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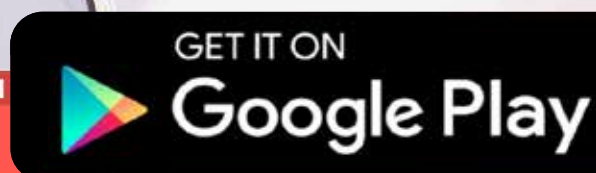
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NCERT Exercise

Question 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.

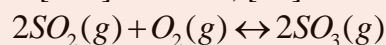
- (a) What is the initial effect of the change on vapour pressure?
- (b) How do rates of evaporation and condensation change initially?
- (c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

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



Solution 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_c for the equilibrium is 12.239 M^{-1} .

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Question 3:

At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms

$I_2(g) \leftrightarrow 2I(g)$. Calculate K_p for the equilibrium.

Solution 3:

Partial pressure of I atoms,

$$\begin{aligned} p_1 &= \frac{40}{100} \times p_{total} \\ &= \frac{40}{100} \times 10^5 \\ &= 4 \times 10^4 \text{ Pa} \end{aligned}$$

Partial pressure of I_2 molecules,

$$\begin{aligned} p_{I_2} &= \frac{60}{100} \times p_{total} \\ &= \frac{60}{100} \times 10^5 \\ &= 6 \times 10^4 \text{ Pa} \end{aligned}$$

Now, for the given reaction,

$$\begin{aligned} K_p &= \frac{(pI)^2}{p_{I_2}} \\ &= \frac{(4 \times 10^4)^2 \text{ Pa}^2}{6 \times 10^4 \text{ Pa}} \\ &= 2.67 \times 10^4 \text{ Pa} \end{aligned}$$

Question 4:

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

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

Solution 4:

$$(i) K_c = \frac{[NO_{(g)}]^2 [Cl_{2(g)}]}{[NOCl_{(g)}]^2}$$

$$(ii) K_c = \frac{[CuO_{(s)}]^2 [NO_{2(g)}]^4 [O_{2(g)}]}{[Cu(NO_3)_{2(s)}]^2}$$

$$= \frac{[NO_{2(g)}]^4 [O_{2(g)}]}{1}$$

$$(iii) K_c = \frac{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}][H_2O_{(l)}]} = \frac{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}]}$$

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

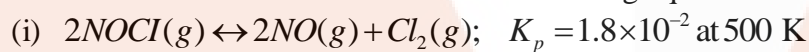
$$= \frac{1}{[Fe^{3+}_{(aq)}][OH^{-}_{(aq)}]^3}$$

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

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

Question 5:

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

**Solution 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,

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

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

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

$$K_p = 167$$

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 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?

Solution 6:

It is given that K_c for the forward reaction is 6.3×10^{14}

Then, K_c for the reverse reaction will be, $K'_c = \frac{1}{K_c}$

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

Question 7:

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

Solution 7:

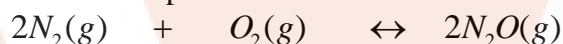
For a pure substance (both solids and liquids),

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

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 8:

Reaction between N_2 and O_2 takes place as follows:

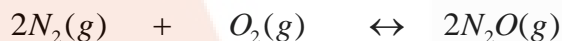


If a mixture of 0.482 mol of N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

Solution 8:

Let the concentration of N_2O at equilibrium be x .

The given reaction is:



Initial conc. 0.482 mol 0.933 mol 0

At equilibrium (0.482-x)mol (1.933-x)mol xmol

Therefore, at equilibrium, in the 10 L vessel:

$$[\text{N}_2] = \frac{0.482 - x}{10}, [\text{O}_2] = \frac{0.933 - x/2}{10}, [\text{N}_2\text{O}] = \frac{x}{10}$$

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,

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

Now,

$$K_c = \frac{[\text{N}_2\text{O}(\text{g})]^2}{[\text{N}_{2(\text{g})}]^2 [\text{O}_{2(\text{g})}]}$$

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

$$\Rightarrow \frac{x^2}{100} = 2.0 \times 10^{-37} \times (0.0482)^2 (0.0933)$$

$$\Rightarrow x^2 = 43.35 \times 10^{-40}$$

$$\Rightarrow x = 6.6 \times 10^{-20}$$

$$[N_2O] = \frac{x}{10} = \frac{6.6 \times 10^{-20}}{10} = 6.6 \times 10^{-21}$$

Question 9:

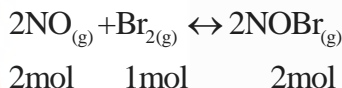
Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:



When 0.087 mol of NO and 0.0437 mol of 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 Br_2 .

Solution9:

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 Br.

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

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

$$[NO] = 0.087 \text{ mol} \quad [Br_2] = 0.0437 \text{ mol}$$

Therefore, the amount of NO present at equilibrium is:

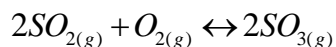
$$[NO] = 0.087 - 0.0518 = 0.0352 \text{ mol}$$

And, the amount of Br present at equilibrium is:

$$[Br_2] = 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

Question 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?

Solution 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,

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

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

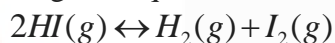
$$\Rightarrow K_c = \frac{2.0 \times 10^{10} \text{ bar}^{-1}}{(0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K})^{-1}}$$

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

$$= 74.79 \times 10^{14} \text{ L mol}^{-1}$$

Question 11:

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

**Solution 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:

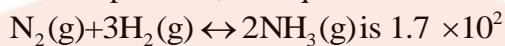
	$2HI_{(g)}$	\leftrightarrow	$H_{2(g)}$	+	$I_{2(g)}$
Initial conc.	0.2 atm		0		0
At equilibrium	0.04atm		$\frac{0.16}{2}$		$\frac{2.15}{2}$
			= 0.08atm		= 0.08atm

Therefore,

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

Question 12:

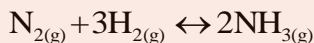
A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction



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

Solution 12:

The given reaction is:



The given concentration of various species is

$$[N_2] = \frac{1.57}{20} \text{ mol L}^{-1} \quad [H_2] = \frac{1.92}{20} \text{ mol L}^{-1}$$

$$[NH_3] = \frac{8.13}{20} \text{ mol L}^{-1}$$

Now, reaction quotient Q_c is:

$$\begin{aligned} Q_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ &= \frac{\left(\frac{8.13}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3} \\ &= 2.4 \times 10^3 \end{aligned}$$

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 13:

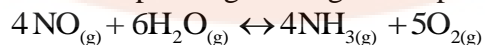
The equilibrium constant expression for a gas reaction is,

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

Write the balanced chemical equation corresponding to this expression.

