

# Chemistry

## (Chapter – 7) (Equilibrium)

(Class – XI)

### Question 7.1:

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

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

### Answer 7.1:

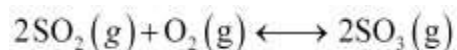
(a) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.

(b) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.

(c) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

### Question 7.2:

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



### Answer 7.2:

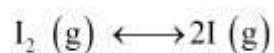
The equilibrium constant ( $K_c$ ) for the give reaction is:

$$\begin{aligned}
 K_c &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} \\
 &= \frac{(1.90)^2 \text{ M}^2}{(0.60)^2 (0.821) \text{ M}^3} \\
 &= 12.239 \text{ M}^{-1} (\text{approximately})
 \end{aligned}$$

Hence,  $K$  for the equilibrium is  $12.239 \text{ M}^{-1}$ .

### Question 7.3:

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.

### Answer 7.3:

Partial pressure of I atoms,

$$\begin{aligned}
 p_{\text{I}} &= \frac{40}{100} \times p_{\text{total}} \\
 &= \frac{40}{100} \times 10^5 \\
 &= 4 \times 10^4 \text{ Pa}
 \end{aligned}$$

Partial pressure of  $\text{I}_2$  molecules,

$$\begin{aligned}
 p_{\text{I}_2} &= \frac{60}{100} \times p_{\text{total}} \\
 &= \frac{60}{100} \times 10^5 \\
 &= 6 \times 10^4 \text{ Pa}
 \end{aligned}$$

Now, for the given reaction,

$$\begin{aligned}
 K_p &= \frac{(p_{\text{I}})^2}{p_{\text{I}_2}} \\
 &= \frac{(4 \times 10^4)^2 \text{ Pa}^2}{6 \times 10^4 \text{ Pa}} \\
 &= 2.67 \times 10^4 \text{ Pa}
 \end{aligned}$$

**Question 7.4:**

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

- (i)  $2 \text{NOCl(g)} \rightleftharpoons 2 \text{NO(g)} + \text{Cl}_2(\text{g})$
- (ii)  $2 \text{Cu(NO}_3)_2(\text{s}) \rightleftharpoons 2 \text{CuO(s)} + 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- (iii)  $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COOH(aq)} + \text{C}_2\text{H}_5\text{OH(aq)}$
- (iv)  $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightleftharpoons \text{Fe(OH)}_3(\text{s})$
- (v)  $\text{I}_2(\text{s}) + 5 \text{F}_2 \rightleftharpoons 2 \text{IF}_5$

**Answer 7.4:**

$$(i) \quad K_c = \frac{[\text{NO}_{(g)}]^2 [\text{Cl}_{2(g)}]}{[\text{NOCl}_{(g)}]^2}$$

$$(ii) \quad K_c = \frac{[\text{CuO}_{(s)}]^2 [\text{NO}_{2(g)}]^4 [\text{O}_{2(g)}]}{[\text{Cu(NO}_3)_{2(s)}]^2}$$

$$= [\text{NO}_{2(g)}]^4 [\text{O}_{2(g)}]$$

$$(iii) \quad K_c = \frac{[\text{CH}_3\text{COOH}_{(aq)}][\text{C}_2\text{H}_5\text{OH}_{(aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_5(aq)][\text{H}_2\text{O}_{(l)}]} = \frac{[\text{CH}_3\text{COOH}_{(aq)}][\text{C}_2\text{H}_5\text{OH}_{(aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_5(aq)]}$$

$$(iv) \quad K_c = \frac{[\text{Fe(OH)}_{3(s)}]}{[\text{Fe}^{3+}_{(aq)}][\text{OH}^-_{(aq)}]^3}$$

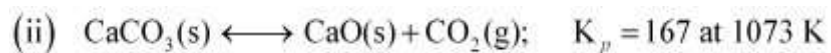
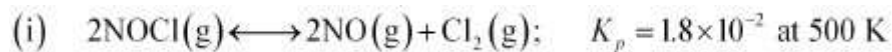
$$= \frac{1}{[\text{Fe}^{3+}_{(aq)}][\text{OH}^-_{(aq)}]^3}$$

$$(v) \quad K_c = \frac{[\text{IF}_5]^2}{[\text{I}_{2(s)}][\text{F}_2]^5}$$

$$= \frac{[\text{IF}_5]^2}{[\text{F}_2]^5}$$

**Question 7.5:**

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

**Answer 7.5:**

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

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

**(a)** Here,

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

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

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

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

Now,

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

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

$$\begin{aligned} \Rightarrow K_c &= \frac{1.8 \times 10^{-2}}{0.0831 \times 500} \\ &= 4.33 \times 10^{-4} \text{ (approximately)} \end{aligned}$$

**(b)** Here,

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

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

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

$$K_p = 167$$

Now,

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

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

$$\begin{aligned} \Rightarrow K_c &= \frac{167}{0.0831 \times 1073} \\ &= 1.87 \text{ (approximately)} \end{aligned}$$

**Question 7.6:**

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?

**Answer 7.6:**

It is given that  $K_c$  for the forward reaction is  $6.3 \times 10^{14}$ .

Then,  $K_c$  for the reverse reaction will be,

$$\begin{aligned} K'_c &= \frac{1}{K_c} \\ &= \frac{1}{6.3 \times 10^{14}} \\ &= 1.59 \times 10^{-15} \end{aligned}$$

**Question 7.7:**

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

**Answer 7.7:**

For a pure substance (both solids and liquids),

$$\begin{aligned} [\text{Pure substance}] &= \frac{\text{Number of moles}}{\text{Volume}} \\ &= \frac{\text{Mass/molecular mass}}{\text{Volume}} \\ &= \frac{\text{Mass}}{\text{Volume} \times \text{Molecular mass}} \\ &= \frac{\text{Density}}{\text{Molecular mass}} \end{aligned}$$

Now, the molecular mass and density (at a particular temperature) of a pure substance is always fixed and is accounted for in the equilibrium constant. Therefore, the values of pure substances are not mentioned in the equilibrium constant expression.

**Question 7.8:**

Reaction between  $N_2$  and  $O_2$  takes place as follows:

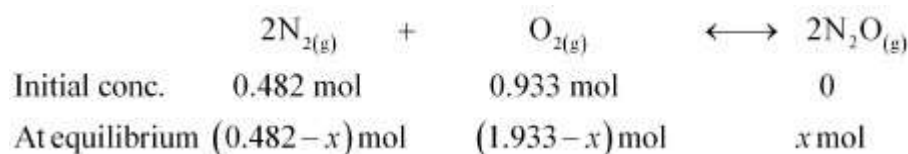


If a mixture of 0.482 mol of  $N_2$  and 0.933 mol of  $O_2$  is placed in a 10 L reaction vessel and allowed to form  $N_2O$  at a temperature for which  $K_c = 2.0 \times 10^{-37}$ , determine the composition of equilibrium mixture.

**Answer 7.8:**

Let the concentration of  $N_2O$  at equilibrium be  $x$ .

The given reaction is:



Therefore, at equilibrium, in the 10 L vessel:

$$[N_2] = \frac{0.482 - x}{10}, [O_2] = \frac{0.933 - x}{10}, [N_2O] = \frac{x}{10}$$

The value of equilibrium constant i.e.  $K_c = 2.0 \times 10^{-37}$  is very small. Therefore, the amount of  $N_2$  and  $O_2$  reacted is also very small. Thus,  $x$  can be neglected from the expressions of molar concentrations of  $N_2$  and  $O_2$ . Then,

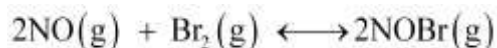
$$[N_2] = \frac{0.482}{10} = 0.0482 \text{ mol L}^{-1} \text{ and } [O_2] = \frac{0.933}{10} = 0.0933 \text{ mol L}^{-1}$$

Now,

$$\begin{aligned}
 K_c &= \frac{[N_2O_{(g)}]^2}{[N_{2(g)}]^2 [O_{2(g)}]} \\
 \Rightarrow 2.0 \times 10^{-37} &= \frac{\left(\frac{x}{10}\right)^2}{(0.0482)^2 (0.0933)} \\
 \Rightarrow \frac{x^2}{100} &= 2.0 \times 10^{-37} \times (0.0482)^2 \times (0.0933) \\
 \Rightarrow x^2 &= 43.35 \times 10^{-40} \\
 \Rightarrow x &= 6.6 \times 10^{-20} \\
 [N_2O] &= \frac{x}{10} = \frac{6.6 \times 10^{-20}}{10} \\
 &= 6.6 \times 10^{-21}
 \end{aligned}$$

**Question 7.9:**

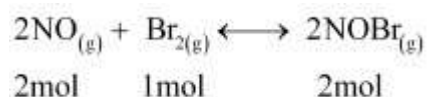
Nitric oxide reacts with  $\text{Br}_2$  and gives nitrosyl bromide as per reaction given below:



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  $\text{Br}_2$ .

**Answer 7.9:**

The given reaction is:



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  $\text{Br}_2$ .

Therefore, 0.0518 mol of NOBr are formed from  $\frac{0.0518}{2}$  mol of  $\text{Br}_2$ , or 0.0259 mol of  $\text{Br}_2$ .

The amount of NO and  $\text{Br}_2$  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:

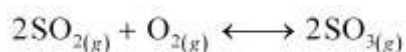
$$[\text{NO}] = 0.087 - 0.0518 = 0.0352 \text{ mol}$$

And, the amount of  $\text{Br}_2$  present at equilibrium is:

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

**Question 7.10:**

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



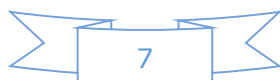
What is  $K_c$  at this temperature?

