NCERT SOLUTIONS
CLASS-XI CHEMISTRY
CHAPTER-7
EQUILIBRIUM

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

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

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

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

Ans.

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

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

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

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

: $[SO_2]$= 0.6 M, $[O_2]$ = 0.82 M and $[SO_3]$ = 1.9 M ?

$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$

Ans.

As per the question,

$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$ (Given)

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

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

$= 12.229 M^{-1}$

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

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

$I_2(g) \leftrightarrow 2I(g)$

Find K_p for the equilibrium.

Ans.

Partial pressure of Iodine atoms (I)

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

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

$= 4 \times 10^4 Pa$

Partial pressure of I_2 molecules,

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

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

$= 6 \times 10^4 Pa$

Now, for the given reaction,

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

$= 2.67 \times 10^4 Pa$

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

(i)$2NOCl(g) \leftrightarrow 2NO(g) + Cl_2(g)$

(ii)$2Cu(NO_3)_2(s) \leftrightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii)$CH_3COOC_2H_5(aq) + H_2O(1) \leftrightarrow CH_3COOH(aq) + C_2H_5OH(aq)$

(iv)$Fe^{3+}(aq) + 3OH^-(aq) \leftrightarrow Fe(OH)_3(s)$

(v)$I_2(s) + 5F_2 \leftrightarrow 2IF_5$

Ans.

$$K_C = \frac{[NO_g]^2[Cl_{2(g)}]}{[NOCl_{(g)}]^2}$$

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

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

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

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

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

(i)$2NOCl(g) \leftrightarrow 2NO(g) + Cl_2(g); \quad K_p = 1.8 \times 10^{-2}\ at\ 500K$

(ii)$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g); \quad K_p = 167\ at\ 1073K$

Ans.

The relation between K_p and K_c is given as:

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

(a) Given,

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

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

T = 500 K

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

Now,

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

$$\Rightarrow 1.8 \times 10^{-2} = K_c(0.0831 \times 500)^1$$
$$\Rightarrow K_c = \frac{1.8 \times 10^{-2}}{0.0831 \times 500}$$
$$= 4.33 \times 10^{-4}(approximately)$$

(b) Here,

$\Delta n = 2 - 1 = 1$

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

T = 1073 K

$K_p = 167$

Now,

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

$$\Rightarrow 167 = K_c(0.0831 \times 1073)^{\Delta n}$$
$$\Rightarrow K_c = \frac{167}{0.0831 \times 1073}$$
$$= 1.87(approximately)$$

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

$NO(g) + O_{3(g)} \leftrightarrow NO_{2(g)} + O_{2(g)}$

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

Ans.

For the reverse reaction, $K_c = \frac{1}{K_c}$

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

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

Ans.

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

Mole concentration= $\frac{Number\ of\ moles}{Volume}$

$$\frac{Mass/molecular\ mass}{Volume}$$
$$= \frac{Mass}{Volume \times Molecular\ mass}$$
$$= \frac{Density}{Molecular\ mass}$$

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

∴Molar concentration are constatnt.

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

$$2N_2(g) + O_2 \leftrightarrow 2N_2O(g)$$

If a solution of 0.933 mol of oxygen and 0.482 mol of nitrogen is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which K_c =2.0×10^{-37}, determine the composition of equilibrium solution.

Ans.

Let the concentration of N_2O at equilibrium be x.

The given reaction is:

$2N_2(g)$ + $O_2(g)$ $2N_2O(g)$

Initial conc. 0.482 mol 0.933 mol 0

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

$$[N_2] = \frac{0.482 - x}{10} \cdot [O_2] = \frac{0.933 - \frac{x}{2}}{10}, [N_2O] = \frac{x}{10}$$

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

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

Now,

$$K_c = \frac{[N_2O_{(g)}]^2}{[N_{2(g)}][O_{2(g)}]}$$
$$\Rightarrow 2.0 \times 10^{-37} = \frac{(\frac{x}{10})^2}{(0.0482)^2 (0.0933)}$$
$$\Rightarrow \frac{x^2}{100} = 2.0 \times 10^{-37} \times (0.0482)^2 \times (0.0933)$$
$$\Rightarrow x^2 = 43.35 \times 10^{-40}$$
$$\Rightarrow x = 6.6 \times 10^{-20}$$

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

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

$2NO(g)+Br_2(g) \Rightarrow 2NOBr(g)$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at a constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

Ans.

The given reaction is:

$2NO(g)+Br_2(g)$ $2NOBr(g)$

2mol 1mol 2mol

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

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

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

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

[NO] = 0.087 mol [Br2] = 0.0437 mol

Therefore, the amount of NO present at equilibrium is:

[NO] = 0.087 – 0.0518 = 0.0352 mol

And, the amount of Br present at equilibrium is:

[Br2] = 0.0437 – 0.0259 = 0.0178 mol

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

$2SO_2(g)+O_2(g) \Rightarrow 2SO_3(g)$

What is K_c at this temperature?

Ans.)

For the given reaction,

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

T = 450 K

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

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

We know that,

$$K_p = K_c(RT)\Delta n$$
$$\Rightarrow 2.0 \times 10^{10} bar^{-1} = K_c(0.0831 L\, bar\, K^{-1} mol^{-1} \times 450K)^{-1}$$
$$\Rightarrow K_c = \frac{2.0\times10^{10} bar^{-1}}{(0.0831 L\, bar\, K^{-1} mol^{-1} \times 450K)^{-1}}$$
$$= (2.0 \times 10^{10} bar^{-1})(0.0831 L\, bar\, K^{-1} mol^{-1} \times 450K)$$
$$= 74.79 \times 10^{10} L\, mol^{-1}$$
$$= 7.48 \times 10^{11} L\, mol^{-1}$$
$$= 7.48 \times 10^{11}\, M^{-1}$$

Q.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?

$2HI(g) \Rightarrow H_2(g)+I_2(g)$

Ans.

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

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

$2HI(g)$		$H_2(g)$ +	$I_2(g)$
Initial conc.	0.2 atm	0	0
At equilibrium	0.4 atm	0.16	2.15

2 2

=0.08atm =0.08atm

Therefore,

$$K_p = \frac{p_{H_2} \times p_{I_2}}{p^2_{HI}}$$
$$= \frac{0.08 \times 0.08}{(0.04)^2}$$
$$= \frac{0.0064}{0.0016}$$
$$= 4.0$$

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

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

$N_2(g)+3H_2(g) \Rightarrow 2NH_3(g)$ is 1.7×10^2

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

Ans.