Solution 13:

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



Question 14:

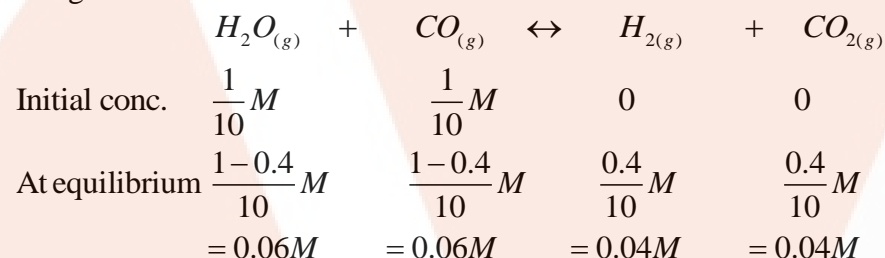
One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,



Calculate the equilibrium constant for the reaction.

Solution 14:

The given reaction is:

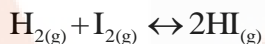


Therefore, the equilibrium constant for the reaction,

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

Question 15:

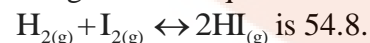
At 700 K, equilibrium constant for the reaction



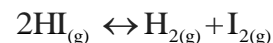
is 54.8. If 0.5 mol L^{-1} of $\text{HI}_{(\text{g})}$ is present at equilibrium at 700 K, what are the concentration of $\text{H}_{2(\text{g})}$ and $\text{I}_{2(\text{g})}$ assuming that we initially started with $\text{HI}_{(\text{g})}$ and allowed it to reach equilibrium at 700 K?

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

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

Therefore, $\frac{[H_2][I_2]}{[HI]^2} = K'_c$

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

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

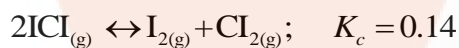
$$\Rightarrow x = 0.06754$$

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

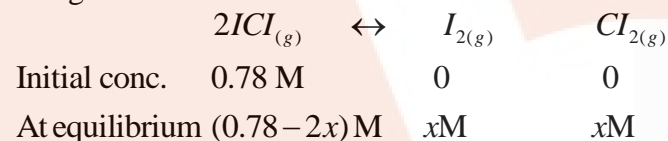
Hence, at equilibrium, $[H_2] = [I_2] = 0.068 \text{ mol L}^{-1}$

Question 16:

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

**Solution 16:**

The given reaction is:



Now, we can write,

$$\frac{[I_2][Cl_2]}{[ICl]^2} = K_c$$

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

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

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

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

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

Hence, at equilibrium,

$$[H_2] = [I_2] = 0.167 M$$

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

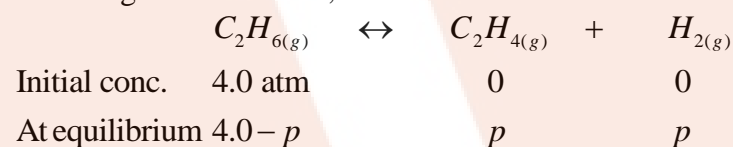
$$= 0.446 M$$

Question 17:

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

**Solution 17:**

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



We can write,

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

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

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

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

$$\text{Now, } p = \frac{-0.04 \pm \sqrt{(0.04)^2 - 4 \times 1 \times (-0.16)}}{2 \times 1}$$

$$= \frac{-0.04 \pm 0.08}{2}$$

$$= \frac{0.76}{2} \quad (\text{Taking positive value})$$

$$= 0.38$$

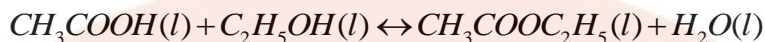
Hence, at equilibrium,

$$[C_2H_6] - 4 - p = 4 - 0.38$$

$$= 3.62 \text{ atm}$$

Question 18:

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



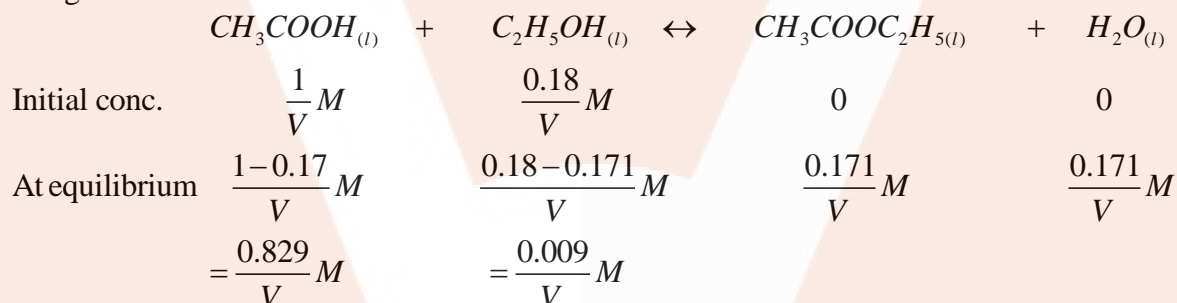
- Write the concentration ratio (reaction quotient), Q_c , for this reaction (note: water is not in excess and is not a solvent in this reaction)
- At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- 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?

Solution 18:

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

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

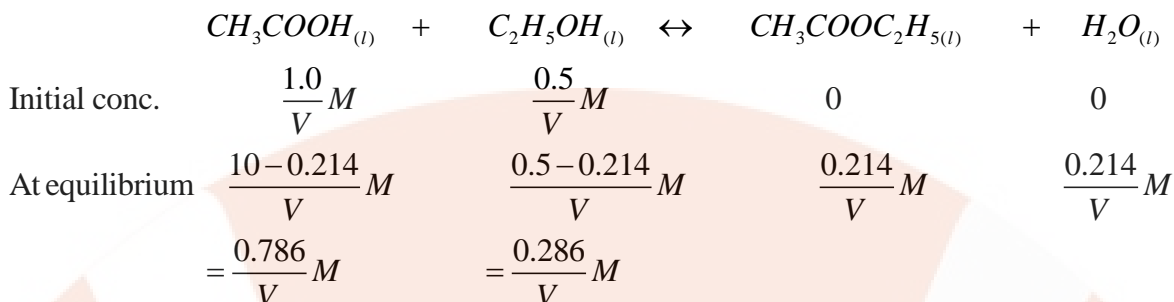
The given reaction is:



Therefore, equilibrium constant for the given reaction is:

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

- Let the volume of the reaction mixture be V .



Therefore, the reaction quotient is,

$$Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.786}{V}} = 3.919$$

$$= 0.2037$$

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

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

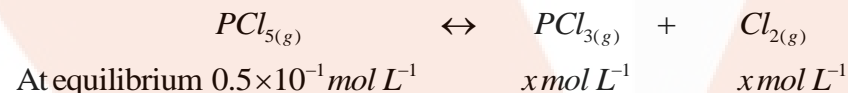
Question 19:

A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If value of K_c is 8.3×10^{-3} , what are the concentrations of PCl_3 and Cl_2 at equilibrium?