**Answer 7.10:**

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,

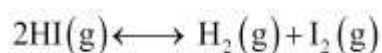
$$K_p = K_c (RT)^{\Delta n}$$

$$\Rightarrow 2.0 \times 10^{10} \text{ bar}^{-1} = K_c (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K})^{-1}$$

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

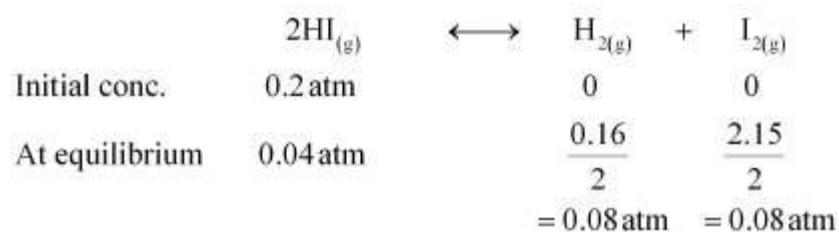
### Question 7.11:

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



### Answer 7.11:

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:



Therefore,

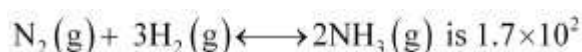


$$\begin{aligned}
 K_p &= \frac{p_{\text{H}_2} \times p_{\text{I}_2}}{p_{\text{HI}}^2} \\
 &= \frac{0.08 \times 0.08}{(0.04)^2} \\
 &= \frac{0.0064}{0.0016} \\
 &= 4.0
 \end{aligned}$$

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

### Question 7.12:

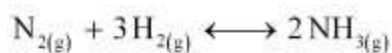
A mixture of 1.57 mol of  $\text{N}_2$ , 1.92 mol of  $\text{H}_2$  and 8.13 mol of  $\text{NH}_3$  is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant,  $K_c$  for the reaction



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

### Answer 7.12:

The given reaction is:



The given concentration of various species is

$$[\text{N}_2] = \frac{1.57}{20} \text{ mol L}^{-1} \quad [\text{H}_2] = \frac{1.92}{20} \text{ mol L}^{-1}$$

$$[\text{NH}_3] = \frac{8.13}{20} \text{ mol L}^{-1}$$

Now, reaction quotient  $Q_c$  is:

$$\begin{aligned}
 Q_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{\left(\frac{8.13}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3} \\
 &= 2.4 \times 10^3
 \end{aligned}$$

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.

**Question 7.13:**

The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

Write the balanced chemical equation corresponding to this expression.

**Answer 7.13:**

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



**Question 7.14:**

One mole of  $\text{H}_2\text{O}$  and one mole of  $\text{CO}$  are taken in 10 L 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.

**Answer 7.14:**

The given reaction is:

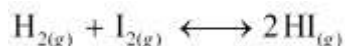
|                |                            |   |                            |                       |                          |   |                          |
|----------------|----------------------------|---|----------------------------|-----------------------|--------------------------|---|--------------------------|
|                | $\text{H}_2\text{O}_{(g)}$ | + | $\text{CO}_{(g)}$          | $\longleftrightarrow$ | $\text{H}_{2(g)}$        | + | $\text{CO}_{2(g)}$       |
| Initial conc.  | $\frac{1}{10}\text{M}$     |   | $\frac{1}{10}\text{M}$     |                       | 0                        |   | 0                        |
| At equilibrium | $\frac{1-0.4}{10}\text{M}$ |   | $\frac{1-0.4}{10}\text{M}$ |                       | $\frac{0.4}{10}\text{M}$ |   | $\frac{0.4}{10}\text{M}$ |
|                | = 0.06 M                   |   | = 0.06 M                   |                       | = 0.04 M                 |   | = 0.04 M                 |

Therefore, the equilibrium constant for the reaction,

$$\begin{aligned} K_c &= \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} \\ &= \frac{0.04 \times 0.04}{0.06 \times 0.06} \\ &= 0.444 \text{ (approximately)} \end{aligned}$$

**Question 7.15:**

At 700 K, equilibrium constant for the reaction



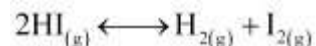
is 54.8. If  $0.5 \text{ mol L}^{-1}$  of  $\text{HI}_{(g)}$  is present at equilibrium at 700 K, what are the concentration of  $\text{H}_{2(g)}$  and  $\text{I}_{2(g)}$  assuming that we initially started with  $\text{HI}_{(g)}$  and allowed it to reach equilibrium at 700 K?

**Answer 7.15:**

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

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

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

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

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

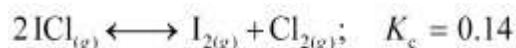
$$\Rightarrow x = 0.06754$$

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

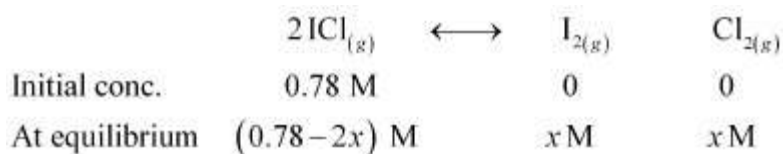
Hence, at equilibrium,  $[\text{H}_2] = [\text{I}_2] = 0.068 \text{ mol L}^{-1}$ .

**Question 7.16:**

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

**Answer 7.16:**

The given reaction is:



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

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

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

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

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

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

Hence, at equilibrium,

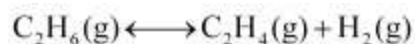
$$[\text{H}_2] = [\text{I}_2] = 0.167 \text{ M}$$

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

$$= 0.446 \text{ M}$$

### Question 7.17:

$K_p = 0.04$  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 atm pressure and allowed to come to equilibrium?



### Answer 7.17:

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

|                |                             |                       |                             |     |                   |
|----------------|-----------------------------|-----------------------|-----------------------------|-----|-------------------|
|                | $\text{C}_2\text{H}_{6(g)}$ | $\longleftrightarrow$ | $\text{C}_2\text{H}_{4(g)}$ | $+$ | $\text{H}_{2(g)}$ |
| Initial conc.  | 4.0atm                      |                       | 0                           |     | 0                 |
| At equilibrium | $4.0 - p$                   |                       | $p$                         |     | $p$               |

We can write,

$$\frac{p_{\text{C}_2\text{H}_4} \times p_{\text{H}_2}}{p_{\text{C}_2\text{H}_6}} = K_p$$

$$\Rightarrow \frac{p \times p}{4.0 - p} = 0.04$$

$$\Rightarrow p^2 = 0.16 - 0.04p$$

$$\Rightarrow p^2 + 0.04p - 0.16 = 0$$

$$\begin{aligned} \text{Now, } p &= \frac{-0.04 \pm \sqrt{(0.04)^2 - 4 \times 1 \times (-0.16)}}{2 \times 1} \\ &= \frac{-0.04 \pm 0.80}{2} \\ &= \frac{0.76}{2} \quad (\text{Taking positive value}) \\ &= 0.38 \end{aligned}$$

Hence, at equilibrium,

$$\begin{aligned} [\text{C}_2\text{H}_6] - 4 - p &= 4 - 0.38 \\ &= 3.62 \text{ atm} \end{aligned}$$

### Question 7.18:

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.

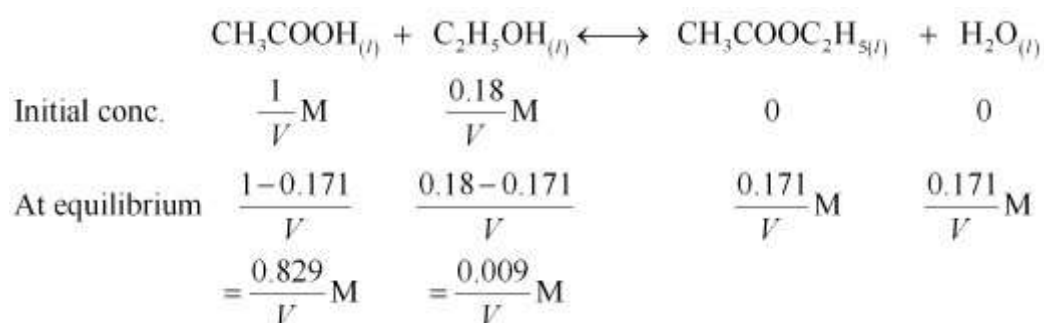
(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

**Answer 7.18:**

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

(ii) Let the volume of the reaction mixture be  $V$ . Also, here we will consider that water is a solvent and is present in excess.

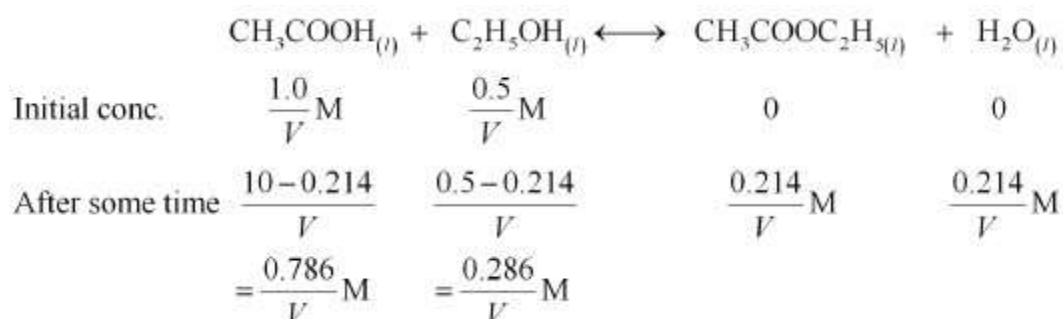
The given reaction is:



Therefore, equilibrium constant for the given reaction is:

$$\begin{aligned} K_c &= \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \\ &= \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.009}{V}} = 3.919 \\ &= 3.92 (\text{approximately}) \end{aligned}$$

(iii) Let the volume of the reaction mixture be  $V$ .



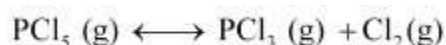
Therefore, the reaction quotient is,

$$\begin{aligned}
 Q_c &= \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \\
 &= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}} \\
 &= 0.2037 \\
 &= 0.204 \text{ (approximately)}
 \end{aligned}$$

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

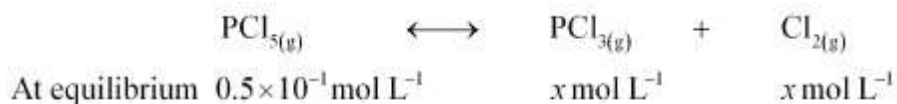
**Question 7.19:**

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  $0.5 \times 10^{-1} \text{ mol L}^{-1}$ . 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?