The given reaction is:

$N_2(g)+3H_2(g) \Rightarrow 2NH_3(g)$

The given concentration of various species is

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

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

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

Now, reaction quotient Q_c is:

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
$$= \frac{(\frac{8.13}{20})^2}{(\frac{1.57}{20})(\frac{1.92}{20})^3}$$
$$= 2.4 \times 10^3$$

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

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

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

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

Write the balanced chemical equation corresponding to this expression.

Ans.

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

$4NO_{(g)}+6H_2o_{(g)} \Rightarrow 4NH_{3(g)}+5O_{2(g)}$

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

$H_2O(g) + CO(g) \Rightarrow H_2(g) + CO_2(g)$

Calculate the equilibrium constant for the reaction.

Ans.

The given reaction is:

$H_2O(g) + CO(g)$ $H_2(g) + CO_2(g)$

Initial conc. 1 M 1 M 0 0

10 10

At equilibrium 1-0.6 M 1-0.6 M 0.6 M 0.6 M

10 10 10 10

=0.04 M =0.04M =0.06 M =0.06M

Therefore, the equilibrium constant for the reaction,

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

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

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

$H_{2(g)}+I_{2(g)} \Rightarrow 2HI_{(g)}$

is 54.8. If 0.5 molL^{-1} of $HI_{(g)}$ is present at equilibrium at 700 K, what are the concentration of $H_{2(g)}$ and $I_{2(g)}$ assuming that we initially started with $HI_{(g)}$ and allowed it to reach equilibrium at 700 K?

Ans.

It is given that equilibrium constant K_c for the reaction

$H_{2(g)}+I_{2(g)}$ $2HI_{(g)}$ is 54.8.

Therefore, at equilibrium, the equilibrium constant K'_c for the reaction

$H_{2(g)}+I_{2(g)}$ $2HI_{(g)}$

[HI]=0.5 molL^{-1} will be 1/54.8.

Let the concentrations of hydrogen and iodine at equilibrium be x molL^{-1}

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

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

$$\Rightarrow \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$$
$$\Rightarrow x^2 = \frac{0.25}{54.8}$$
$$\Rightarrow x = 0.06754$$
$$x = 0.068 mol L^{-1} (approximately)$$

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

Q.16. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?

$2ICl_{(g)} \Rightarrow I_{2(g)}+Cl_{2(g)}$; K_c =0.14

Ans.

The given reaction is:

$2ICl_{(g)}$		$I_{2(g)}$ +	$Cl_{2(g)}$
Initial conc.	0.78 M	0	0
At equilibrium	(0.78-2x) M	x M	x M

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]= $(0.78 - 2 \times 0.167) M$
$= 0.446 M$

Q.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?

$C_2H_6(g) \Rightarrow C_2H_4(g) + H_2(g)$

Ans.

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

$C_2H_6(g)$		$C_2H_4(g)$ +	$H_2(g)$
Initial conc.	4.0 M	0	0

At equilibrium (4.0-p) p p

We can write,

$$\frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} = K_P$$
$$\Rightarrow \frac{p \times p}{40-p} = 0.04$$
$$\Rightarrow p^2 = 0.16 - 0.04p$$
$$\Rightarrow p^2 + 0.04p - 0.16 = 0$$

Now,

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

Hence, at equilibrium,

$[C_2H_6]$ – 4 – p = 4 – 0.38

= 3.62 atm

Q.18. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$CH_3COOH(l) + c_2H_5OH(l) \Rightarrow CH_3COOC_2H_5(l) + H_2O(l)$

(i)Write the concentration ratio (reaction quotient), Q_c, for this reaction (note: water is not in excess and is not a solvent in this reaction)

(ii)At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

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

Ans.

(i)Reaction quotient,

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

(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:

$CH_3COOH(l) + c_2H_5OH(l)$ $CH_3COOC_2H_5(l) + H_2O(l)$

Initial conc. 0 0

At equilibrium

= =

Therefore, equilibrium constant for the given reaction is:

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$
$$= \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.009}{V}} = 3.919$$
$$= 3.92(approximately)$$

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

$CH_3COOH(l) + c_2H_5OH(l) \Rightarrow CH_3COOC_2H_5(l) + H_2O(l)$

Initial conc. 0 0

At equilibrium

= =

Therefore, the reaction quotient is,

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$
$$= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}} = 0.2037$$

$= 0.204(approximately)$

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

Q.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 0.5×10^{-1} 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?

$PCl_5(g) \Rightarrow PCl_{3(g)}$ + $Cl_{2(g)}$

Ans.

Consider the conc. Of both PCl_3 and Cl_2 at equilibrium be x molL^{-1}. The given reaction is:

$PCl_5(g) \Rightarrow PCl_{3(g}$ + $Cl_{2(g)}$

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

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

Now we can write the expression for equilibrium as:

$$\frac{[PCl_2][Cl_2]}{[PCl_3]} = K_c$$
$$\Rightarrow \frac{x \times x}{0.5 \times 10^{-10}} = 8.3 \times 10^{-3}$$
$$\Rightarrow x^2 = 4.15 \times 10^{-4}$$
$$\Rightarrow x = 2.04 \times 10^{-2}$$
$$= 0.0204$$
$$= 0.02(approximately)$$

Therefore, at equilibrium,

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

Q.20. One of the reactions that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

FeO (s) + CO (g) ⇒ Fe (s) + CO2 (g); K_p= 0.265 at 1050 K.

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: p_{CO} = 1.4 atm and p_{CO2}= 0.80 atm?

Ans.

For the given reaction,

$FeO_{(g)}$	+ $CO_{(g)}$	$Fe_{(s)}$	+	$CO_{2(g)}$
Initialy,	1.4 atm			0.80 atm

$$Q_p = \frac{p_{CO_2}}{p_{CO}}$$
$$= \frac{0.80}{1.4}$$
$$= 0.571$$

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,

$$K_p = \frac{p_{CO_2}}{p_{CO}}$$
$$\Rightarrow 0.265 = \frac{0.80-p}{1.4+p}$$
$$\Rightarrow 0.371 + 0.265p = 0.80 - p$$
$$\Rightarrow 1.265p = 0.429$$
$$\Rightarrow p = 0.339 atm$$

Therefore, equilibrium partial of CO_2,p_{CO}=0.80-0.339=0.461 atm

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

Q.21. A reaction is given:

$N_2(g)+3H_2(g) \Rightarrow 2NH_3$

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

At a specific time, from the analysis we can conclude that composition of the reaction mixture is, 2.0 mol L^{-1} H_2 , 3.0 mol L^{-1} N_2 and 0.5 mol L^{-1} NH_3. Find out whether the reaction is at equilibrium or not? Find in which direction the reaction proceeds to reach equilibrium.