Solution 19:

Let the concentrations of both PCl_3 and 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 8.3×10^{-3} .

Now we can write the expression for equilibrium as:

$$\frac{[PCl_3][Cl_2]}{[PCl_5]} = K_c$$

$$\Rightarrow \frac{x \times x}{0.5 \times 10^{-1}} = 8.3 \times 10^{-3}$$

$$\Rightarrow x^2 = 4.15 \times 10^{-4}$$

$$\Rightarrow x = 2.04 \times 10^{-2}$$

$$= 0.0204$$

$$= 0.02 \text{ (approximately)}$$

Therefore, at equilibrium,

$$[PCl_3] = [Cl_2] = 0.02 \text{ mol L}^{-1}.$$

Question 20:

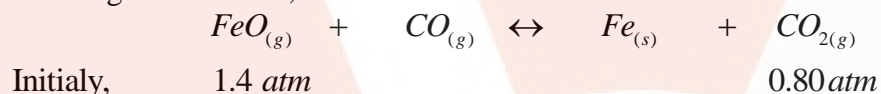
One of the reactions that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2 .



What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: $p_{CO} = 1.4 \text{ atm}$ and $p_{CO_2} = 0.80 \text{ atm}$?

Solution 20:

For the given reaction,



$$\begin{aligned} Q_p &= \frac{p_{CO_2}}{p_{CO}} \\ &= \frac{0.80}{1.4} \\ &= 0.571 \end{aligned}$$

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 CO_2 will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO_2 be p . Then, we can write,

$$K_p = \frac{p_{CO_2}}{p_{CO}}$$

$$\Rightarrow 0.265 = \frac{0.80 - p}{1.4 + p}$$

$$\Rightarrow 0.371 + 0.265p = 0.80 - p$$

$$\Rightarrow 1.265p = 0.429$$

$$\Rightarrow p = 0.339 \text{ atm}$$

Therefore, equilibrium partial of CO_2 , $p_{CO_2} = 0.80 - 0.339 = 0.461 \text{ atm}$.

And, equilibrium partial pressure of CO , $p_{CO} = 1.4 - 0.339 = 1.061 \text{ atm}$.

Question 21:

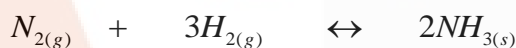
Equilibrium constant, K_c for the reaction

$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ at 500 K is 0.061.

At a particular time, the analysis shows that composition of the reaction mixture is $3.0 \text{ mol L}^{-1} N_2$, $2.0 \text{ mol L}^{-1} H_2$ and $0.5 \text{ mol L}^{-1} NH_3$. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

Solution 21:

The given reaction is:



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

Now, we know that,

$$\begin{aligned} Q_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ &= \frac{(0.5)^2}{(3.0)(2.0)^3} \\ &= 0.0104 \end{aligned}$$

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 22:

Bromine monochloride, $BrCl$ decomposes into bromine and chlorine and reaches the equilibrium:

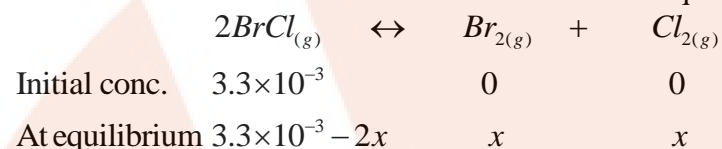


for which $K_c = 32$ at 500 K.

If initially pure 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?

Solution 22:

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



Now, we can write,

$$\frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} = K_c$$

$$\Rightarrow \frac{x \times x}{(3.3 \times 10^{-3} - 2x)^2} = 32$$

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

$$\Rightarrow x = 18.678 \times 10^{-3} - 11.32x$$

$$\Rightarrow 12.32x = 18.678 \times 10^{-3}$$

$$\Rightarrow x = 1.5 \times 10^{-3}$$

Therefore, at equilibrium

$$[\text{BrCl}] = 3.3 \times 10^{-3} - (2 \times 1.5 \times 10^{-3})$$

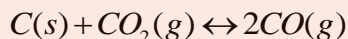
$$= 3.3 \times 10^{-3} - 3.0 \times 10^{-3}$$

$$= 0.3 \times 10^{-3}$$

$$= 3.0 \times 10^{-4} \text{ mol L}^{-1}$$

Question 23:

At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass



Calculate K_c for this reaction at the above temperature.

Solution 23:

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

Mass of CO = 90.55 g

And, mass of $\text{CO}_2 = (100 - 90.55) = 9.45 \text{ g}$

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

Number of moles of CO₂, $n_{CO_2} = \frac{9.45}{44} = 0.215 \text{ mol}$

Partial pressure of CO, $p_{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2}} \times p_{total}$

$$= \frac{3.234}{3.234 + 0.215} \times 1$$

$$= 0.938 \text{ atm}$$

Partial pressure of CO₂, $p_{CO_2} = \frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \times p_{total}$

$$= \frac{0.215}{3.234 + 0.215} \times 1$$

$$= 0.062 \text{ atm}$$

Therefore,

$$K_p = \frac{[CO]^2}{[CO_2]}$$

$$= \frac{(0.938)^2}{0.062}$$

$$= 14.19$$

For the given reaction,

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

We know that,

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

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

$$\Rightarrow K_c = \frac{14.19}{0.082 \times 1127}$$

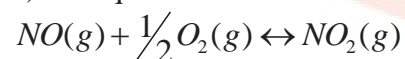
$$= 0.154 \text{ (approximately)}$$

Question 24:

Calculate

a) ΔG° and

b) the equilibrium constant for the formation of NO₂ from NO and O₂ at 298 K



Where:

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

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

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

Solution 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,

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

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

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

$$= 6.134$$

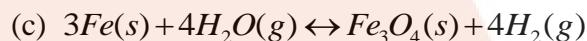
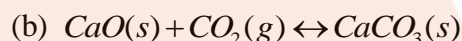
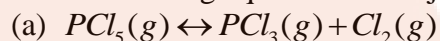
$$\therefore K_c = \text{antilog}(6.134)$$

$$= 1.36 \times 10^6$$

Hence, the equilibrium constant for the given reaction K_c is 1.36×10^6 .

Question 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?

**Solution 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 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.

- (i) $\text{COCl}_2(g) \leftrightarrow \text{CO}(g) + \text{Cl}_2(g)$
- (ii) $\text{CH}_4(g) + 2\text{S}_2(g) \leftrightarrow \text{CS}_2(g) + 2\text{H}_2\text{S}(g)$
- (iii) $\text{CO}_2(g) \leftrightarrow \text{C}(s) + 2\text{CO}(g)$
- (iv) $2\text{H}_2(g) + \text{CO}(g) \leftrightarrow \text{CH}_3\text{OH}(g)$
- (v) $\text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g)$
- (vi) $4\text{NH}_3(g) + 5\text{O}_2(g) \leftrightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$

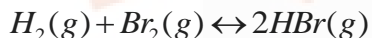
Solution 26:

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 27:

The equilibrium constant for the following reaction is 1.6×10^5 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.