**Answer 7.19:**

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



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

Now we can write the expression for equilibrium as:

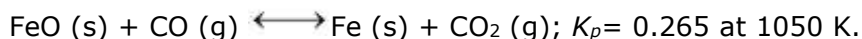
$$\begin{aligned}
 \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} &= K_c \\
 \Rightarrow \frac{x \times x}{0.5 \times 10^{-1}} &= 8.3 \times 10^{-3} \\
 \Rightarrow x^2 &= 4.15 \times 10^{-4} \\
 \Rightarrow x &= 2.04 \times 10^{-2} \\
 &= 0.0204 \\
 &= 0.02 \text{ (approximately)}
 \end{aligned}$$

Therefore, at equilibrium,

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

**Question 7.20:**

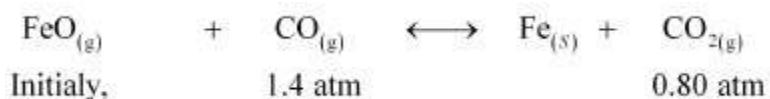
One of the reactions that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and  $\text{CO}_2$ .



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  $p_{\text{CO}_2} = 0.80 \text{ atm}$ ?

**Answer 7.20:**

For the given reaction,



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

It is given that  $K_p = 0.265$ .

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,

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

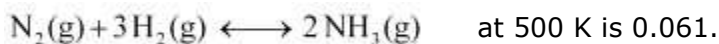
Therefore, equilibrium partial of  $\text{CO}_2$ ,  $p_{\text{CO}_2} = 0.80 - 0.339 = 0.461 \text{ atm}$ .

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



**Question 7.21:**

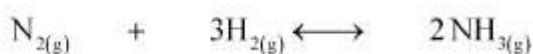
Equilibrium constant,  $K_c$  for the reaction



At a particular time, the analysis shows that composition of the reaction mixture is  $3.0 \text{ mol L}^{-1} \text{ N}_2$ ,  $2.0 \text{ mol L}^{-1} \text{ H}_2$  and  $0.5 \text{ mol L}^{-1} \text{ NH}_3$ . Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

**Answer 7.21:**

The given reaction is:



At a particular time:  $3.0 \text{ mol L}^{-1}$        $2.0 \text{ mol L}^{-1}$        $0.5 \text{ mol L}^{-1}$

Now, we know that,

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

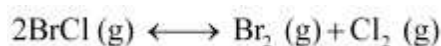
It is given that  $K_c = 0.061$ .

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

Since  $Q_c < K_c$  , the reaction will proceed in the forward direction to reach equilibrium.

**Question 7.22:**

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

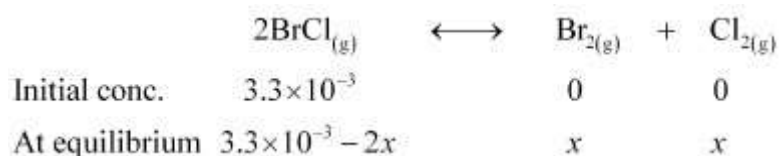


for which  $K_c = 32$  at  $500 \text{ K}$ .

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?

**Answer 7.22:**

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



Now, we can write,

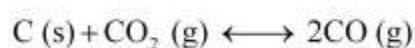
$$\begin{aligned} \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} &= K_c \\ \Rightarrow \frac{x \times x}{(3.3 \times 10^{-3} - 2x)^2} &= 32 \\ \Rightarrow \frac{x}{3.3 \times 10^{-3} - 2x} &= 5.66 \\ \Rightarrow x &= 18.678 \times 10^{-3} - 11.32x \\ \Rightarrow 12.32x &= 18.678 \times 10^{-3} \\ \Rightarrow x &= 1.5 \times 10^{-3} \end{aligned}$$

Therefore, at equilibrium,

$$\begin{aligned} [\text{BrCl}] &= 3.3 \times 10^{-3} - (2 \times 1.5 \times 10^{-3}) \\ &= 3.3 \times 10^{-3} - 3.0 \times 10^{-3} \\ &= 0.3 \times 10^{-3} \\ &= 3.0 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$$

**Question 7.23:**

At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO<sub>2</sub> in equilibrium with solid carbon has 90.55% CO by mass



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

**Answer 7.23:**

Let the total mass of the gaseous mixture be 100 g.

Mass of CO = 90.55 g

And, mass of CO<sub>2</sub> = (100 - 90.55) = 9.45 g

Now, number of moles of CO,  $n_{\text{CO}} = \frac{90.55}{28} = 3.234 \text{ mol}$

Number of moles of CO<sub>2</sub>,  $n_{\text{CO}_2} = \frac{9.45}{44} = 0.215 \text{ mol}$

Partial pressure of CO,

$$\begin{aligned} p_{\text{CO}} &= \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2}} \times p_{\text{total}} \\ &= \frac{3.234}{3.234 + 0.215} \times 1 \\ &= 0.938 \text{ atm} \end{aligned}$$

Partial pressure of CO<sub>2</sub>,

$$\begin{aligned} p_{\text{CO}_2} &= \frac{n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \times p_{\text{total}} \\ &= \frac{0.215}{3.234 + 0.215} \times 1 \\ &= 0.062 \text{ atm} \end{aligned}$$

$$\begin{aligned} \text{Therefore, } K_p &= \frac{[\text{CO}]^2}{[\text{CO}_2]} \\ &= \frac{(0.938)^2}{0.062} \\ &= 14.19 \end{aligned}$$

For the given reaction,

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

We know that,

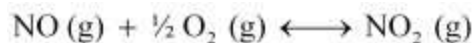
$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} \\ \Rightarrow 14.19 &= K_c (0.082 \times 1127)^1 \\ \Rightarrow K_c &= \frac{14.19}{0.082 \times 1127} \\ &= 0.154 (\text{approximately}) \end{aligned}$$

**Question 7.24:**

Calculate

**a)**  $\Delta G^\circ$  and

**b)** the equilibrium constant for the formation of  $\text{NO}_2$  from  $\text{NO}$  and  $\text{O}_2$  at 298 K



Where:

$$\Delta_f G^\circ (\text{NO}_2) = 52.0 \text{ kJ/mol}$$

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

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

**Answer 7.24:**

**(a)** For the given reaction,

$$\Delta G^\circ = \Delta G^\circ (\text{Products}) - \Delta G^\circ (\text{Reactants})$$

$$\Delta G^\circ = 52.0 - \{87.0 + 0\}$$

$$= -35.0 \text{ kJ mol}^{-1}$$

**(b)** We know that,

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

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

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

$$= 6.134$$

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

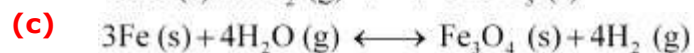
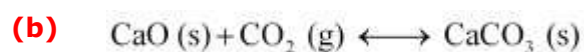
$$= 1.36 \times 10^6$$

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

**Question 7.25:**

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?





**Answer 7.25:**

(a) 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.

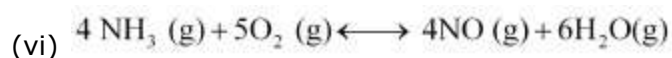
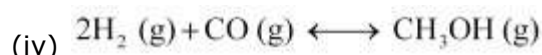
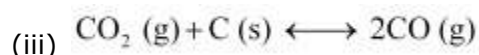
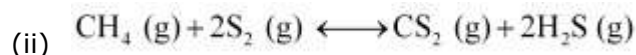
(b) The number of moles of reaction products will decrease.

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

**Question 7.26:**

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.



**Answer 7.26:**

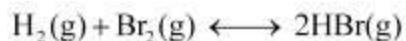
The reactions given in (i), (iii), (iv), (v), and (vi) will get affected by increasing the pressure.

The reaction given in (iv) will proceed in the forward direction because the number of moles of gaseous reactants is more than that of gaseous products.

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

**Question 7.27:**

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.

**Answer 7.27:**

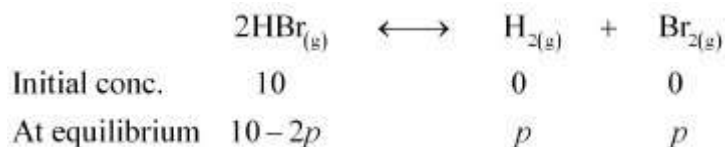
Given,

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

Therefore, for the reaction  $2\text{HBr}_{(\text{g})} \longleftrightarrow \text{H}_{2(\text{g})} + \text{Br}_{2(\text{g})}$ , 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.



Now, we can write,

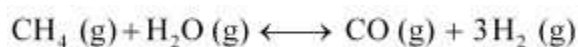
$$\begin{aligned} \frac{p_{\text{HBr}} \times p_{\text{H}_2}}{p_{\text{HBr}}^2} &= K'_p \\ \frac{p \times p}{(10 - 2p)^2} &= 6.25 \times 10^{-6} \\ \frac{p}{10 - 2p} &= 2.5 \times 10^{-3} \\ p &= 2.5 \times 10^{-2} - (5.0 \times 10^{-3})p \\ p + (5.0 \times 10^{-3})p &= 2.5 \times 10^{-2} \\ (1005 \times 10^{-3})p &= 2.5 \times 10^{-2} \\ p &= 2.49 \times 10^{-2} \text{ bar} = 2.5 \times 10^{-2} \text{ bar (approximately)} \end{aligned}$$

Therefore, at equilibrium,

$$\begin{aligned}
 [\text{H}_2] &= [\text{Br}_2] = 2.49 \times 10^{-2} \text{ bar} \\
 [\text{HBr}] &= 10 - 2 \times (2.49 \times 10^{-2}) \text{ bar} \\
 &= 9.95 \text{ bar} = 10 \text{ bar (approximately)}
 \end{aligned}$$

**Question 7.28:**

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?

**Answer 7.28:**

- (a) For the given reaction,

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

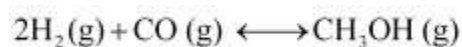
(b)

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

**Question 7.29:**

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:

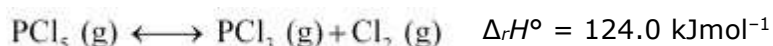


**Answer 7.29:**

- (a) According to Le Chatelier's principle, on addition of  $\text{H}_2$ , the equilibrium of the given reaction will shift in the forward direction.
- (b) On addition of  $\text{CH}_3\text{OH}$ , the equilibrium will shift in the backward direction.
- (c) On removing  $\text{CO}$ , the equilibrium will shift in the backward direction.
- (d) On removing  $\text{CH}_3\text{OH}$ , the equilibrium will shift in the forward direction.

**Question 7.30:**

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?

**Answer 7.30:**

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

- (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.