Ans.

$N_2(g)$ + $3H_2(g)$ $2NH_3$

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

So,

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

It is given that K_c=0.061

$\because$ $Qc \neq K_c$, the reaction is not at equilibrium.

$\because$ $Qc < K_c$, the reaction preceeds in the forward direction to reach at equilibrium.

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

$2BrCl(g) \Rightarrow Br_2(g) + Cl_2(g)$

For which K_c= 42 at 600 K.

If initially pure BrCl is present at a concentration of 5.5×10^{-5} molL^{-1} , what is its molar concentration in the mixture at equilibrium?

Ans.)

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

$2BrCl(g)$ $Br_2(g)$ + $Cl_2(g)$

Initial conc. 5.5×10^{-5} 0 0

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

Now, we can write,

$$
\begin{aligned}
&\frac{[Br_2][Cl_2]}{[BrCl]^2} = K_c \\
&\Rightarrow \frac{x \times x}{(5.5 \times 10^{-5} - 2x)^2} = 42 \\
&\Rightarrow \frac{x}{5.5 \times 10^{-5} - 2x} = 6.48 \\
&\Rightarrow x = 35.64 \times 10^{-5} - 12.96x \\
&\Rightarrow 13.96x = 35.64 \times 10^{-5} \\
&\Rightarrow x = \frac{35.64}{13.96} \times 10^{-5} = 2.55 \times 10^{-5}
\end{aligned}
$$

So,at equilibrium

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

Q.23. Find out K_c for the given reaction at temperature 1127K where the pressure is 1 atm. A solution of CO and CO_2 is in equilibrium with carbon(solid). It has 93.55% CO by mass.

$C(s)+CO_2 (g) \Rightarrow 2CO (g)$

Ans.)

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

Given, mass of CO = 93.55 g

Now, the mass of CO_2 =(100 – 93.55)=6.45 g

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

Number of moles of CO_2, $n_{CO_2} = \frac{[illegible]}{44} = 0.146\, mol$

Partial pressure of CO,

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

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

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,

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

$$\Rightarrow 14.19 = K_c(0.082 \times 1127)^1$$
$$\Rightarrow K_c = \frac{14.19}{0.082 \times 1127}$$
$$= 0.154 (approximately)$$

Q.24.Find out

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

(II) $\Delta G°$

$$NO(g) + \frac{1}{2}O_2(g) \leftrightarrow NO_2(g)$$

Where;

$\Delta_f G°$ (NO_2) = 52.0 kJ/mol

$\Delta_f G°$ (NO) = 87.0 kJ/mol

$\Delta_f G°$ (O_2) = 0 kJ/mol

Ans.)

(I)We know that,

$\Delta G° = RT \log K_c$

$\Delta G° = 2.303\, RT \log K_c$

$$K_c = \frac{-35.0 \times 10^{-3}}{-2.303 \times 8.314 \times 298}$$
$$= 6.134$$
$$\therefore K_c = antilog(6.134)$$
$$= 1.36 \times 10^6$$

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

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

(I) $PCl_5(g) \Rightarrow PCl_3 + Cl_2\,(g)$

(II) Cao(s) + CO_2 (g) $\Rightarrow$ $CaCO_3$(s)

(III) 3Fe (s) + $4H_2O$ (g) $\Rightarrow$ Fe_3O_4 (s) +$4H_2$ (g)

Ans.

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

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

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

Q.26. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

(I)$COCl_2$ (g) ⇒ CO (g) +Cl_2 (g)

(II)CH_4 (g) +2S_2 (g) ⇒ CS_2 (g) + 2H_2S (g)

(III)CO_2 (g) +C (s) ⇒ 2CO (g)

(IV)2H_2 (g) +CO (g) ⇒ CH_3OH(g)

(V)$CaCO_3$ (s) ⇒ Cao (s) + CO_2 (g)

(VI)4NH_3 (g) +5O_2 (g) ⇒ 4NO (g) + 6H_2O (g)

Ans.)

When pressure is increased:

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

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

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

Q.27. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K.

H_2 (g) + Br_2 (g) ⇒ 2HBr (g)

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

Ans.

Given, K_p for the reaction i.e., H_2 (g) + Br_2 (g) ⇒ 2HBr (g) is 1.6×10^5.

Therefore, for the reaction 2HBr (g) ⇒ H_2 (g) + Br_2 (g) the equilibrium constant will be,

$$K'_p = \frac{1}{K_p}$$
$$= \frac{1}{1.6\times10^5}$$
$$= 6.25 \times 10^{-6}$$

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

	2HBr (g)	H_2 (g)	+ Br_2 (g)
Initial conc.	10	0	0
At equilibrium	10-2p	p	p

Now, we can write,

$$\frac{p_{HBr} \times p_2}{p^2_{HBr}} = K'_p$$
$$\frac{p\times p}{(10-2p)^2} = 6.25 \times 10^{-6}$$
$$\frac{p}{10-2p} = 2.5 \times 10^{-3}$$
$$p = 2.5 \times 10^{-2} - (5.0 \times 10^{-3})p$$
$$p + (5.0 \times 10^{-3})p = 2.5 \times 10^{-2}$$
$$(1005 \times 10^{-3}) = 2.5 \times 10^{-2}$$
$$p = 2.49 \times 10^{-2} bar = 2.5 \times 10^{-2} bar (approximately)$$

Therefore, at equilibrium,

$[H_2]$=$[Br_2]$= $2.49 \times 10^{-2} bar$

$$[HBr] = 10 - 2 \times (2.49 \times 10^{-2}) bar$$
$$= 9.95 bar = 10 bar (approximately)$$

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

$$CH_4(g) + H_2O(g) \leftrightarrow CO(g) + 3H_2(g)$$

(I)Write as expression for K_p for the above reaction.

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

(i)Increasing the pressure

(ii)Increasing the temperature

(iii)Using a catalyst?

Ans.)

(I)For the given reaction,

$K_p = \frac{p_{CO} \times p_{H_2}^3}{p_{CH_4} \times p_{H_2O}}$

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

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

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

Q.29. Describe the effect of:

I) Removal of CO

II) Addition of H_2

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

IV) Addition of CH_3OH

$2H_2$ (g)+CO (g) ⇒ CH_3OH (g)

Ans.)

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

(II) According to Le Chatelier's principle, on addition of H2, the equilibrium of the given reaction will shift in the forward direction.