Solution 27:

Given,

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

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

$$K'_p = \frac{1}{K_p}$$

$$= \frac{1}{1.6 \times 10^5}$$

$$= 6.25 \times 10^{-6}$$

Now, let p be the pressure of both H_2 and Br_2 at equilibrium.

	$2\text{HBr}_{(g)}$	\leftrightarrow	$\text{H}_{2(g)}$	+	$\text{Br}_{2(g)}$
Initial conc.	10		0		0
At equilibrium	$10 - 2p$		p		p

Now, we can write,

$$\frac{P_{\text{HBr}} \times P_2}{P_{\text{HBr}}^2} = K_p'$$

$$\frac{p \times p}{(10 - 2p)^2} = 6.25 \times 10^{-6}$$

$$\frac{p}{10 - 2p} = 2.5 \times 10^{-3}$$

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

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

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

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

Therefore, at equilibrium,

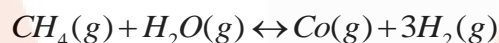
$$[\text{H}_2] = [\text{Br}_2] = 2.49 \times 10^{-2} \text{ bar}$$

$$[\text{HBr}] = 10 - 2 \times (2.49 \times 10^{-2}) \text{ bar}$$

$$= 9.95 \text{ bar} = 10 \text{ bar (approximately)}$$

Question 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
 - (i) Increasing the pressure
 - (ii) Increasing the temperature
 - (iii) Using a catalyst?

Solution 28:

- (a) For the given reaction,

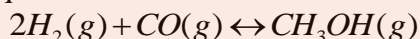
$$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}^3}{P_{\text{CH}_4} \times P_{\text{H}_2\text{O}}}$$

- (b)
 - (i) According to Le Chatelier's principle, the equilibrium will shift in the backward direction.
 - (ii) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.
 - (iii) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increases the rate of a reaction. Thus, equilibrium will be attained quickly.

Question 29:

Describe the effect of:

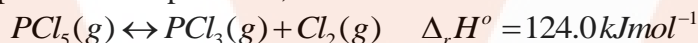
- Addition of H_2
- Addition of CH_3OH
- Removal of CO
- Removal of CH_3OH on the equilibrium of the reaction:

**Solution 29:**

- According to Le Chatelier's principle, on addition of H_2 , the equilibrium of the given reaction will shift in the forward direction.
- On addition of CH_3OH , the equilibrium will shift in the backward direction.
- On removing CO , the equilibrium will shift in the backward direction.
- On removing CH_3OH , the equilibrium will shift in the forward direction.

Question 30:

At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as,



- Write an expression for K_c for the reaction.
- What is the value of K_c for the reverse reaction at the same temperature?
- What would be the effect on K_c if
 - more PCl_5 is added
 - pressure is increased?
 - The temperature is increased?

Solution 30:

$$(a) K_c = \frac{[PCl_{3(g)}][Cl_{2(g)}]}{[PCl_{5(g)}]}$$

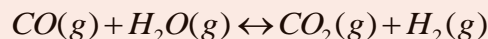
- Value of K_c for the reverse reaction at the same temperature is:

$$\begin{aligned} K'_c &= \frac{1}{K_c} \\ &= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2 \\ &= 120 - 48 \end{aligned}$$

- K_c would remain the same because in this case, the temperature remains the same.
 - K_c is constant at constant temperature. Thus, in this case, K_c would not change.
 - 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 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 H₂. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

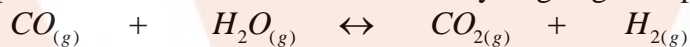


If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H₂ at equilibrium?

$K_p = 10.1$ at 400°C

Solution 31:

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



Initial conc. 4.0 bar 4.0 bar 0 0

At equilibrium 4.0 – p 4.0 – p p p

It is given that $K_p = 10.1$

Now,

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

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

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

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

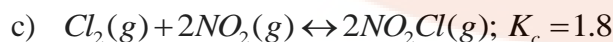
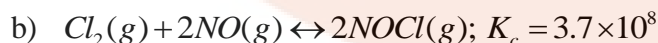
$$\Rightarrow 4.178p = 12.712$$

$$\Rightarrow p = 3.04$$

Hence, at equilibrium, the partial pressure of H₂ will be 3.04 bar.

Question 32:

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

**Solution 32:**

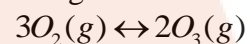
If the value of K_c lies between 10^{-3} and 10^3 , a reaction has appreciable concentration of reactants and products. Thus, the reaction given in (c) will have appreciable concentration of reactants and products.

Question 33:

The value of K_c for the reaction $3O_2(g) \leftrightarrow 2O_3(g)$ is 2.0×10^{-50} at 25°C . If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} , what is the concentration of O_3 ?

Solution 33:

The given reaction is:



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

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

Then, we have,

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

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

$$\Rightarrow [O_{3(g)}]^2 = 8.192 \times 10^{-50}$$

$$\Rightarrow [O_{3(g)}] = 2.86 \times 10^{-28} M$$

Hence, the concentration of O_3 is $2.86 \times 10^{-28} M$.

Question 34:

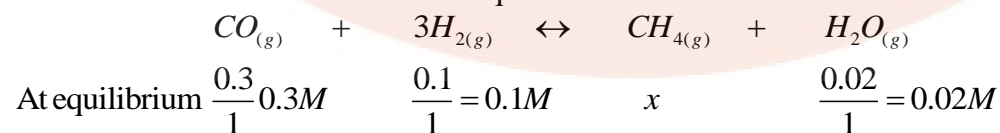
The reaction, $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1L flask.

It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture.

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

Solution 34:

Let the concentration of methane at equilibrium be x.



It is given that $K_c = 3.90$.

Therefore,

$$\frac{[CH_{4(g)}][H_2O_{(g)}]}{[CO_{(g)}][H_{2(g)}]^3} = K_c$$

$$\Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} = 3.90$$

$$\Rightarrow x = \frac{3.90 \times 0.3 \times (0.1)^3}{0.02}$$

$$= \frac{0.00117}{0.02}$$

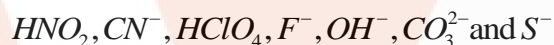
$$= 0.0585M$$

$$= 5.85 \times 10^{-2} M$$

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

Question 35:

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



Solution 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**

HNO_2 NO_3^- (base)

CN^- HCN (acid)

$HClO_4$ ClO_4^- (base)

F^- HF (acid)

OH^- H_2O (acid) / O^{2-} (base)

CO_3^{2-} HCO_3^- (acid)

S^{2-} HS^- (acid)

Question 36:

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

Solution 36:

Lewis acids are those acids which can accept a pair of electrons. For example, BF_3 , H^+ , and

NH_4^+ are Lewis acids.