### Question 7.31:

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  $H_2$ . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

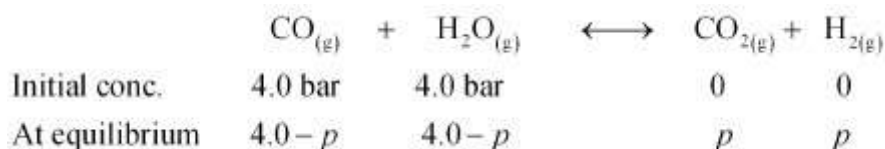


If a reaction vessel at  $400^\circ C$  is charged with an equimolar mixture of CO and steam such that  $p_{CO} = p_{H_2O} = 4.0$  bar, what will be the partial pressure of  $H_2$  at equilibrium?

$K_p = 10.1$  at  $400^\circ C$

### Answer 7.31:

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



It is given that  $K_p = 10.1$ .

Now,

$$\begin{aligned} \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} &= K_p \\ \Rightarrow \frac{p \times p}{(4.0 - p)(4.0 - p)} &= 10.1 \\ \Rightarrow \frac{p}{4.0 - p} &= 3.178 \\ \Rightarrow p &= 12.712 - 3.178p \\ \Rightarrow 4.178p &= 12.712 \\ \Rightarrow p &= 3.04 \end{aligned}$$

Hence, at equilibrium, the partial pressure of  $H_2$  will be 3.04 bar.

**Question 7.32:**

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

- a)  $\text{Cl}_2 (\text{g}) \longleftrightarrow 2 \text{Cl} (\text{g}) ; K_c = 5 \times 10^{-39}$   
 b)  $\text{Cl}_2 (\text{g}) + 2 \text{NO} (\text{g}) \longleftrightarrow 2 \text{NOCl} (\text{g}) ; K_c = 3.7 \times 10^8$   
 c)  $\text{Cl}_2 (\text{g}) + 2 \text{NO}_2 (\text{g}) \longleftrightarrow 2 \text{NO}_2\text{Cl} (\text{g}) ; K_c = 1.8$

**Answer 7.32:**

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.

**Question 7.33:**

The value of  $K_c$  for the reaction  $3\text{O}_2 (\text{g}) \longleftrightarrow 2\text{O}_3 (\text{g})$  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  $\text{O}_3$ ?

**Answer 7.33:**

The given reaction is:



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

$$\text{It is given that } K_c = 2.0 \times 10^{-50} \text{ and } [\text{O}_{2(\text{g})}] = 1.6 \times 10^{-2}.$$

Then, we have,

$$\begin{aligned} 2.0 \times 10^{-50} &= \frac{[\text{O}_{3(\text{g})}]^2}{[1.6 \times 10^{-2}]^3} \\ \Rightarrow [\text{O}_{3(\text{g})}]^2 &= 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3 \\ \Rightarrow [\text{O}_{3(\text{g})}]^2 &= 8.192 \times 10^{-56} \\ \Rightarrow [\text{O}_{3(\text{g})}] &= 2.86 \times 10^{-28} \text{ M} \end{aligned}$$

Hence, the concentration of  $\text{O}_3$  is  $2.86 \times 10^{-28} \text{ M}$ .

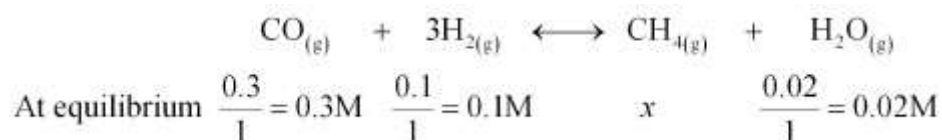
**Question 7.34:**

The reaction,  $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$  is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of  $\text{H}_2$  and 0.02 mol of  $\text{H}_2\text{O}$  and an unknown amount of  $\text{CH}_4$  in the flask. Determine the concentration of  $\text{CH}_4$  in the mixture.

The equilibrium constant,  $K_c$  for the reaction at the given temperature is 3.90.

**Answer 7.34:**

Let the concentration of methane at equilibrium be  $x$ .



It is given that  $K_c = 3.90$ .

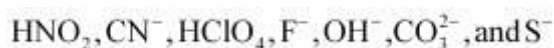
Therefore,

$$\begin{aligned} \frac{[\text{CH}_{4(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{H}_{2(\text{g})}]^3} &= K_c \\ \Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} &= 3.90 \\ \Rightarrow x &= \frac{3.90 \times 0.3 \times (0.1)^3}{0.02} \\ &= \frac{0.00117}{0.02} \\ &= 0.0585\text{M} \\ &= 5.85 \times 10^{-2}\text{M} \end{aligned}$$

Hence, the concentration of  $\text{CH}_4$  at equilibrium is  $5.85 \times 10^{-2}\text{M}$ .

**Question 7.35:**

What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:



**Answer 7.35:**

A conjugate acid-base pair is a pair that differs only by one proton. The conjugate acid-base for the given species is mentioned in the table below.

**Species Conjugate acid-base**

|                    |  |
|--------------------|--|
| $\text{HNO}_2$     | $\text{NO}_2^-$ (base)                               |
| $\text{CN}^-$      | $\text{HCN}$ (acid)                                  |
| $\text{HClO}_4$    | $\text{ClO}_4^-$ (base)                              |
| $\text{F}^-$       | $\text{HF}$ (acid)                                   |
| $\text{OH}^-$      | $\text{H}_2\text{O}$ (acid) / $\text{O}^{2-}$ (base) |
| $\text{CO}_3^{2-}$ | $\text{HCO}_3^-$ (acid)                              |
| $\text{S}^{2-}$    | $\text{HS}^-$ (acid)                                 |

**Question 7.36:**

Which of the followings are Lewis acids?  $\text{H}_2\text{O}$ ,  $\text{BF}_3$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$

**Answer 7.36:**

Lewis acids are those acids which can accept a pair of electrons. For example,  $\text{BF}_3$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$  are Lewis acids.

**Question 7.37:**

What will be the conjugate bases for the Brönsted acids:  $\text{HF}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCO}_3^-$ ?

**Answer 7.37:**

The table below lists the conjugate bases for the given Bronsted acids.

**Bronsted acid Conjugate base**

|                         |                    |
|-------------------------|--------------------|
| $\text{HF}$             | $\text{F}^-$       |
| $\text{H}_2\text{SO}_4$ | $\text{HSO}_4^-$   |
| $\text{HCO}_3^-$        | $\text{CO}_3^{2-}$ |

**Question 7.38:**

Write the conjugate acids for the following Brönsted bases:  $\text{NH}_2^-$ ,  $\text{NH}_3$  and  $\text{HCOO}^-$ .

**Answer 7.38:**

The table below lists the conjugate acids for the given Bronsted bases.

**Bronsted base Conjugate acid**

|                 |                 |
|-----------------|-----------------|
| $\text{NH}_2^-$ | $\text{NH}_3$   |
| $\text{NH}_3$   | $\text{NH}_4^+$ |
| $\text{HCOO}^-$ | $\text{HCOOH}$  |

**Question 7.39:**

The species:  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ , and  $\text{NH}_3$  can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

**Answer 7.39:**

The table below lists the conjugate acids and conjugate bases for the given species.

| Species              | Conjugate acid          | Conjugate base     |
|----------------------|-------------------------|--------------------|
| $\text{H}_2\text{O}$ | $\text{H}_3\text{O}^+$  | $\text{OH}^-$      |
| $\text{HCO}_3^-$     | $\text{H}_2\text{CO}_3$ | $\text{CO}_3^{2-}$ |
| $\text{HSO}_4^-$     | $\text{H}_2\text{SO}_4$ | $\text{SO}_4^{2-}$ |
| $\text{NH}_3$        | $\text{NH}_4^+$         | $\text{NH}_2^-$    |

**Question 7.40:**

Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base:

**(a)**  $\text{OH}^-$

**(b)**  $\text{F}^-$

**(c)**  $\text{H}^+$

**(d)**  $\text{BCl}_3$ .

**Answer 7.40:**

**(a)**  $\text{OH}^-$  is a Lewis base since it can donate its lone pair of electrons.

**(b)**  $\text{F}^-$  is a Lewis base since it can donate a pair of electrons.

**(c)**  $\text{H}^+$  is a Lewis acid since it can accept a pair of electrons.

**(d)**  $\text{BCl}_3$  is a Lewis acid since it can accept a pair of electrons.

**Question 7.41:**

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

**Answer 7.41:**

Given,

$$[H^+] = 3.8 \times 10^{-3} \text{ M}$$

∴ pH value of soft drink

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

$$= -\log(3.8 \times 10^{-3})$$

$$= -\log 3.8 - \log 10^{-3}$$

$$= -\log 3.8 + 3$$

$$= -0.58 + 3$$

$$= 2.42$$

**Question 7.42:**

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

**Answer 7.42:**

Given, pH

$$= 3.76$$

It is known that,

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

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

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

$$= \text{antilog}(-3.76)$$

$$= 1.74 \times 10^{-4} \text{ M}$$

Hence, the concentration of hydrogen ion in the given sample of vinegar is  $1.74 \times 10^{-4}$  M.

**Question 7.43:**

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

**Answer 7.43:**

It is known that,

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

Given,

$$K_a \text{ of HF} = 6.8 \times 10^{-4}$$

Hence,  $K_b$  of its conjugate base  $F^-$

$$\begin{aligned} &= \frac{K_w}{K_a} \\ &= \frac{10^{-14}}{6.8 \times 10^{-4}} \\ &= 1.5 \times 10^{-11} \end{aligned}$$

Given,

$$K_a \text{ of HCOOH} = 1.8 \times 10^{-4}$$

Hence,  $K_b$  of its conjugate base  $HCOO^-$

$$\begin{aligned} &= \frac{K_w}{K_a} \\ &= \frac{10^{-14}}{1.8 \times 10^{-4}} \\ &= 5.6 \times 10^{-11} \end{aligned}$$

Given,

$$K_a \text{ of HCN} = 4.8 \times 10^{-9}$$

Hence,  $K_b$  of its conjugate base  $CN^-$

$$\begin{aligned} &= \frac{K_w}{K_a} \\ &= \frac{10^{-14}}{4.8 \times 10^{-9}} \\ &= 2.08 \times 10^{-6} \end{aligned}$$

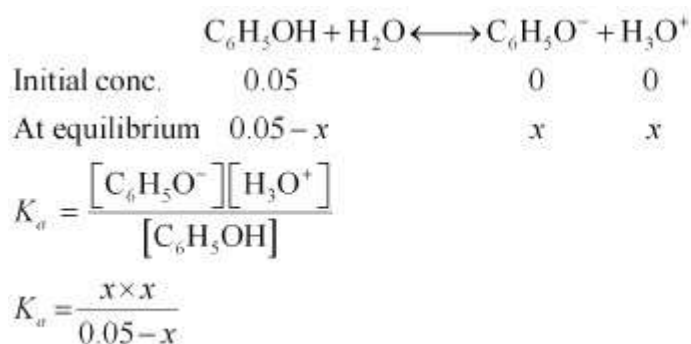


**Question 7.44:**

The ionization 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 ionization if the solution is also 0.01M in sodium phenolate?