(III) On removing CH3OH, the equilibrium will shift in the forward direction.

(IV) On addition of CH3OH, the equilibrium will shift in the backward direction.

Q.30. At 473 K, equilibrium constant Kc for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$

$\Delta_rH°$ = 124.0 $kJmol^{-1}$

a) Write an expression for Kc for the reaction.

b) What is the value of Kc for the reverse reaction at the same temperature?

c) What would be the effect on Kc if

(i) more PCl5 is added

(ii) pressure is increased?

(iii) The temperature is increased?

Ans.)

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

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

$$K_c^{\prime} = \frac{1}{K_c}$$
$$= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2$$
$$= 120.48$$

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

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

Q.31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that P_{co}=P_{H2O} = 4.0 bar, what will be the partial pressure of H2 at equilibrium? K_p= 10.1 at 400°C

Ans.)

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

$CO(g)$ +	$H_2O \Rightarrow$	$CO_2(g)$ +	$H_2(g)$	
Initial conc.	4.0 bar	4.0 bar	0	0
At equilibrium	4.0-p	4.0-p	p	p

Given K_p = 10.1

$$\frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}} = K_P$$
$$\Rightarrow \frac{p \times p}{(4.0-p)(4.0-p)} = 10.1$$
$$\Rightarrow \frac{p}{4.0-p} = 3.178$$
$$\Rightarrow p = 12.712 - 3.178p$$
$$4.178p = 12.712$$
$$p = \frac{12.712}{4.178}$$
$$p = 3.04$$

So, partial pressure of H_2 is 3.04 bar at equilibrium.

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

(a)$Cl_2(g) \leftrightarrow 2Cl(g); K_c = 5 \times 10^{-39}$

(b)$Cl_2(g) + 2NO(g) \leftrightarrow 2NOCl(g); K_c = 3.7 \times 10^8$

(c)$Cl_2(g) + 2NO_2(g) \leftrightarrow 2NO_2Cl(g); K_c = 1.8$

Ans.)

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

Q.33. The value of Kc for the reaction $3O_2$ (g) ⇒ $2O_3$ (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?

Ans.)

Given,

$3O_2$ (g) ⇒ $2O_3$ (g)

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

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

Then,

$$2.0 \times 10^{-50} = \frac{[O_3(g)]^2}{[1.6 \times 10^{-2}]^3}$$
$$\Rightarrow [O_3(g)]^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3$$
$$\Rightarrow [O_3(g)]^2 = 8.192 \times 10^{-56}$$
$$\Rightarrow [O_3(g)]^2 = 2.86 \times 10^{-28} M$$

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

Q.34. The reaction, $CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$ at 1300K is at equilibrium in a 1L container. It has 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and y amount of CH_4 in the container. Find the concentration of CH_4 in the mixture.

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

Ans.)

Let the concentration of CH_4 at equilibrium be y.

$CO_{(g)} \; + \; 3H_{2(g)} \; \rightarrow \; CH_{4(g)} \; + \; H_{2}O_{(g)}$

At equilibrium,

For CO – $\frac{0.3}{1} = 0.3M$

For H_2 – $\frac{0.1}{1} = 0.1M$

For H_2O – $\frac{0.02}{1} = 0.02M$

K_c = 3.90

Therefore,

$$\frac{[CH_{4(g)}][H_2O_{(g)}]}{[CO_{(g)}][H_{2(g)}]^3} = K_c \; \frac{y\times 0.02}{0.3\times(0.1)^3} = 3.9 \; y = \frac{3.9\times 0.3\times(0.1)^3}{0.02} \; y = \frac{0.00117}{0.02} \; y = 0.0585M$$
$$y = 5.85\times 10^{-2}M$$

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

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

(i) HNO_2

(ii) CN^-

(iii) $HClO_4$

(iv) F^-

(v) OH^-

(vi) CO_3^{2-}

(vii) S^-

Ans.)

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

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

(i) HNO_2 – NO_2^- (Base)

(ii) CN^- – HCN (Acid)

(iii) $HClO_4$ – ClO_4^- (Base)

(iv) F^- – HF (Acid)

(v) OH^- – H_2O (Acid)/ O^{2-} (Base)

(vi) CO_3^{2-} – HCO_3^- (Acid)

(vii) S^- – HS^- (Acid)

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

(i) H_2O

(ii) BF_3

(iii) H^+

(iv) NH_4^+

Ans.)

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

(i) H_2O – Not Lewis acid

(ii) BF_3 – Lewis acid

(iii) H^+ – Lewis acid

(iv) NH_4^+ – Lewis acid

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

(i) HF

(ii) H_2SO_4

(iii) HCO_3

Ans.)

The following shows the conjugate bases for the Bronsted acids:

(i) HF – F^-

(ii) H_2SO_4 – HSO_4^-

(iii) HCO_3 – CO_3^{2-}

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

1. NH_3
2. $HCOO^-$
3. NH_2^-

Ans.)

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

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

1. HCO_3^-
2. HSO_4^-
3. NH_3
4. H_2O

Ans.)

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

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

1. BCl_3
2. H^+
3. OH^-
4. F^-

Ans.)

1. BCl_3:

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

2. H^+

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

3. OH^-

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

4. F^{-}

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

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

Ans.)

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

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

Ans.)

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

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

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

HF = 5.7×10^{-5} at 298K

HCOOH = 1.7×10^{-3} at 298K

HCN = 3.7×10^{-8} at 298K

Find out the conjugate bases for the above acids.

Ans.)

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

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

For CN⁻ = $K_b = \frac{10^{-14}}{(3.7 \times 10^{-8})} = \times 10^{-11} = 2.70 \times 10^{-6}$

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

Ans.)

C_6H_5OH	$C_6H_5O^{-}$ + H^{+}		
Initial	0.06M		
After dissociation	0.06-x	x	x

$$\therefore K_a = \frac{x \times x}{0.06 - x} = 1.0 \times 10^{-8}$$
$$\Rightarrow \frac{x^2}{0.06} = 1.0 \times 10^{-8}$$
$$\Rightarrow x^2 = 6 \times 10^{-10}$$
$$\Rightarrow x = 2.4 \times 10^{5} M$$

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

$[C_6H_5OH]$ = 0.06 – y $\simeq$ 0.06,

$[C_6H_5O^{-}]$ = 0.02 + y $\simeq$0.01M,

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

(0.02)(y) ... 8

$\therefore K_a = \frac{(0.02)(y)}{0.06} = 1.0 \times 10^{-8}$
$\Rightarrow y = \frac{1.0 \times 0.06}{(0.02)} \times 10^{-8}$
$\Rightarrow y = 6 \times 10^{-8}$

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

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

Q.45 Given, 9.1×10^{-8} is the initial(first) ionization constant of the gas H_2S.Find out concentration of the ion HS^- in 0.1M solution of H_2S . Find the changes in concentration if the concentration is 0.1M in HCl. Find the concentration of S^{2-} under both conditions, if 1.2×10^{-13} is the second dissociation constant of H_2S.