Question 37:

What will be the conjugate bases for the Brønsted acids: HF, H_2SO_4 and HCO_3^- ?

Solution 37:

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

Brønsted acid	Conjugate base
HF	F^-
H_2SO_4	HSO_4^-
HCO_3^-	CO_3^{2-}

Question 38:

Write the conjugate acids for the following Brønsted bases: NH_2^- , NH_3 and HCOO^- .

Solution 38:

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

Brønsted base	Conjugate acid
NH_2^-	NH_3
NH_3	NH_4^+
HCOO^-	HCOOH

Question 39:

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

Solution 39:

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

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

Question 40:

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

- (a) OH^-
- (b) F^-
- (c) H^+
- (d) BCl_3 .

Solution 40:

- (a) OH^- is a Lewis base since it can donate its lone pair of electrons.
- (b) F^- is a Lewis base since it can donate a pair of electrons.
- (c) H^+ is a Lewis acid since it can accept a pair of electrons.
- (d) BCl_3 is a Lewis acid since it can accept a pair of electrons.

Question 41:

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

Solution 41:

Given,

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

\therefore pH Value of soft drink

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

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

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

$$= -\log 3.8 + 3$$

$$= -0.58 + 3$$

$$= 2.42$$

Question 42:

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

Solution 42:

Given, pH

$$= 3.76$$

It is known that,

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

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

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

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

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

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

Question 43:

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

Solution 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^-

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

$$= \frac{10^{-14}}{6.8 \times 10^{-4}}$$

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

Given,

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

Hence, K_b of its conjugate base HCOO^-

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

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

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

Given,

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

Hence, K_b of its conjugate base CN^-

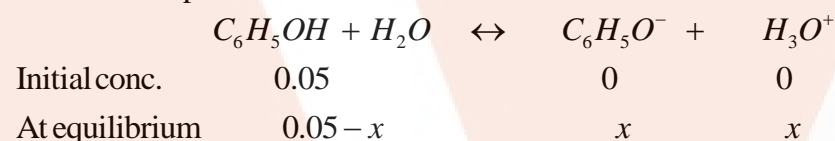
$$\begin{aligned}
 &= \frac{K_w}{K_a} \\
 &= \frac{10^{-14}}{4.8 \times 10^{-9}} \\
 &= 2.08 \times 10^{-6}
 \end{aligned}$$

Question 44:

The ionization constant of phenol is 1.0×10^{-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?

Solution 44:

Ionization of phenol:



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

$$K_a = \frac{x \times x}{0.05 - x}$$

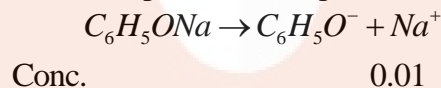
As the value of the ionization constant is very less, x will be very small. Thus, we can ignore x in the denominator.

$$\begin{aligned}
 \therefore x &= \sqrt{1 \times 10^{-10} \times 0.05} \\
 &= \sqrt{5 \times 10^{-12}} \\
 &= 2.2 \times 10^{-6} M = [H_3O^+]
 \end{aligned}$$

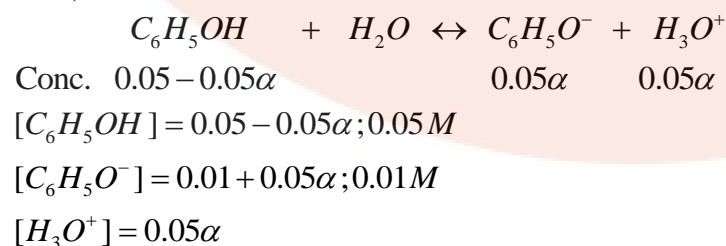
Since $[H_3O^+] = [C_6H_5O^-]$

$$[C_6H_5O^-] = 2.2 \times 10^{-6} M$$

Now, let α be the degree of ionization of phenol in the presence of 0.01 M C_6H_5ONa .



Also,



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

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

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

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

Question 45:

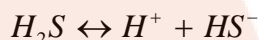
The first ionization constant of H_2S is 9.1×10^{-8} . Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13} , calculate the concentration of S^{2-} under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

Solution 45:

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

Case I (in the absence of HCl):

Let the concentration of HS^- be x M.



$$C_i \quad 0.1 \quad 0 \quad 0$$

$$C_f \quad 0.1-x \quad x \quad x$$

Then,

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

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

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

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

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

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

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

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

Case II (in the presence of HCl):

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

Then, $H_2S \leftrightarrow HS^- + H^+$

$$C_i \quad 0.1 \quad 0 \quad 0$$

$$C_f \quad 0.1 - y \quad y \quad y$$

$$\text{Now, } K_{a_1} = \frac{[HS^-][H^+]}{[H_2S]}$$

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

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

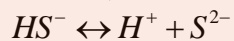
$$(\text{and } 0.1 + y ; 0.1M)$$

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

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

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.

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

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

$$[S^{2-}] X'$$

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

$$1.2 \times 10^{-13} = \frac{(0.1)(X')}{9.1 \times 10^{-8}}$$

$$10.92 \times 10^{-21} = 0.1 X'$$

$$\frac{10.92 \times 10^{-21}}{0.1} = X'$$

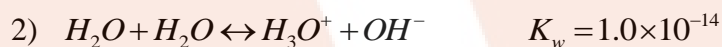
$$X' = \frac{1.092 \times 10^{-20}}{0.1}$$

$$= 1.092 \times 10^{-10} M$$

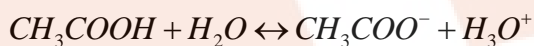
$$\Rightarrow K_{a_1} = 1.74 \times 10^{-5}$$

Question 46:

The ionization constant of acetic acid is 1.74×10^{-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.

Solution 46:**Method 1**

Since $K_a \gg K_w$,



$C_i = 0.05$	0	0
$0.05 - 0.05\alpha$	0.05α	0.05α

$$K_a = \frac{(.05\alpha)(.05\alpha)}{(0.05 - 0.05\alpha)}$$

$$= \frac{(.05\alpha)(0.05\alpha)}{.05(1 - \alpha)}$$

$$= \frac{.05\alpha^2}{1 - \alpha}$$

$$1.74 \times 10^{-5} = \frac{.05\alpha^2}{1 - \alpha}$$

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

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

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

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

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

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

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

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

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

$$= CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

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

$$[CH_3COO^-] = 0.05 \times 1.86 \times 10^{-3}$$

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

$$= .000093$$

Method 2

Degree of dissociation,

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

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

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

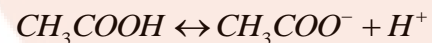
Then,

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

$$\alpha = \sqrt{3.48 \times 10^{-5}}$$

$$\alpha = \sqrt{3.48} \times 10^{-4}$$

$$\alpha = 1.8610^{-2}$$

Thus, concentration of $CH_3COO^- = c \cdot \alpha$

$$= .05 \times 1.86 \times 10^{-2}$$

$$= .093 \times 10^{-2}$$

$$= .00093 \text{ M}$$

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

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

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

$$= -\log(0.093 \times 10^{-2}),$$

$$\therefore pH = 3.03$$

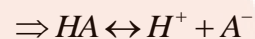
Hence, the concentration of acetate ion in the solution is 0.00093 M and its pH is 3.03.