**Answer 7.44:**

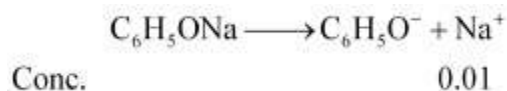
Ionization of phenol:



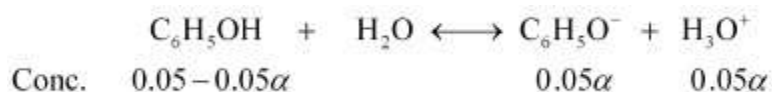
As the value of the ionization constant is very less,  $x$  will be very small. Thus, we can ignore  $x$  in the denominator.

$$\begin{aligned} \therefore x &= \sqrt{1 \times 10^{-10} \times 0.05} \\ &= \sqrt{5 \times 10^{-12}} \\ &= 2.2 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+] \\ \text{Since } [\text{H}_3\text{O}^+] &= [\text{C}_6\text{H}_5\text{O}^-], \\ [\text{C}_6\text{H}_5\text{O}^-] &= 2.2 \times 10^{-6} \text{ M}. \end{aligned}$$

Now, let  $\alpha$  be the degree of ionization of phenol in the presence of 0.01 M  $\text{C}_6\text{H}_5\text{ONa}$ .



Also,



$$[C_6H_5OH] = 0.05 - 0.05\alpha ; 0.05 \text{ M}$$

$$[C_6H_5O^-] = 0.01 + 0.05\alpha ; 0.01 \text{ M}$$

$$[H_3O^+] = 0.05\alpha$$

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$K_a = \frac{(0.01)(0.05\alpha)}{0.05}$$

$$1.0 \times 10^{-10} = .01\alpha$$

$$\alpha = 1 \times 10^{-8}$$

**Question 7.45:**

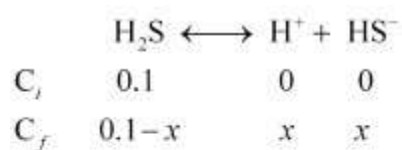
The first ionization constant of  $H_2S$  is  $9.1 \times 10^{-8}$ . Calculate the concentration of  $HS^-$  ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of  $H_2S$  is  $1.2 \times 10^{-13}$ , calculate the concentration of  $S^{2-}$  under both conditions.

**Answer 7.45:**

(i) To calculate the concentration of  $HS^-$  ion:

**Case I (in the absence of HCl):**

Let the concentration of  $HS^-$  be x M.



$$\text{Then, } K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$9.1 \times 10^{-8} = \frac{(x)(x)}{0.1-x}$$

$$(9.1 \times 10^{-8})(0.1-x) = x^2$$

Taking  $0.1-x \text{ M}$  ;  $0.1 \text{ M}$ , we have  $(9.1 \times 10^{-8})(0.1) = x^2$ .

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

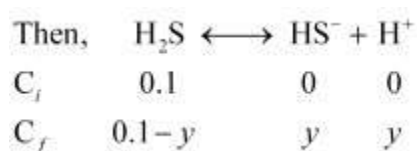
$$x = \sqrt{9.1 \times 10^{-9}}$$

$$= 9.54 \times 10^{-5} \text{ M}$$

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

### Case II (in the presence of HCl):

In the presence of  $0.1 \text{ M}$  of  $\text{HCl}$ , let  $[\text{HS}^-]$  be  $y \text{ M}$



$$\text{Now, } K_{a_1} = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]}$$

$$K_{a_1} = \frac{[y](0.1+y)}{(0.1-y)}$$

$$9.1 \times 10^{-8} = \frac{y \times 0.1}{0.1} \quad (\because 0.1-y ; 0.1 \text{ M})$$

(and  $0.1+y ; 0.1 \text{ M}$ )

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

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

To calculate the concentration of  $[S^{2-}]$

**Case I (in the absence of 0.1 M HCl):**



$$[HS^-] = 9.54 \times 10^{-5} M \quad (\text{From first ionization, case I})$$

Let  $[S^{2-}]$  be  $X$ .

$$\text{Also, } [H^+] = 9.54 \times 10^{-5} M \quad (\text{From first ionization, case I})$$

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$K_{a_2} = \frac{(9.54 \times 10^{-5})(X)}{9.54 \times 10^{-5}}$$

$$1.2 \times 10^{-13} = X = [S^{2-}]$$

**Case II (in the presence of 0.1 M HCl):**

Again, let the concentration of  $HS^-$  be  $X'$  M.

$$[HS^-] = 9.1 \times 10^{-8} M \quad (\text{From first ionization, case II})$$

$$[H^+] = 0.1 M \quad (\text{From HCl, case II})$$

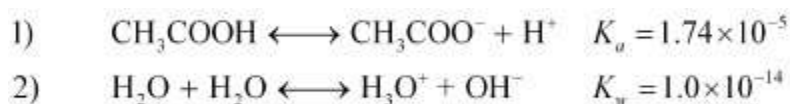
$$\begin{aligned}
 [S^{2-}] &= X' \\
 \text{Then, } K_{a_2} &= \frac{[H^+][S^{2-}]}{[HS^-]} \\
 1.2 \times 10^{-13} &= \frac{(0.1)(X')}{9.1 \times 10^{-8}} \\
 10.92 \times 10^{-21} &= 0.1X' \\
 \frac{10.92 \times 10^{-21}}{0.1} &= X' \\
 X' &= \frac{1.092 \times 10^{-20}}{0.1} \\
 &= 1.092 \times 10^{-19} \text{ M} \\
 \Rightarrow K_{a_1} &= 1.74 \times 10^{-5}
 \end{aligned}$$

**Question 7.46:**

The ionization 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.

**Answer 7.46:**

**Method 1**



Since  $K_a \gg K_w$ :

$$\begin{aligned}
 & \text{CH}_3\text{COOH} + \text{H}_2\text{O} \longleftrightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \\
 C_i = & \begin{array}{ccc} 0.05 & 0 & 0 \\ 0.05 - 0.05\alpha & 0.05\alpha & 0.05\alpha \end{array} \\
 K_a = & \frac{(0.05\alpha)(0.05\alpha)}{(0.05 - 0.05\alpha)} \\
 & = \frac{(0.05\alpha)(0.05\alpha)}{0.05(1 - \alpha)} \\
 & = \frac{0.05\alpha^2}{1 - \alpha}
 \end{aligned}$$

$$1.74 \times 10^{-5} = \frac{0.05\alpha^2}{1-\alpha}$$

$$1.74 \times 10^{-5} - 1.74 \times 10^{-5} \alpha = 0.05\alpha^2$$

$$0.05\alpha^2 + 1.74 \times 10^{-5} \alpha - 1.74 \times 10^{-5}$$

$$D = b^2 - 4ac$$

$$= (1.74 \times 10^{-5})^2 - 4(.05)(1.74 \times 10^{-5})$$

$$= 3.02 \times 10^{-25} + .348 \times 10^{-5}$$

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

$$\alpha = \sqrt{\frac{1.74 \times 10^{-5}}{.05}}$$

$$= \sqrt{\frac{34.8 \times 10^{-5} \times 10}{10}}$$

$$= \sqrt{3.48 \times 10^{-6}}$$

$$= \text{CH}_3\text{COOH} \longleftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$$

$$\alpha 1.86 \times 10^{-3}$$

$$[\text{CH}_3\text{COO}^-] = 0.05 \times 1.86 \times 10^{-3}$$

$$= \frac{0.93 \times 10^{-3}}{1000}$$

$$= .000093$$

## Method 2

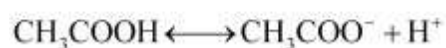
Degree of dissociation,

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

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

$$K_a = 1.74 \times 10^{-5}$$

$$\begin{aligned}\text{Then, } \alpha &= \sqrt{\frac{1.74 \times 10^{-5}}{.05}} \\ \alpha &= \sqrt{34.8 \times 10^{-5}} \\ \alpha &= \sqrt{3.48} \times 10^{-4} \\ \alpha &= 1.8610^{-2}\end{aligned}$$



Thus, concentration of  $\text{CH}_3\text{COO}^- = \text{c.a}$

$$\begin{aligned}&= .05 \times 1.86 \times 10^{-2} \\ &= .093 \times 10^{-2} \\ &= .00093 \text{ M}\end{aligned}$$

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

$$[\text{H}^+] = .00093 = .093 \times 10^{-2}.$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log (.093 \times 10^{-2})\end{aligned}$$

$$\therefore \text{pH} = 3.03$$

Hence, the concentration of acetate ion in the solution is 0.00093 M and its Ph is 3.03.

#### Question 7.47:

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  $\text{p}K_a$ .

#### Answer 7.47:

Let the organic acid be HA.



Concentration of HA = 0.01 M  
pH = 4.15

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

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

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Now,

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

$$[HA] = 0.01$$

Then,

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

$$K_a = 5.01 \times 10^{-7}$$

$$pK_a = -\log K_a$$

$$= -\log(5.01 \times 10^{-7})$$

$$pK_a = 6.3001$$

#### Question 7.48:

Assuming complete dissociation, calculate the pH of the following solutions:

(i) 0.003 M HCl

(ii) 0.005 M NaOH

(iii) 0.002 M HBr

(iv) 0.002 M KOH

#### Answer 7.48:

(i) 0.003M HCl:



Since HCl is completely ionized,

$$[H_3O^+] = [HCl].$$

$$\Rightarrow [H_3O^+] = 0.003$$

Now,



$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] = -\log (.003) \\ &= 2.52\end{aligned}$$

Hence, the pH of the solution is 2.52.