Ans.)

To calculate $[HS^-]$

H_2S $H^+ + HS^-$

Intial 0.1 M

After dissociation 0.1-x x x

$\simeq 0.1\ K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8}$
$\Rightarrow x^2 = 9.1 \times 10^{-9}$
$\Rightarrow x = 9.54 \times 10^{-5}$

In the presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium, $[H_2S]$ =0.1-y $\simeq 0.1$,

$[H^+]$=0.1 + y $\simeq 0.1$,

$[HS^-]$ = y M

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

K_{a2}

K_{a1}

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

H_2S $H^+ + HS^-$, HS^- $H^+ + S^{2-}$

For the overall reaction,

H_2S $2H^+ + S^{2-}$

$K_a = K_{a_1} \times K_{a_2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20}\ K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$

In the absence of 0.1M HCl,

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

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

$$\therefore \frac{(2x)^2}{0.1} = 1.092 \times 10^{-20}$$
$$\Rightarrow 4x^3 = 1.092 \times 10^{-21}$$
$$\Rightarrow x^3 = \frac{1.092}{4} \times 10^{-21} = 273 \times 10^{-24}$$
$$\Rightarrow log\, x^3 = log\, 273 - log\, 10^{-24} = 2.4362 - 24$$
$$\Rightarrow 3logx = 2.4362 - 24$$
$$\Rightarrow log\, x = \frac{2.4362}{3} - \frac{24}{3}$$
$$\Rightarrow x = 0.8127 - 8 = -7.1873$$
$$\Rightarrow x = Antilog\, -7.1873 = 6.497 \times 10^{-8} = 6.5 \times 10^{-8}$$

In presence of 0.1M HCl,

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

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

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

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20}$$
$$y = 1.09 \times 10^{-19} M$$

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

Ans.)

$CH_3COOH \Rightarrow CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$
$$\Rightarrow [H^+] = \sqrt{K_a[CH_3COOH]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4} M$$
$$[CH_3COO^-] = [H^+] = 9.33 \times 10^{-4} M$$
$$pH = -log(9.33 \times 1.0^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$$

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

Ans.)

HA $\quad\quad$ $H^+ + A^-$

pH=-log$[H^+]$

log$[H^+]$=-4.15

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

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

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.08\times10^{-5})(7.08\times10^{-5})}{10^{-2}} = 5.0 \times 10^{-7}$$
$$p_{K_a} = -log\, K_a = -log\,(5.0 \times 10^{-7}) = 7 - 0.699 = 6.301$$

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

(I)0.004 M HCl

(II)0.003 M NaOH

(III)0.002 M HBr

(IV)0.002 M KOH

Ans.)

(I)HCl + aq $\quad\quad$ $H^+ + Cl^-$

$$\therefore [H^+] = [HCl] = 4 \times 10^{-3} M$$
$$pH = -log(4 \times 10^{-3}) = 2.398$$

(II)NaOH + aq $\quad\quad$ $Na^+ + OH^-$

$\therefore [OH^-] = 3 \times 10^{-3} M$
$[H^+] = \frac{10^{-14}}{(3 \times 10^{-3})} = 3 \times 10^{-12} M$
$pH = -log(3 \times 10^{-12}) = 11.52$

(III)HBr + aq H$^+$ + Br$^-$

$\therefore [H^+] = 2 \times 10^{-3} M$
$pH = -log(2 \times 10^{-3} M) = 2.70$

(IV)KOH + aq K$^+$ + OH$^-$

$\therefore [OH^+] = 2 \times 10^{-3} M$
$[H^+] = \frac{10^{-14}}{(2 \times 10^{-3})} = 5 \times 10^{-12}$
$pH = -log(5 \times 10^{-12}) = 11.30$

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

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

(II)0.3g of $Ca(OH)_2$ dissolved in water to given 500mL of the solution

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

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

Ans.)

(I)Molar conc. Of TlOH = $\frac{2g}{(204+16+1)g\ mol^{-1}} \times \frac{1}{2L} = 4.52 \times 10^{-3} M$
$[OH_-] = [TlOH] = 4.52 \times 10^{-3} M$
$[H^+] = \frac{10^{-14}}{(4.52 \times 10^{-3})} = 2.21 \times 10^{-12} M$
$\therefore pH = -log(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$

(II)Molar conc. Of $Ca(OH)_2$=$\frac{0.3g}{(40+34)g\ mol^{-1}} \times \frac{1}{0.5L} = 8.11 \times 10^{-3} M$
$[OH_-] = 2[Ca(OH)_2] = 2 \times (8.11 \times 10^{-3})M = 16.22 \times 10^{-3} M$
$pOH = -log(16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$
$pH = 14 - 1.79 = 12.21$

(III)Molar conc. of NaOH = $\frac{0.3g}{(40+34)g\ mol^{-1}} \times \frac{1}{0.2L} = 3.75 \times 10^{-2} M$
$[OH_-] = 3.75 \times 10^{-2} M$
$pOH = -log(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$
$pH = 14 - 1.43 = 12.57$

(IV)$M_1V_1 = M_2V_2$

$\therefore 13.6M \times \times 1mL = M_2 \times 1000mL$
$\therefore M_2 = 1.36 \times 10^{-2} M$
$[H^+] = [HCl] = 1.36 \times 10^{-2} M$
$pH = -log(1.36 \times 10^{-2}) = 2 - 0.1335 \simeq 1.87$

Q.50. The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the p_{Ka} of bromoacetic acid.

Ans.)

$CH_2(Br)COOH$ $CH_2(Br)COO^-$ + H^+

Initial conc.	C	0	0
Conc. at eqm.	C – Cα	Cα	Cα

$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$
$p_{K_a} = -log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$
$[H^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} M$
$pH = -log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$

Q.51. The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the p_{Ka} of bromoacetic acid.

Ans.)

$CH_2(Br)COOH$ $\quad$ $CH_2(Br)COO^- + H^+$

Initial conc.	C	0	0
Conc. at eqm.	C – Cα	Cα	Cα

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$
$$p_{K_a} = -log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$
$$[H^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} M$$
$$pH = -log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$$

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

Ans.)