Question 47:

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

Solution 47:

Let the organic acid be HA.



Concentration of HA = 0.01 M

pH = 4.15

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

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

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

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

$$[HA] = 0.01$$

Then,

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

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

$$pK_a = -\log K_a$$

$$= -\log K_a$$

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

$$pK_a = 6.3001$$

Question 48:

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

(i) 0.003 M HCl

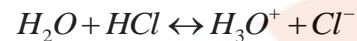
(ii) 0.005 M NaOH

(iii) 0.002 M HBr

(iv) 0.002 M KOH

Solution 48:

(i) 0.003 M HCl:



Since HCl is completely ionized,

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

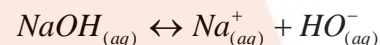
$$\Rightarrow [H_3O^+] = 0.003$$

Now,

$$\begin{aligned} pH &= -\log[H_3O^+] = -\log(.003) \\ &= 2.52 \end{aligned}$$

Hence, the pH of the solution is 2.52.

(ii) 0.005 M NaOH:



$$[HO^-] = [NaOH]$$

$$\Rightarrow [HO^-] = .005$$

$$pOH = -\log[HO^-] = -\log(.005)$$

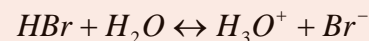
$$pOH = 2.30$$

$$\therefore pH = 14 - 2.30$$

$$= 11.70$$

Hence, the pH of the solution is 11.70.

(iii) 0.002 M HBr:



$$[H_3O^+] = [HBr]$$

$$\Rightarrow [H_3O^+] = .002$$

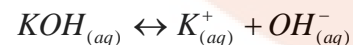
$$\therefore pH = \log[H_3O^+]$$

$$= -\log(0.002)$$

$$= 2.69$$

Hence, the pH of the solution is 2.69.

(iv) 0.002 M KOH:



$$[OH^-] = [KOH]$$

$$\Rightarrow [OH^-] = .002$$

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

$$= 2.69$$

$$\therefore pH = 14 - 2.69$$

$$= 11.31$$

Hence, the pH of the solution is 11.31.

Question 49:

Calculate the pH of the following solutions:

- 2 g of TIOH dissolved in water to give 2 litre of solution.
- 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.
- 0.3 g of NaOH dissolved in water to give 200 mL of solution.
- 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

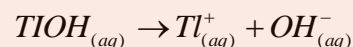
Solution 49:

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

$$[TIOH_{(aq)}] = \frac{2}{2} g / L$$

$$= \frac{2}{2} \times \frac{1}{221} M$$

$$= \frac{1}{221} M$$



$$[OH^-_{(aq)}] = [TIOH_{(aq)}] = \frac{1}{221} M$$

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

$$10^{-14} = [H^+] \left(\frac{1}{221} \right)$$

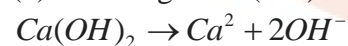
$$221 \times 10^{-14} = [H^+]$$

$$\Rightarrow pH = -\log[H^+] = -\log(221 \times 10^{-14})$$

$$= -\log(2.21 \times 10^{-12})$$

$$= 11.65$$

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



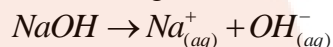
$$[Ca(OH)_2] = 0.3 \times \frac{1000}{500} = 0.6M$$

$$[OH^-]_{aq} = 2 \times [Ca(OH)_{2aq}] = 2 \times 0.6 \\ = 1.2M$$

$$[H^+] = \frac{K_w}{[OH^-]_{aq}} \\ = \frac{10^{-14}}{1.2} M \\ = 0.833 \times 10^{-14}$$

$$pH = -\log(0.833 \times 10^{-14}) \\ = -\log(8.33 \times 10^{-13}) \\ = (-0.902 + 13) \\ = 12.098$$

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



$$[NaOH] = 0.3 \times \frac{1000}{200} = 1.5M$$

$$[OH^-]_{aq} = 1.5M$$

$$\text{Then, } [H^+] = \frac{10^{-14}}{1.5} \\ = 6.66 \times 10^{-13}$$

$$pH = -\log(6.66 \times 10^{-13}) \\ = 12.18$$

(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)

$$13.6 \times 10^{-3} = M_2 \times 1L \\ = 1.36 \times 10^{-2} [H^+] = 1.36 \times 10^{-2} \text{ pH} = -\log(1.36 \times 10^{-2}) \\ = (-0.1335 + 2) = 1.866 \approx 1.87$$

Question 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.

Solution 50:

Degree of ionization, $\alpha = 0.132$

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

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

$$= 0.1 \times 0.132$$

$$= 0.0132$$

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

$$= -\log(0.0132)$$

$$= 1.879 : 1.88$$

Now,

$$K_a = C\alpha^2$$

$$= 0.1 \times (0.132)^2$$

$$K_a = .0017$$

$$\text{p}K_a = 2.75$$

Question 51:

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

Solution 51:

Degree of ionization, $\alpha = 0.132$

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

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

$$= 0.1 \times 0.132$$

$$= 0.0132$$

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

$$= -\log(0.0132)$$

$$= 1.879 : 1.88$$

Now,

$$K_a = C\alpha^2$$

$$= 0.1 \times (0.132)^2$$

$$K_a = .0017$$

$$\text{p}K_a = 2.75$$

Question 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.

Solution 52:

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

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

$$\text{pH} = ?$$

$$\alpha = ?$$

$$K_a = C\alpha^2$$

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

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

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

$$\begin{aligned}\text{Then, [anion]} &= c\alpha = 0.01 \times 6.53 \times 10^{-5} \\ &= 0.65 \times 10^{-5}\end{aligned}$$

$$\begin{aligned}\text{pOH} &= -\log(0.65 \times 10^{-5}) \\ &= 6.187\end{aligned}$$

$$\text{pH} = 7.813$$

Now,

$$K_a \times K_b = K_w$$

$$\therefore 4.27 \times 10^{-10} \times K_a = K_w$$

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

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

Question 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?

Solution 53:

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

$$\text{pK}_a = 4.74$$

$$\text{pK}_a = -\log(K_a)$$

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

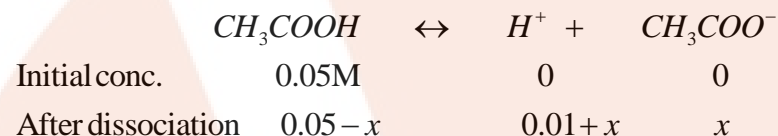
$$K_a = c\alpha^2 \quad \alpha = \sqrt{\frac{K_a}{c}}$$

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

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.