**(ii)** 0.005MNaOH:

$$\begin{aligned}\text{NaOH}_{(aq)} &\longleftrightarrow \text{Na}_{(aq)}^+ + \text{HO}_{(aq)}^- \\ [\text{HO}^-] &= [\text{NaOH}] \\ \Rightarrow [\text{HO}^-] &= .005 \\ \text{pOH} &= -\log [\text{HO}^-] = -\log (.005) \\ \text{pOH} &= 2.30 \\ \therefore \text{pH} &= 14 - 2.30 \\ &= 11.70\end{aligned}$$

Hence, the pH of the solution is 11.70.

**(iii)** 0.002 HBr:

$$\begin{aligned}\text{HBr} + \text{H}_2\text{O} &\longleftrightarrow \text{H}_3\text{O}^+ + \text{Br}^- \\ [\text{H}_3\text{O}^+] &= [\text{HBr}] \\ \Rightarrow [\text{H}_3\text{O}^+] &= .002 \\ \therefore \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (0.002) \\ &= 2.69\end{aligned}$$

Hence, the pH of the solution is 2.69.

**(iv)** 0.002 M KOH:

$$\begin{aligned}\text{KOH}_{(aq)} &\longleftrightarrow \text{K}_{(aq)}^+ + \text{OH}_{(aq)}^- \\ [\text{OH}^-] &= [\text{KOH}] \\ \Rightarrow [\text{OH}^-] &= .002 \\ \text{Now, pOH} &= -\log [\text{OH}^-] \\ &= 2.69 \\ \therefore \text{pH} &= 14 - 2.69 \\ &= 11.31\end{aligned}$$

Hence, the pH of the solution is 11.31.

**Question 7.49:**

Calculate the pH of the following solutions:

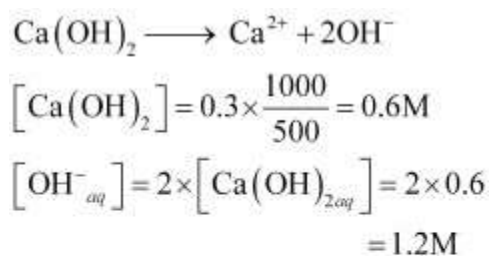
- a)** 2 g of TIOH dissolved in water to give 2 litre of solution.
- b)** 0.3 g of  $\text{Ca}(\text{OH})_2$  dissolved in water to give 500 mL of solution.
- c)** 0.3 g of NaOH dissolved in water to give 200 mL of solution.
- d)** 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

**Answer 7.49:**

**(a)** For 2g of TIOH dissolved in water to give 2 L of solution:

$$\begin{aligned}
 [\text{TIOH}_{(aq)}] &= \frac{2}{2} \text{ g/L} \\
 &= \frac{2}{2} \times \frac{1}{221} \text{ M} \\
 &= \frac{1}{221} \text{ M} \\
 \text{TIOH}_{(aq)} &\longrightarrow \text{TI}^+_{(aq)} + \text{OH}^-_{(aq)} \\
 [\text{OH}^-_{(aq)}] &= [\text{TIOH}_{(aq)}] = \frac{1}{221} \text{ M} \\
 K_w &= [\text{H}^+][\text{OH}^-] \\
 10^{-14} &= [\text{H}^+] \left( \frac{1}{221} \right) \\
 221 \times 10^{-14} &= [\text{H}^+] \\
 \Rightarrow \text{pH} &= -\log [\text{H}^+] = -\log (221 \times 10^{-14}) \\
 &= -\log (2.21 \times 10^{-12}) \\
 &= 11.65
 \end{aligned}$$

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



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

$$= \frac{10^{-14}}{1.2}\text{M}$$

$$= 0.833 \times 10^{-14}$$

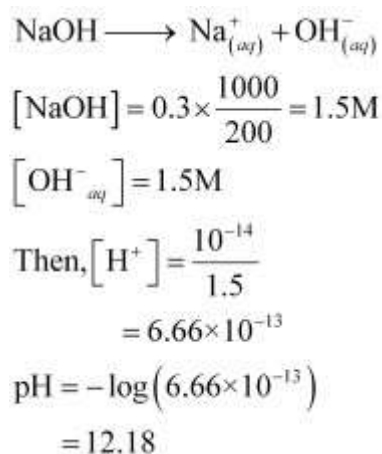
$$\text{pH} = -\log(0.833 \times 10^{-14})$$

$$= -\log(8.33 \times 10^{-13})$$

$$= (-0.902 + 13)$$

$$= 12.098$$

**(c)** For 0.3 g of NaOH dissolved in water to give 200 mL of solution:



**(d)** For 1mL of 13.6 M HCl diluted with water to give 1 L of solution:

$$13.6 \times 1 \text{ mL} = M_2 \times 1000 \text{ mL}$$

(Before dilution) (After dilution)

$$13.6 \times 10^{-3} = M_2 \times 1\text{L}$$

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

$$= (-0.1335 + 2) = 1.866 \dots 1.87$$

**Question 7.50:**

The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the  $pK_a$  of bromoacetic acid.

**Answer 7.50:**

Degree of ionization,  $\alpha = 0.132$

Concentration,  $c = 0.1 \text{ M}$

Thus, the concentration of  $\text{H}_3\text{O}^+ = c \cdot \alpha$

$$= 0.1 \times 0.132$$

$$= 0.0132$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log(0.0132) \\ &= 1.879 : 1.88\end{aligned}$$

Now,

$$\begin{aligned}K_a &= C\alpha^2 \\ &= 0.1 \times (0.132)^2 \\ K_a &= .0017 \\ pK_a &= 2.75\end{aligned}$$

**Question 7.51:**

The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the  $pK_a$  of bromoacetic acid.

**Answer 7.51:**

Degree of ionization,  $\alpha = 0.132$

Concentration,  $c = 0.1 \text{ M}$

Thus, the concentration of  $\text{H}_3\text{O}^+ = c \cdot \alpha$

$$= 0.1 \times 0.132$$

$$= 0.0132$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log(0.0132) \\ &= 1.879 : 1.88\end{aligned}$$

Now,

$$\begin{aligned}K_a &= C\alpha^2 \\&= 0.1 \times (0.132)^2 \\K_a &= .0017 \\pK_a &= 2.75\end{aligned}$$

**Question 7.52:**

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.

**Answer 7.52:**

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

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

pH = ?

$\alpha$  = ?

$$\begin{aligned}K_b &= c\alpha^2 \\4.27 \times 10^{-10} &= 0.001 \times \alpha^2 \\4270 \times 10^{-10} &= \alpha^2 \\65.34 \times 10^{-5} &= \alpha = 6.53 \times 10^{-4}\end{aligned}$$

$$\begin{aligned}\text{Then, [anion]} &= c\alpha = .001 \times 65.34 \times 10^{-5} \\&= .065 \times 10^{-5}\end{aligned}$$

$$\begin{aligned}\text{pOH} &= -\log(.065 \times 10^{-5}) \\&= 6.187\end{aligned}$$

$$\text{pH} = 7.813$$

Now,

$$\begin{aligned}K_a \times K_b &= K_w \\ \therefore 4.27 \times 10^{-10} \times K_a &= K_w \\ K_a &= \frac{10^{-14}}{4.27 \times 10^{-10}} \\&= 2.34 \times 10^{-5}\end{aligned}$$

Thus, the ionization constant of the conjugate acid of aniline is  $2.34 \times 10^{-5}$ .

**Question 7.53:**

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 (a) 0.01 M (b) 0.1 M in HCl?

**Answer 7.53:**

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

$$pK_a = 4.74$$

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

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

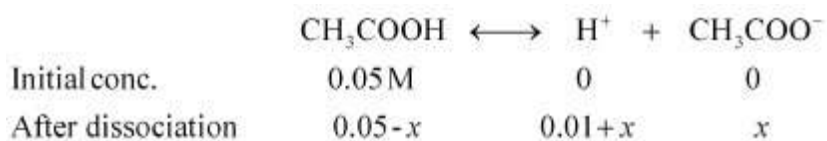
$$K_a = c\alpha^2 \quad \alpha = \sqrt{\frac{K_a}{c}}$$

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

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

**Case I:** When 0.01 M HCl is taken.

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



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.

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

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

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

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

Now,

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

**Case II:** 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:

$$[\text{CH}_3\text{COOH}] = 0.05 - X ; 0.05 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = X$$

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

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

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

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

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

Now,

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

**Question 7.54:**

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?

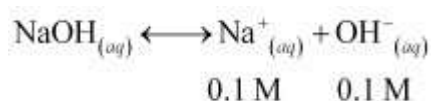
**Answer 7.54:**

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

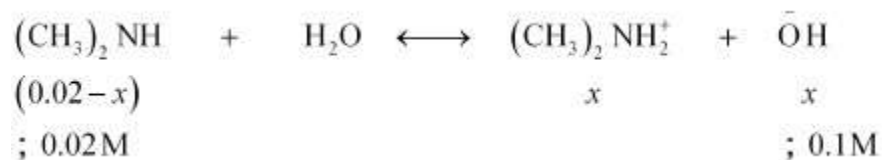
$$c = 0.02 \text{ M}$$

$$\begin{aligned} \text{Then, } \alpha &= \sqrt{\frac{K_b}{c}} \\ &= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} \\ &= 0.1643 \end{aligned}$$

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



And,



$$\text{Then, } [(\text{CH}_3)_2\text{NH}_2^+] = x$$

$$[\text{OH}^-] = x + 0.1 ; 0.1$$

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

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

$$x = 0.0054$$

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



**Question 7.55:**

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.

**Answer 7.55:**

**(a) Human muscle fluid 6.83:**

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

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

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

**(b) Human stomach fluid, 1.2:**

$$\text{pH} = 1.2$$

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

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

**(c) Human blood, 7.38:**

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

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

**(d) Human saliva, 6.4:**

$$\text{pH} = 6.4$$

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

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

**Question 7.56:**

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.

**Answer 7.56:**

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

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

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

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

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

(v) pH of egg white = 7.8

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

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

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

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

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

### Question 7.57:

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?