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

c = 0.001M

pH =?

α =?

$$K_b = c\alpha^2$$
$$4.27 \times 10^{-10} = 0.001 \times \alpha^2$$
$$4270 \times 10^{-10} = \alpha^2$$
$$65.34 \times 10^{-5} = \alpha = 6.53 \times 10^{-4}$$
$$Then, [anion] = c\alpha = 0.001 \times 65.34 \times 10^{-5} = 0.065 \times 10^{-5}$$

$$pOH = -log(0.065 \times 10^{-5})$$
$$= 6.187$$
$$pH = 7.813$$
$$Now,$$
$$K_a \times K_b = K_w$$
$$K_a = \frac{10^{-14}}{4.27 \times 10^{-10}}$$
$$= 2.34 \times 10^{-5}$$

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

Q.53. Calculate the degree of ionization of 0.05M acetic acid if its p_{Ka} value is 4.74. How is the degree of dissociation affected when its solution also contains

(I)0.01 M

(II)0.1 M in HCl?

Ans.)

c=0.05M

p_{Ka}=4.74

p_{Ka}=-log(K_a)

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

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

Case 1: When 0.01 M HCl is taken.

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

CH_3COOH $\quad$ $H^+ + CH_3COO^-$

Initial conc.	0.05M	0	0
After dissociation	0.05-x	0.01+x	x

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$
$$\therefore = \frac{(0.01)x}{0.05}$$
$$x = \frac{1.82 \times 10^{-5} \times 0.05}{0.01}$$

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

Now,

$\alpha = \frac{Amoun\ of\ acid\ dissociation}{Amount\ of\ acid\ taken}$
$= \frac{1.82 \times 10^{-3} \times 0.05}{0.05}$
$= 1.82 \times 10^{-3}$

Case 2: When 0.1 M HCl is taken.

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

$[CH_3COOH]$=0.05 – X; 0.05 M

$[CH_3COO^-]$=X

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

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$
$\therefore K_a = \frac{(0.1)X}{0.05}$
$x = \frac{1.82 \times 10^{-5} \times 0.05}{0.1}$
$x = 1.82 \times 10^{-4} \times 0.05M$

Now,

$\alpha = \frac{Amoun\ of\ acid\ dissociation}{Amount\ of\ acid\ taken}$
$= \frac{1.82 \times 10^{-4} \times 0.05}{0.05}$
$= 1.82 \times 10^{-4}$

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

Ans.)

$K_b = 5.4 \times 10^{-4}$
$c = 0.02M$
$Then, \alpha = \sqrt{\frac{K_b}{c}}$
$= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 0.1643$

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

$NaOH_{(aq)}$ $Na^+_{(aq)}$ + $OH^-_{(aq)}$

0.1M 0.1M

And,

$(CH_3)_2$ NH + H_2O $(CH_3)_2$ NH_2^+ + OH

(0.02-x) x x

;0.02M ;0.1M

Then,[$(CH_3)_2$ $NH^+{}_2$]=x

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

$\Rightarrow K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$
$5.4 \times 10^{-4} = \frac{x \times 0.1}{0.02}$
$x = 0.0054$

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

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

(I)Human saliva, 6.4

(II)Human stomach fluid, 1.2

(III)Human muscle-fluid, 6.83

(IV)Human blood, 7.38

Ans.)

(I)Human saliva, 6.4:

pH = 6.4

6.4 = – log [H$^+$]

[H$^+$] = 3.98×10^{-7}

(II)Human stomach fluid, 1.2:

pH =1.2

1.2 = – log [H$^+$]

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

(III)Human muscle fluid 6.83:

pH = 6.83

pH = – log [H$^+$]

6.83 = – log [H$^+$]

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

(IV) Human blood, 7.38:

pH = 7.38 = – log [H$^+$]

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

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

Ans.)

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

(I)pH of milk = 6.8

Since, pH = –log [H$^+$]

6.8 = –log [H$^+$] log

[H$^+$] = –6.8

[H$^+$] = anitlog(–6.8)

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

(II)pH ofblack coffee = 5.0

Since, pH = –log [H$^+$]

5.0 = –log [H$^+$] log

[H$^+$] = –5.0

[H$^+$] = anitlog(–5.0)

= $10^{-5} M$

(III)pH of tomato= 4.2

Since, pH = –log [H$^+$]

4.2 = –log [H$^+$] log

[H$^+$] = –4.2

[H$^+$] = anitlog(–4.2)

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

(IV)pH of lemon juice= 2.2

Since, pH = –log [H$^+$]

2.2 = –log [H$^+$] log

$[H^+]$ = –2.2

$[H^+]$ = anitlog(–2.2)

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

(V)pH of egg white= 7.8

Since, pH = –log $[H^+]$

7.8 = –log $[H^+]$ log

$[H^+]$ = –7.8

$[H^+]$ = anitlog(–7.8)

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

Q.57. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Ans.)

$[KOH_{aq}]$= $\frac{0.561}{\frac{1}{5}} g/L$

$$= 2.805 g/L$$
$$= 2.805 \times \frac{1}{56.11} M$$
$$= 0.05 M$$

$KOH_{(aq)}$ $K^+_{(aq)} + OH^-_{(aq)}$

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

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

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

$$= \frac{10^{-14}}{0.05} = 2 \times 10^{-13} M$$
$$\therefore pH = 12.70$$

Q.58. The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

Ans.)

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

Then, concentration of $Sr(OH)_2$

=$\frac{19.23}{121.63} M$

$$= 0.1581 M$$

$Sr(OH)_{2(aq)}$ $Sr^{2+}_{(aq)} + 2(OH^-)_{(aq)}$

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

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

Now,

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

$$\frac{10^{-14}}{0.3126} = [H^+]$$
$$\Rightarrow [H^+] = 3.2 \times 10^{-14}$$
$$\therefore pH = 13.495; 13.50$$

Q.59. The ionization constant of propanoic acid is $1.32 \times \times 10^{-15}$. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

Ans.)

Let the degree of ionization of propanoic acid be α.