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

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

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

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

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:

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

$$[CH_3COO^-] = X$$

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

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

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

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

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

Now,

$$\alpha = \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}}$$

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

$$= 1.82 \times 10^{-4}$$

Question 54:

The ionization constant of dimethylamine is 5.4×10^{-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?

Solution 54:

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

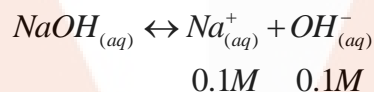
$$c = 0.02 \text{ M}$$

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

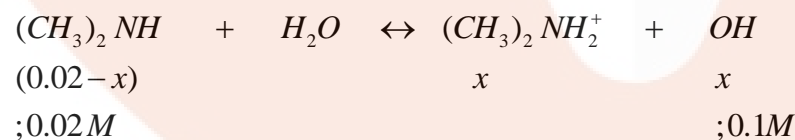
$$= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}}$$

$$= 0.1643$$

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



And,



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

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

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

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

$$x = 0.0054$$

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

Question 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.

Solution 55:**(a) Human muscle fluid 6.83:**

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

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

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

(b) Human stomach fluid, 1.2:

$$pH = 1.2$$

$$1.2 = -\log [H^+]$$

$$\therefore [H^+] = 0.063$$

(c) Human blood, 7.38:

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

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

(d) Human saliva, 6.4:

$$pH = 6.4$$

$$6.4 = -\log [H^+]$$

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

Question 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.

Solution 56:

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

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

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

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

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

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

(v) pH of egg white = 7.8

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

$$7.8 = -\log [\text{H}^+] \log$$

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

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

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

Question 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?

Solution 57:

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

$$\begin{aligned}
 &= 2.805 \times \frac{1}{56.11} M \\
 &= .05 M \\
 KOH_{aq} &\rightarrow K_{(aq)}^{+} + OH_{(aq)}^{-} \\
 [OH^{-}] &= .05 M = [K^{+}] \\
 [H^{+}][H^{-}] &= K_w \\
 [H^{+}] &= \frac{K_w}{[OH^{-}]} \\
 &= \frac{10^{-14}}{0.05} = 2 \times 10^{-11} M \\
 \therefore pH &= 12.70
 \end{aligned}$$

Question 58:

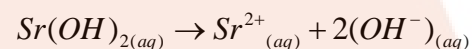
The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

Solution 58:

Solubility of $Sr(OH)_2 = 19.23$ g/L

Then, concentration of $Sr(OH)_2$

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



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

$$[OH^{-}] = 2 \times 0.1581 M = 0.3126 M$$

Now,

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

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

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

$$\therefore pH = 13.495 ; 13.50$$

Question 59:

The ionization constant of propanoic acid is 1.32×10^{-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?

Solution 59:

Let the degree of ionization of propanoic acid be α .

Then, representing propionic acid as HA, we have:



$$(.05 - 0.0\alpha) \approx 0.5 \qquad .05\alpha \qquad .05\alpha$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{(.05\alpha)(.05\alpha)}{0.05} = .05\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{.05}} = 1.63 \times 10^{-2}$$

$$\text{Then, } [H_3O^+] = .05\alpha = .05 \times 1.63 \times 10^{-2} = K_b \cdot 15 \times 10^{-4} M$$

$$\therefore \text{pH} = 3.09$$

In the presence of 0.1M of HCl, let α' be the degree of ionization.

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

$$[A^-] = .005\alpha'$$

$$[HA] = .05$$

$$K_a = \frac{0.01 \times .05\alpha'}{.05}$$

$$1.32 \times 10^{-5} = .01 \times \alpha'$$

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

Question 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.

Solution 60:

$$c = 0.1 M$$

$$\text{pH} = 2.34$$

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

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

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

Also,

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

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

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

$$\alpha = 4.5 \times 10^{-3} = .045$$

Then,

$$K_a = c\alpha^2$$

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

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

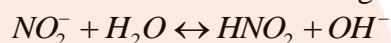
$$= 2.02 \times 10^{-4}$$

Question 61:

The ionization constant of nitrous acid is 4.5×10^{-4} . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

Solution 61:

NaNO_2 is the salt of a strong base (NaOH) and a weak acid (HNO_2).



$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$$

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5 \times 10^{-4}} = .22 \times 10^{-10}$$

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

$$[\text{NO}_2^-] = .04 - x ; 0.04$$

$$[\text{HNO}_2] = x$$

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

$$K_b = \frac{x^2}{0.04} = 0.22 \times 10^{-10}$$

$$x^2 = .0088 \times 10^{-10}$$

$$x = .093 \times 10^{-5}$$

$$\therefore [OH^-] = 0.093 \times 10^{-5} M$$

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

$$\Rightarrow pH = -\log(10.75 \times 10^{-9})$$

$$= 7.96$$

Therefore, degree of hydrolysis

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

$$= 2.325 \times 10^{-5}$$

Question 62:

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

Solution 62:

$$pH = 3.44$$

We know that,

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

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

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

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

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

$$\Rightarrow K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{6.6 \times 10^{-6}}$$

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

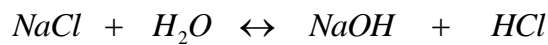
Question 63:

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

NaCl, KBr, NaCN, NH_4NO_3 , $NaNO_2$ and KF

Solution 63:

(i) NaCl:



Strong base Strong base

Therefore, it is a neutral solution.

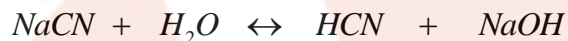
(ii) KBr:



Strong base Strong base

Therefore, it is a neutral solution.

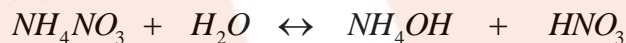
(iii) NaCN:



Weak acid Strong base

Therefore, it is a basic solution.

(iv) NH_4NO_3



Weak acid Strong base

Therefore, it is an acidic solution.

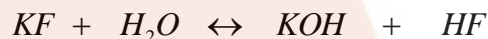
(v) NaNO_2



Strong base Weak acid

Therefore, it is a basic solution.

(vi) KF



Strong base Weak acid

Therefore, it is a basic solution.

Question 64:

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

Solution 64:

It is given that K_a for ClCH_2COOH is 1.35×10^{-3} .

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

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

$$= \sqrt{\frac{1.35 \times 10^{-3}}{0.1}} \quad (\because \text{concentration of acid} = 0.1\text{M})$$

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

$$= 0.116$$

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

$$= 0.116$$

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

$\text{ClCH}_2\text{COONa}$ is the salt of a weak acid i.e., ClCH_2COOH and a strong base i.e., NaOH .