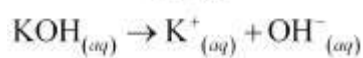
### Answer 7.57:

$$[KOH]_{aq} = \frac{0.561}{\frac{1}{5}} \text{ g/L}$$

$$= 2.805 \text{ g/L}$$

$$= 2.805 \times \frac{1}{56.11} \text{ M}$$

$$= .05 \text{ M}$$



$$[OH^-] = .05 \text{ M} = [K^+]$$

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

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

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

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

**Question 7.58:**

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.

**Answer 7.58:**

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

Then, concentration of  $\text{Sr}(\text{OH})_2$

$$\begin{aligned}
 &= \frac{19.23}{121.63} \text{ M} \\
 &= 0.1581 \text{ M} \\
 \text{Sr}(\text{OH})_{2(aq)} &\longrightarrow \text{Sr}^{2+}_{(aq)} + 2(\text{OH}^-)_{(aq)} \\
 \therefore [\text{Sr}^{2+}] &= 0.1581 \text{ M} \\
 [\text{OH}^-] &= 2 \times 0.1581 \text{ M} = 0.3162 \text{ M} \\
 \text{Now,} \\
 K_w &= [\text{OH}^-][\text{H}^+] \\
 \frac{10^{-14}}{0.3162} &= [\text{H}^+] \\
 \Rightarrow [\text{H}^+] &= 3.2 \times 10^{-14} \\
 \therefore \text{pH} &= 13.495 ; 13.50
 \end{aligned}$$

**Question 7.59:**

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?

**Answer 7.59:**

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

Then, representing propionic acid as HA, we have:

$$\begin{array}{rclcl}
 \text{HA} & + & \text{H}_2\text{O} & \longleftrightarrow & \text{H}_3\text{O}^+ & + & \text{A}^- \\
 (.05 - 0.05\alpha) \approx .05 & & & & .05\alpha & & .05\alpha \\
 K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} & & & & & & \\
 = \frac{(.05\alpha)(.05\alpha)}{0.05} = .05\alpha^2 & & & & & & \\
 \alpha = \sqrt{\frac{K_a}{.05}} = 1.63 \times 10^{-2} & & & & & & \\
 \text{Then, } [\text{H}_3\text{O}^+] = .05\alpha = .05 \times 1.63 \times 10^{-2} = K_b, 15 \times 10^{-4} \text{ M} & & & & & & \\
 \therefore \text{pH} = 3.09 & & & & & & 
 \end{array}$$

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

$$\begin{array}{l}
 \text{Then, } [\text{H}_3\text{O}^+] = 0.01 \\
 [\text{A}^-] = 0.05\alpha' \\
 [\text{HA}] = .05 \\
 K_a = \frac{0.01 \times 0.05\alpha'}{.05} \\
 1.32 \times 10^{-5} = .01 \times \alpha' \\
 \alpha' = 1.32 \times 10^{-3}
 \end{array}$$

**Question 7.60:**

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.

**Answer 7.60:**

$$c = 0.1 \text{ M}$$

$$\text{pH} = 2.34$$

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

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

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

Also,

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

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

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

$$\alpha = 45 \times 10^{-3} = .045$$

Then,

$$K_a = c\alpha^2$$

$$= 0.1 \times (45 \times 10^{-3})^2$$

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

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

**Question 7.61:**

The ionization 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.

**Answer 7.61:**

$\text{NaNO}_2$  is the salt of a strong base ( $\text{NaOH}$ ) and a weak acid ( $\text{HNO}_2$ ).

$$\begin{aligned}\text{NO}_2^- + \text{H}_2\text{O} &\longleftrightarrow \text{HNO}_2 + \text{OH}^- \\ K_h &= \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} \\ \Rightarrow \frac{K_w}{K_a} &= \frac{10^{-14}}{4.5 \times 10^{-4}} = .22 \times 10^{-10}\end{aligned}$$

Now, If  $x$  moles of the salt undergo hydrolysis, then the concentration of various species present in the solution will be:

$$\begin{aligned}[\text{NO}_2^-] &= .04 - x ; 0.04 \\ [\text{HNO}_2] &= x \\ [\text{OH}^-] &= x \\ K_h &= \frac{x^2}{0.04} = 0.22 \times 10^{-10} \\ x^2 &= .0088 \times 10^{-10} \\ x &= .093 \times 10^{-5} \\ \therefore [\text{OH}^-] &= 0.093 \times 10^{-5} \text{ M} \\ [\text{H}_3\text{O}^+] &= \frac{10^{-14}}{.093 \times 10^{-5}} = 10.75 \times 10^{-9} \text{ M} \\ \Rightarrow \text{pH} &= -\log(10.75 \times 10^{-9}) \\ &= 7.96\end{aligned}$$

Therefore, degree of hydrolysis

$$\begin{aligned}&= \frac{x}{0.04} = \frac{.093 \times 10^{-5}}{.04} \\ &= 2.325 \times 10^{-5}\end{aligned}$$

**Question 7.62:**

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

**Answer 7.62:**

$$\text{pH} = 3.44$$

We know that,

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

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

$$\text{Then, } K_h = \frac{(3.63 \times 10^{-4})^2}{0.02} \quad (\because \text{concentration} = 0.02 \text{ M})$$

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

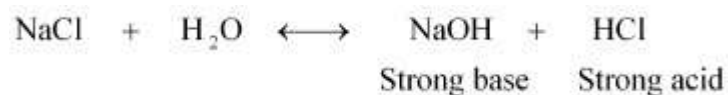
$$\text{Now, } K_h = \frac{K_w}{K_a}$$

$$\begin{aligned} \Rightarrow K_a &= \frac{K_w}{K_h} = \frac{10^{-14}}{6.6 \times 10^{-6}} \\ &= 1.51 \times 10^{-9} \end{aligned}$$

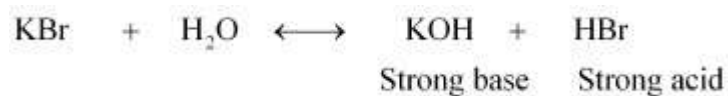
**Question 7.63:**

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

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

**Answer 7.63:****(i) NaCl:**

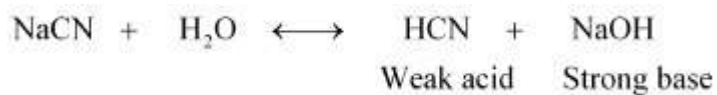
Therefore, it is a neutral solution.

**(ii) KBr:**



Therefore, it is a neutral solution.

**(iii) NaCN:**



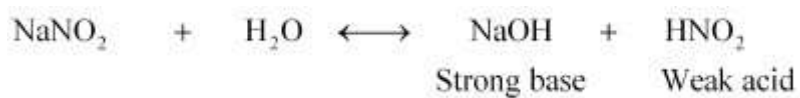
Therefore, it is a basic solution.

**(iv)  $\text{NH}_4\text{NO}_3$**



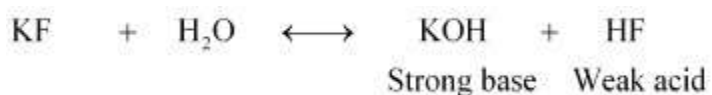
Therefore, it is an acidic solution.

**(v)  $\text{NaNO}_2$**



Therefore, it is a basic solution.

**(vi) KF**



Therefore, it is a basic solution.

**Question 7.64:**

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

**Answer 7.64:**

It is given that  $K_a$  for  $\text{ClCH}_2\text{COOH}$  is  $1.35 \times 10^{-3}$ .

$$\Rightarrow K_a = c\alpha^2$$

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

$$= \sqrt{\frac{1.35 \times 10^{-3}}{0.1}}$$

( $\therefore$  concentration of acid = 0.1m)

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

$$= 0.116$$

$$\therefore [\text{H}^+] = c\alpha = 0.1 \times 0.116$$

$$= .0116$$

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

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



$$K_b = \frac{[\text{ClCH}_2\text{COOH}][\text{OH}^-]}{[\text{ClCH}_2\text{COO}^-]}$$

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

$$K_b = \frac{10^{-14}}{1.35 \times 10^{-3}}$$

$$= 0.740 \times 10^{-11}$$

$$\text{Also, } K_b = \frac{x^2}{0.1} \quad (\text{where } x \text{ is the concentration of } \text{OH}^- \text{ and } \text{ClCH}_2\text{COOH})$$

$$0.740 \times 10^{-11} = \frac{x^2}{0.1}$$

$$0.074 \times 10^{-11} = x^2$$

$$\Rightarrow x^2 = 0.74 \times 10^{-12}$$

$$x = 0.86 \times 10^{-6}$$

$$[\text{OH}^-] = 0.86 \times 10^{-6}$$

$$\therefore [\text{H}^+] = \frac{K_w}{0.86 \times 10^{-6}}$$

$$= \frac{10^{-14}}{0.86 \times 10^{-6}}$$

$$[\text{H}^+] = 1.162 \times 10^{-8}$$

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

$$= 7.94$$

**Question 7.65:**

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

**Answer 7.65:**

Ionic product,

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

$$\text{Let } [\text{H}^+] = x.$$

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

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

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

$$\Rightarrow x = 1.64 \times 10^{-7}$$

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

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

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

$$= 6.78$$

Hence, the pH of neutral water is 6.78.

**Question 7.66:**

Calculate the pH of the resultant mixtures:

- a)** 10 mL of 0.2M  $\text{Ca}(\text{OH})_2$  + 25 mL of 0.1M HCl
- b)** 10 mL of 0.01M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.01M  $\text{Ca}(\text{OH})_2$
- c)** 10 mL of 0.1M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.1M KOH

**Answer 7.66:**

**(a)** Moles of  $\text{H}_3\text{O}^+ = \frac{25 \times 0.1}{1000} = .0025 \text{ mol}$

$$\text{Moles of OH}^- = \frac{10 \times 0.2 \times 2}{1000} = .0040 \text{ mol}$$

Thus, excess of  $\text{OH}^- = .0015 \text{ mol}$

$$[\text{OH}^-] = \frac{.0015}{35 \times 10^{-3}} \text{ mol/L} = .0428$$

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

$$= 1.36$$

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

$$= 12.63 \quad (\text{not matched})$$

**(b)**  $\text{Moles of H}_3\text{O}^+ = \frac{2 \times 10 \times 0.01}{1000} = .0002 \text{ mol}$

$$\text{Moles of OH}^- = \frac{2 \times 10 \times .01}{1000} = .0002 \text{ mol}$$

Since there is neither an excess of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$

**(c)**  $\text{Moles of H}_3\text{O}^+ = \frac{2 \times 10 \times 0.1}{1000} = .002 \text{ mol}$

$$\text{Moles of OH}^- = \frac{10 \times 0.1}{1000} = 0.001 \text{ mol}$$

Excess of  $\text{H}_3\text{O}^+ = .001 \text{ mol}$

$$\text{Thus, } [\text{H}_3\text{O}^+] = \frac{.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = .05$$

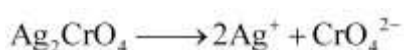
$$\therefore \text{pH} = -\log(0.05)$$

$$= 1.30$$

The solution is neutral. Hence,  $\text{pH} = 7$ .