Then, representing propionic acid as HA, we have:

HA + H_2O H_3O^+ + A^-

(0.05-0.0α) ≈0.05 0.05α 0.05α

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

Then,[H_3O^+]= 0.05α =$0.05 \times 1.63 \times 10^{-2} = K_b \cdot 15 \times 10^{-4} M$
$\therefore pH = 3.09$

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

Then,[H_3O^+]=0.01

[A^-]=0.05 α´

[HA]=0.05

$K_\alpha = \frac{0.01 \times 0.05\alpha'}{0.05}$
$1.32 \times 10^{-5} = 0.01 \times \alpha'$
$\alpha' = 1.32 \times 10^{-3}$

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

Ans.)

c = 0.1 M

pH = 2.34

-log [H^+] = pH

-log [H^+] = 2.34

[H^+]=4.5×10^{-3}

Also,

[H^+]=cα

$4.5 \times 10^{-3} = 0.1 \times \alpha$
$\frac{4.5 \times 10^{-3}}{0.1} = \alpha$
$\alpha = 4.5 \times 10^{-3} = 0.045$

Then,

$K_a = c\alpha^2$
$= 0.1 \times (45 \times 10^{-3})^2$
$= 202.5 \times 10^{-6}$
$= 2.02 \times 10^{-4}$

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

Ans.)

Sodium nitrite is a salt of NaOH (strong base) and HNO2 (weak acid).

$NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$ $K_h = \frac{[HNO_2][OH^-]}{[NO_2^-]} \Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5 \times 10^{-4}} = 22 \times 10^{-10}$

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

$[NO_2^-] = 0.04 - y; 0.04$ $[HNO_2] = y$ $[OH^-] = y$ $K_h = \frac{y^2}{0.04} = 0.22 \times 10^{-10}$ $y^2 = 0.0088 \times 10^{-10}$
$y = 0.093 \times 10^{-5} \therefore [OH^-] = 0.093 \times 10^{-5} M$ $[H_3O^+] = \frac{10^{-10}}{0.093 \times 10^{-5}} = 10.75 \times 10^{-9} M$

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

= 7.96

Thus, the degree of hydrolysis is

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

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

Ans.)

pH = 3.44

As we know,

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

Now, $K_h = \frac{3.63\times10^{-4}}{0.02}$; (Given that concentration = 0.02M)

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

As we know that,

$K_h = \frac{K_w}{K_a}\ K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6\times10^{-6}}$

= 1.51×10^{-9}

Q.63. Few salts are given below;

1. **KBr**
2. **NH_4NO_3**
3. **KF**
4. **NaNO2**
5. **NaCN**
6. **NaCl**

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

Ans.)

1. KBr

KBr + H_2O ↔ KOH (Strong base)+ HBr (Strong acid)

Thus, it is a neutral solution.

2. NH_4NO_3

NH_4NO_3 + H_2O ↔ NH_4OH(Weak base) + HNO_2 (Strong acid)

Thus, it is an acidic solution.

3. KF

KF + H_2O ↔ KOH (Strong base) + HF (weak acid)

Thus, it is a basic solution.

4. $NaNO_2$

$NaNO_2$ + H_2O ↔ NH_4OH(Strong base) + HNO_2(Weak acid)

Thus, it is a basic solution.

5. NaCN

NaCN + H_2O ↔ HCN (Weak acid) + NaOH (Strong base)

Thus, it is a basic solution.

6. NaCl

NaCl + $H_2O \leftrightarrow$ NaOH (Strong base) + HCL (Strong acid)

Thus, it is a neutral solution.

Q.64. Find the pH of 0.1M acid and its 0.1M NaCl solution. The Ka for chloroacetic acid is 1.35×10^{-3}.

Ans.)

The Ka for chloroacetic acid ($ClCH_2COOH$) is 1.35×10^{-3}.

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

= $\sqrt{\frac{1.35\times10^{-3}}{0.1}}$; (given concentration = 0.1M)

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

= 0.116

$\therefore [H^+] = c\alpha = 0.1 * 0.116 = 0.0116$
pH = $-\log[H^+]$ = 1.94

ClCH2COONa is a salt of strong base i.e. NaOH, and weak acid i.e. ClCH2COOH

$ClCH_2COO^- + H_2O \leftrightarrow ClCH_2COOH + OH^-$ $K_h = \frac{[ClCH_2COO][OH^-]}{[ClCH_2COO^-]}$

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

$K_h = \frac{10^{-14}}{1.35\times10^{-3}} = 0.740 \times 10^{-11}$

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

$\Rightarrow\ 0.740 \times 10^{-11} = \frac{y^2}{0.1} \Rightarrow\ 0.0740 \times 10^{-11} = y^2$ $y = 0.86 \times 10^{-6}$ $[OH^-] = 0.86 \times 10^{-6}$
$\therefore [H^+] = \frac{K_w}{0.86\times10^{-6}} = \frac{10^{-14}}{0.86\times10^{-6}}$ $[H^+] = 1.162 \times 10^{-3}$

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

= 7.94

Q.65. Determine the pH of neutral water at 310K temperature. Ionic product of H_2O is 2.7×10^{-14}.

Ans.)

Ionic Product,

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

Assuming, $[H^+]$ = y

As, $[H^+] = [OH^-]$, $K_w = y^2$.

K_w at 310K is 2.7×10^{-14}.

$\therefore 2.7 \times 10^{-14} = y^2$
y = 1.64×10^{-7}
$[H^+] = 1.64 \times 10^{-7}$
pH = $-\log[H^+]$

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

= 6.78

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

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

i) n10 ml of 0.02M H_2SO_4 + 10 ml of 0.02M $Ca(OH)_2$

ii) 10 ml of 0.1M H_2SO_4 + 10 ml of 0.1M KOH

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

Ans.)

i) Moles of OH^-

= $\frac{2*10*0.02}{1000} = 0.0004mol$

Moles of H_3O^+

= $\frac{2*10*0.02}{1000} = 0.0004mol$

ii) Moles of OH^-

= $\frac{2*10*0.1}{1000} = 0.002mol$

Moles of H_3O^+

= $\frac{2*10*0.1}{1000} = 0.001mol$

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

So, $[H_3O^+] = \frac{0.001}{20\times10^{-3}} = \frac{10^{-3}}{20\times10^{-3}} = 0.5$

Thus, pH = -log(0.05)

= 1.3

As the solution id neutral pH = 7.

iii) Moles of OH^-

= $\frac{2*10*0.2}{1000} = 0.004mol$

Moles of H_3O^+

= $\frac{25*0.1}{1000} = 0.0025mol$

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

So, $[OH^-] = \frac{0.0015}{35\times10^{-3}} = 0.0428$

Thus, pH = -log(OH)

= 1.36

pH = 14 – 1.36 = 12.63

As the solution id neutral pH = 12.63.