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

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

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

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

Also, $K_b = \frac{x^2}{0.1}$ (where x is the concentration of OH^- and ClCH_2COOH)

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

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

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

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

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

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

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

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

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

$$= 7.94$$

Question 65:

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

Solution 65:

Ionic product,

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

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

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

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

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

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

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

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

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

$$= 6.78$$

Hence, the pH of neutral water is 6.78.

Question 66:

Calculate the pH of the resultant mixtures:

- 10 mL of 0.2M Ca(OH)_2 + 25 mL of 0.1M HCl
- 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M Ca(OH)_2
- 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

Solution 66:

$$\text{(a) Moles of } H_3O^+ = \frac{25 \times 0.1}{1000} = .0025 \text{ mol}$$

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

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

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

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

$$= 1.36$$

$$pH = 14 - 1.36$$

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

$$\text{(b) Moles of } H_3O^+ = \frac{2 \times 10 \times 0.1}{1000} = .0002 \text{ mol}$$

$$\text{Moles of } OH^- = \frac{2 \times 10 \times 0.1}{1000} = .0002 \text{ mol}$$

Since there is neither an excess of H_3O^+ or OH^-

The solution is neutral. Hence, $pH = 7$.

$$(c) \text{ Moles of } H_3O^+ = \frac{2 \times 10 \times 0.1}{1000} = .002 \text{ mol}$$

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

Excess of $H_3O^+ = .001 \text{ mol}$

$$\text{Thus, } [H_3O^+] = \frac{.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = .05$$

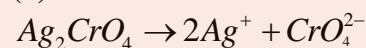
$$\therefore pH = -\log(0.05) \\ = 1.30$$

Question 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.

Solution 67:

(1) Silver chromate:



Then,

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$

Let the solubility of Ag_2CrO_4 be s .

$$\Rightarrow [Ag^+] = 2s \text{ and } [CrO_4^{2-}] = s$$

Then,

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

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

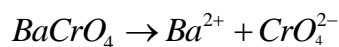
$$.275 \times 10^{-12} = s^3$$

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

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

$$\text{Molarity of } CrO_4^{2-} = s = 0.65 \times 10^{-4} \text{ M}$$

(2) Barium chromate:



$$\text{Then, } K_{sp} = [Ba^{2+}][CrO_4^{2-}]$$

Let the solubility of $BaCrO_4$ be s .

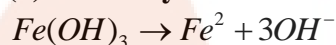
$$\text{So, } [Ba^{2+}] = s \text{ and } [CrO_4^{2-}] = s \Rightarrow K_{sp} = s^2$$

$$\Rightarrow 1.2 \times 10^{-10} = s^2$$

$$\Rightarrow s = 1.09 \times 10^{-5} M$$

$$\text{Molarity of } Ba^{2+} = \text{Molarity of } CrO_4^{2-} = s = 1.09 \times 10^{-5} M$$

(3) Ferric hydroxide:



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

Let s be the solubility of $Fe(OH)_3$

$$\text{Thus, } [Fe^{3+}] = s \text{ and } [OH^{-}] = 3s$$

$$\Rightarrow K_{sp} = s.(3s)^3$$

$$= s.27s^3$$

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

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

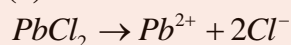
$$.037 \times 10^{-38} = 27s^4$$

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

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

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

(4) Lead chloride:



$$K_{SP} = [Pb^{2+}][Cl^{-}]^2$$

Let K_{SP} be the solubility of $PbCl_2$.

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

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

$$= 4s^3$$

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

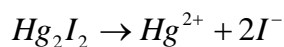
$$\Rightarrow 0.4 \times 10^{-5} = s^3$$

$$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} M = S.1$$

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

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

(5) Mercurous iodide:



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

Let s be the solubility of Hg_2I_2 .

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

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

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

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

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

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

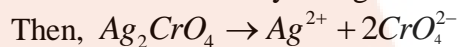
$$\text{Molarity of } \text{I}^- = 2s = 4.48 \times 10^{-10} \text{ M}$$

Question 68:

The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Solution 68:

Let s be the solubility of Ag_2CrO_4 .

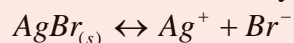


$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

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

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

Let s' be the solubility of 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 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?

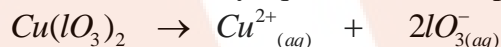
(For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

Solution 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:

$$= [Cu^{2+}] \times [IO_3^-]^2$$

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

$$= 1 \times 10^{-9}$$

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

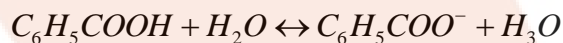
Question 70:

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

Solution 70:

Since pH = 3.19,

$$[H_3O^+] = 6.46 \times 10^{-4} M$$



$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

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

Let the solubility of C_6H_5COOAg be x mol/L.

Then,

$$[Ag^+] = x$$

$$[C_6H_5COOH] + [C_6H_5COO^-] = x$$

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

$$[C_6H_5COO^-] = \frac{x}{11}$$

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

$$2.5 \times 10^{-13} = x \left(\frac{x}{11} \right)$$

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

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

Now, let the solubility of C_6H_5COOAg be $x' \text{ mol/L}$.

Then, $[Ag^+] = x' M$ and $[C_6H_5COO^-] = x' M$.

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

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

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

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

Hence, C_6H_5COOAg is approximately 3.317 times more soluble in a low pH solution.

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

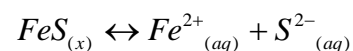
Solution 71:

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

$$\therefore [FeSO_4] = [Na_2S] = \frac{x}{2} M$$

$$\text{Then, } [Fe^{2+}] = [FeSO_4] = \frac{x}{2} M$$

$$\text{Also, } [S^{2-}] = [Na_2S] = \frac{x}{2} M$$



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

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

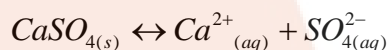
$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

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

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

Question 72:

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

Solution 72:

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

Let the solubility of $CaSO_4$ 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 $CaSO_4 = 136 \text{ g/mol}$

Solubility of $CaSO_4$ 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 $CaSO_4$

Therefore, to dissolve 1g of $CaSO_4$ we require $= \frac{1}{0.41} \text{ L} = 2.44 \text{ L}$ of water.

Question 73:

The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following:

$FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

Given K_{sp} for $Fes = 6.3 \times 10^{-18}$, $MnS = 2.5 \times 10^{-13}$, $ZnS = 1.6 \times 10^{-24}$,

$$CdS = 8.0 \times 10^{-27}$$

Solution 73:

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

Before mixing:

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

volume = 10 mL

volume = 5 mL

After mixing:

$$[S^{2-}] = ? \quad [M^{2+}] = ?$$

volume = (10+5) = 15 mL

volume = 15 mL

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

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

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

This ionic product exceeds the K_{sp} of ZnS and CdS. Therefore, precipitation will occur in $CdCl_2$ and $ZnCl_2$ solutions.

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