**Question 7.67:**

Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9 (page 221). Determine also the molarities of individual ions.

**Answer 7.67:****(1) Silver chromate:**

Then,

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

Let the solubility of  $\text{Ag}_2\text{CrO}_4$  be  $s$ .

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

Then,

$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

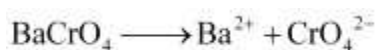
$$\Rightarrow 1.1 \times 10^{-12} = 4s^3$$

$$.275 \times 10^{-12} = s^3$$

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

$$\text{Molarity of } \text{Ag}^+ = 2s = 2 \times 0.65 \times 10^{-4} = 1.30 \times 10^{-4} \text{ M}$$

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

**(2) Barium chromate:**

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

Let the solubility of  $\text{BaCrO}_4$  be  $s$ .

$$\begin{aligned} \text{So, } [\text{Ba}^{2+}] = s \text{ and } [\text{CrO}_4^{2-}] = s & \Rightarrow K_{sp} = s^2 \\ & \Rightarrow 1.2 \times 10^{-10} = s^2 \\ & \Rightarrow s = 1.09 \times 10^{-5} \text{ M} \end{aligned}$$

Molarity of  $\text{Ba}^{2+}$  = Molarity of  $\text{CrO}_4^{2-} = s = 1.09 \times 10^{-5} \text{ M}$

### (3) Ferric hydroxide:



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

Let  $s$  be the solubility of  $\text{Fe}(\text{OH})_3$ .

$$\text{Thus, } [\text{Fe}^{3+}] = s \text{ and } [\text{OH}^-] = 3s \Rightarrow K_{sp} = s.(3s)^3$$

$$= s.27s^3$$

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

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

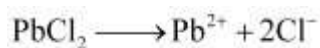
$$.037 \times 10^{-38} = s^4$$

$$.00037 \times 10^{-36} = s^4 \Rightarrow 1.39 \times 10^{-10} \text{ M} = s$$

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

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

### (4) Lead chloride:



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

Let  $K_{sp}$  be the solubility of  $\text{PbCl}_2$ .

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

$$\text{Thus, } K_{sp} = s.(2s)^2$$

$$= 4s^3$$

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

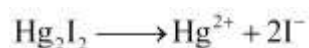
$$\Rightarrow 0.4 \times 10^{-5} = s^3$$

$$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} \text{ M} = s$$

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

Molarity of chloride =  $2s = 3.16 \times 10^{-2} \text{ M}$

**(5) Mercurous iodide:**



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

Let  $s$  be the solubility of  $\text{Hg}_2\text{I}_2$ .

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

$$\text{Thus, } K_{sp} = s(2s)^2 \Rightarrow K_{sp} = 4s^3$$

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

$$1.125 \times 10^{-29} = s^3$$

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

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

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

**Question 7.68:**

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.

**Answer 7.68:**

Let  $s$  be the solubility of  $\text{Ag}_2\text{CrO}_4$ .



$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

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

$$s = 6.5 \times 10^{-5} \text{ M}$$

Let  $s'$  be the solubility of  $\text{AgBr}$ .



$$K_{sp} = s'^2 = 5.0 \times 10^{-13}$$

$$\therefore s' = 7.07 \times 10^{-7} \text{ M}$$

Therefore, the ratio of the molarities of their saturated solution is

$$\frac{s}{s'} = \frac{6.5 \times 10^{-5} \text{ M}}{7.07 \times 10^{-7} \text{ M}} = 91.9.$$

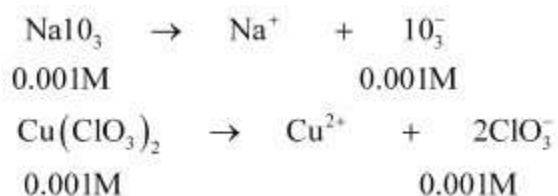
**Question 7.69:**

Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate?

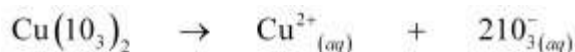
(For cupric iodate  $K_{sp} = 7.4 \times 10^{-8}$ ).

**Answer 7.69:**

When equal volumes of sodium iodate and cupric chlorate solutions are mixed together, then the molar concentrations of both solutions are reduced to half i.e., 0.001 M. Then,



Now, the solubility equilibrium for copper iodate can be written as:



Ionic product of copper iodate:

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

Since the ionic product ( $1 \times 10^{-9}$ ) is less than  $K_{sp}$  ( $7.4 \times 10^{-8}$ ), precipitation will not occur.

**Question 7.70:**

The ionization 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?

**Answer 7.70:**

Since pH = 3.19,



$$\begin{aligned}
 [\text{H}_3\text{O}^+] &= 6.46 \times 10^{-4} \text{ M} \\
 \text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} &\longleftrightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+ \\
 K_a \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} &= 6.46 \times 10^{-5} \\
 \frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} &= \frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10
 \end{aligned}$$

Let the solubility of  $\text{C}_6\text{H}_5\text{COOAg}$  be  $x$  mol/L.

Then,

$$\begin{aligned}
 [\text{Ag}^+] &= x \\
 [\text{C}_6\text{H}_5\text{COOH}] + [\text{C}_6\text{H}_5\text{COO}^-] &= x \\
 10[\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COO}^-] &= x \\
 [\text{C}_6\text{H}_5\text{COO}^-] &= \frac{x}{11} \\
 K_{sp} [\text{Ag}^+] [\text{C}_6\text{H}_5\text{COO}^-] &= 2.5 \times 10^{-13} \\
 2.5 \times 10^{-13} &= x \left( \frac{x}{11} \right) \\
 x &= 1.66 \times 10^{-6} \text{ mol/L}
 \end{aligned}$$

Thus, the solubility of silver benzoate in a pH 3.19 solution is  $1.66 \times 10^{-6}$  mol/L.

Now, let the solubility of  $\text{C}_6\text{H}_5\text{COOAg}$  be  $x'$  mol/L.

$$\begin{aligned}
 \text{Then, } [\text{Ag}^+] &= x' \text{ M and } [\text{CH}_3\text{COO}^-] = x' \text{ M.} \\
 K_{sp} &= [\text{Ag}^+] [\text{CH}_3\text{COO}^-] \\
 K_{sp} &= (x')^2 \\
 x' &= \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ mol/L} \\
 \therefore \frac{x}{x'} &= \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32
 \end{aligned}$$

Hence,  $\text{C}_6\text{H}_5\text{COOAg}$  is approximately 3.317 times more soluble in a low pH solution.

**Question 7.71:**

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,  $K_{sp} = 6.3 \times 10^{-18}$ ).

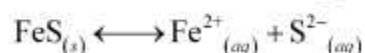
**Answer 7.71:**

Let the maximum concentration of each solution be  $x$  mol/L. After mixing, the volume of the concentrations of each solution will be reduced to half i.e.,  $x/2$ .

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

$$\text{Then, } [\text{Fe}^{2+}] = [\text{FeSO}_4] = \frac{x}{2} \text{ M}$$

$$\text{Also, } [\text{S}^{2-}] = [\text{Na}_2\text{S}] = \frac{x}{2} \text{ M}$$



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

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

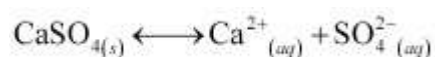
$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

$$\Rightarrow x = 5.02 \times 10^{-9}$$

If the concentrations of both solutions are equal to or less than  $5.02 \times 10^{-9} \text{ M}$ , then there will be no precipitation of iron sulphide.

**Question 7.72:**

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

**Answer 7.72:**

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

Let the solubility of  $\text{CaSO}_4$  be  $s$ .

$$\text{Then, } K_{sp} = s^2$$

$$9.1 \times 10^{-6} = s^2$$

$$s = 3.02 \times 10^{-3} \text{ mol/L}$$

Molecular mass of  $\text{CaSO}_4 = 136 \text{ g/mol}$

Solubility of  $\text{CaSO}_4$  in gram/L

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

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

This means that we need 1L of water to dissolve 0.41g of  $\text{CaSO}_4$

Therefore, to dissolve 1g of  $\text{CaSO}_4$  we require  $= \frac{1}{0.41} \text{ L} = 2.44 \text{ L}$  of water.

### Question 7.73:

The concentration of sulphide ion in 0.1M 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?

$$\text{Given } K_{sp} \text{ for } \text{FeS} = 6.3 \times 10^{-18}, \text{MnS} = 2.5 \times 10^{-13}, \text{ZnS} = 1.6 \times 10^{-24}, \\ \text{CdS} = 8.0 \times 10^{-27}$$

### Answer 7.73:

For precipitation to take place, it is required that the calculated ionic product exceeds the  $K_{sp}$  value.

Before mixing:

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

$$\text{volume} = 10 \text{ mL} \quad \text{volume} = 5 \text{ mL}$$

After mixing:

$$\begin{array}{ll} [S^{2-}] = ? & [M^{2+}] = ? \\ \text{volume} = (10 + 5) = 15 \text{ mL} & \text{volume} = 15 \text{ mL} \end{array}$$

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

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

$$\begin{aligned} \text{Ionic product} &= [M^{2+}][S^{2-}] \\ &= (1.33 \times 10^{-2})(6.67 \times 10^{-20}) \\ &= 8.87 \times 10^{-22} \end{aligned}$$

This ionic product exceeds the  $K_{sp}$  of ZnS and CdS. Therefore, precipitation will occur in CdCl<sub>2</sub> and ZnCl<sub>2</sub> solutions.