Q.67. Calculate the solubilities of

a) barium chromate

b) ferric hydroxide

c) lead chloride

d) mercurous iodide

e) silver chromate

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

Ans.)

a) Barium Chromate

$BaCrO_4$ à Ba^{2+} + CrO_4^{2-}

Now, K_{sp} = $[Ba^{2+}][CrO_4^{2-}]$

Aumming the solubility of $BaCrO_4$ is 'x'.

Thus,

$[Ba^{2+}]$ = x and CrO_4^{2-} = x

$K_{sp} = x^2$
$1.2 \times 10^{-10} = x^2$
x = $1.09 \times 10^{-10}M$

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

b) Ferric Hydroxide

$Fe(OH)_3$ à Fe^{3+} + OH^-

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

Aumming the solubility of $Fe(OH)_3$ is 'x'.

Thus,

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

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

$= x*27x^3$

$K_{sp} = 27x^4$

$1.0 \times 10^{-38} = 27x^4$
x = $0.00037 \times 10^{-36} M$

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

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

c) Lead Chloride

$PbCl_2$ à Pb^{2+} + $2Cl^-$

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

Aumming the solubility of $PbCl_2$ is 'x'.

Thus,

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

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

$= x*4x^2$

$K_{sp} = 4x^3$

$1.6 \times 10^{-5} = 4x^3$
x = $1.58 \times 10^{-2} M$

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

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

d) Mercurous iodide

Hg_2I_2 à Hg^{2+} + $2I^-$

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

Aumming the solubility of Hg_2I_2 is 'x'.

Thus,

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

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

$= x*4x^2$

$K_{sp} = 4x^3$

$4.5 \times 10^{-29} = 4x^3$
x = $2.24 \times 10^{-10} M$

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

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

e) Silver Chromate

Ag_2CrO_4 à $2Ag^{2+}$ + CrO_4^{2-}

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

Aumming the solubility of Ag_2CrO_4 is 'x'.

Thus,

[Ag^{2+}] = 2x and CrO_4^{2-} = x

K_{sp} = (2x)^2*x
$1.1 \times 10^{-12} = 4x^3$
x = $0.65 \times 10^{-4} M$

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

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

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

Ag_2CrO_4 and AgBr

The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} *and* 5.0×10^{-13} respectively.

Ans.)

Ag_2CrO_4 à $2Ag^{2+}$ + CrO_4^-

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

Asuming the solubility of Ag_2CrO_4 is 'x'.

Thus,

[Ag^{2+}] = 2x and CrO_4^- = x

K_{sp} = (2x)^2*x
$1.1 \times 10^{-12} = 4x^3$
x = $0.65 \times 10^{-4} M$

Assuming the solubility of AgBr is y.

$AgBr_{(s)}$ à Ag^{2+} + $2CrO_4^-$

K_{sp} = (y)^2
$5.0 \times 10^{-13} = y^2$

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

The ratio of molarities to their saturated solution is:

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

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

Ans.)

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

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

$Na(IO_3)_2$ à Na^+ + IO_3^-

0.0001M 0.001M

$Cu(ClO_3)_2$ à Cu2+ + $2CIO_3^-$

0.001M 0.001M

The Solubility for $Cu(IO_3)_2 \Rightarrow Cu^{2+}$ (aq) + $2IO_3^-$ (aq)

Now, the ionic product of the copper iodate is:

= [Cu2+] [IO_3^-]^2

= (0.001)(0.001)^2

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

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

Thus, the precipitation will not occur.

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

$2.5\times10^{-5}M$. **Give relation between the solubility of silver benzoate in buffer of pH = 3.19 and its solubility in water.**

Ans.)

Here, pH = 3.19

[H3O+] = $6.46\times10^{-5}M$

C6H5COOH + H2O à $C6H5COO^-$ + H3O

$K_a\frac{[C_6H_5COO^-][H_3O^+]}{C_6H_5COOH}\ K_a\frac{[C_6H_5COOH]}{C_6H_5COO^-}=\frac{[H_3O^+]}{K_a}=\frac{6.46\times10^{-4}}{6.46\times10^{-5}}=10$

Assuming the solubility of silver benzoate (C6H5COOAg) is y mol/L.

Now, $[Ag^+]$ = y

[C6H5COOH] = $[C6H5COO^-]$ = y

10$[C6H5COO^-]$ + $[C6H5COO^-]$ = y

$[C6H5COO^-]$ = y/11

$K_{sp}[Ag^+][C6H5COO^-]$ = y

$2.5\times10^{13}=y\frac{y}{11}$

y = 1.66×10^{-6} mol/L

Hence, solubility of C6H5COOAg in buffer of pH = 3.19 is 1.66×10^{-6} mol/L.

For, water:

Assuming the solubility of silver benzoate (C6H5COOAg) is x mol/L.

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

K_{sp} = $[Ag^+][C6H5COO^-]$

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

y = $\sqrt{K_{sp}}=\sqrt{2.5\times10^{-13}}=5\times10^{-7}mol/L$

$\therefore\frac{y}{x}=\frac{1.66\times10^{-6}}{5\times10^{-7}}=3.32$

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

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

Ans.)

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

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

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

Thus, $[FeSO_4]$ = $[Na_2S]$ = y/2 M

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

FeS(s) $\leftrightarrow Fe^{2+}_{(aq)}+S^{2-}_{(aq)}$

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

$6.3\times10^{-18}=(\frac{y}{2})(\frac{y}{2})\ \frac{y^2}{4}=6.3\times10^{-18}$

Thus, y = 5.02×10^{-9}

Thus, if the concentration of $FeSO_4$ and Na_2SO_4 are equal to or less than that of $5.02\times10^{-9}M$, then there won't be precipitation of FeS.

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

K_{sp} for $CaSO_4$ is 9.1×10^{-6}

Ans.)

$CaSO_{4(s)}\leftrightarrow Ca^{2+}_{(aq)}+SO_4^{2-}(aq)$

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

Assuming the solubility of calcium sulphate is x.

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

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

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

Solubility in calcium sulphate in g/mol is

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

= 0.41 g/L

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

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

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

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

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

In which of the above solution the precipitation takes place?

For MnS, K_{sp} = 2.5×10^{-13}

For ZnS, K_{sp} = 1.6×10^{-24}

For CdS, K_{sp} = 8.0×10^{-27}

For FeS, K_{sp} = 6.3×10^{-18}

Ans.)

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

Before mixing:

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

Volume = 10mL Volume = 5mL

After mixing:

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

Total volume = (10 + 5) = 15mL Volume = 15mL

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

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

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

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

= 8.87×10^{-22}

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

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