$$\text{So, } [Fe^{2+}] = [FeSO_4] = y/2 \text{ M}$$



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

$$6.3 \times 10^{-18} = \left(\frac{y}{2}\right)\left(\frac{y}{2}\right) \frac{y^2}{4} = 6.3 \times 10^{-18}$$

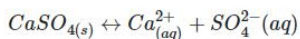
$$\text{Thus, } y = 5.02 \times 10^{-9}$$

Thus, if the concentration of  $FeSO_4$  and  $Na_2SO_4$  are equal to or less than that of  $5.02 \times 10^{-9} M$ , then there won't be precipitation of  $FeS$ .

**Q.72. Find the minimum volume of  $H_2O$  required to dissolve 1 gram of  $CaSO_4$  at 298K?**

$$K_{sp} \text{ for } CaSO_4 \text{ is } 9.1 \times 10^{-6}$$

Ans.)



$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

Assuming the solubility of calcium sulphate is  $x$ .

$$\text{So, } K_{sp} = x^2$$

$$\therefore 9.1 \times 10^{-6} = x^2 \therefore x = 3.02 \times 10^{-3} \text{ mol/L}$$

Now, molecular mass of calcium sulphate is 136g/mol.

Solubility in calcium sulphate in g/mol is

$$= 3.02 \times 10^{-3} \times 136$$

$$= 0.41 \text{ g/L}$$

i.e. 1 litre  $H_2O$  will be required to dissolve 0.41g of calcium sulphate.

Thus, minimum volume of  $H_2O$  required to dissolve 1 gram of  $CaSO_4$  at 298K is

$$= \frac{1}{0.41} L = 2.44L$$

**Q.73. The concentration of  $S^{2-}$  in 0.1M HCl solution saturated with  $H_2S$  is  $1.0 \times 10^{-19} M$ . If 10mL of this added to 5mL of 0.04M solution given below:**

1.  $MnCl_2$
2.  $ZnCl_2$
3.  $CdCl_2$
4.  $FeSO_4$

In which of the above solution the precipitation takes place?

$$\text{For MnS, } K_{sp} = 2.5 \times 10^{-13}$$

$$\text{For ZnS, } K_{sp} = 1.6 \times 10^{-24}$$

$$\text{For CdS, } K_{sp} = 8.0 \times 10^{-27}$$

$$\text{For FeS, } K_{sp} = 6.3 \times 10^{-18}$$

**Ans.)**

If the ionic product exceeds the  $K_{sp}$  value, then only precipitation can take place.

Before mixing:

$$[S^{2-}] = K_{sp} = 1.0 \times 10^{-19} M \quad [M^{2+}] = 0.04M$$

Volume = 10mL

Volume = 5mL

After mixing:

$$[S^{2-}] = ? \text{ and}$$

$$[M^{2+}] = ?$$

$$\text{Total volume} = (10 + 5) = 15mL$$

$$\text{Volume} = 15mL$$

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

$$[M^{2+}] = \frac{0.04 \times 5}{15} = 1.33 \times 10^{-2} M$$

Now, the ionic product =  $[M^{2+}][S^{2-}]$

$$= (1.33 \times 10^{-2})(6.67 \times 10^{-20})$$

$$= 8.87 \times 10^{-22}$$

Here, the ionic product of CdS and ZnS exceeds its corresponding  $K_{sp}$  value.

Thus, precipitation will occur in  $ZnCl_2$  and  $CdCl_2$  solutions.

