Q.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?

Ans.

(a) 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.

(b) 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.

(c) 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.

Q.2.What is Kc for the following equilibrium when the equilibrium concentration of each substance is: [SO_2] = 0.60M, [O_2] = 0.82M and [SO_3] = 1.90M?

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

Ans.

As per the question,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ (Given)}$$

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

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

$$= 12.229 M^{-1} \text{ (approximately)}$$

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

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

$I_2(g) \rightleftharpoons 2I\ (g)$ Calculate 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.Write the expression for the equilibrium constant, K_c for each of the following reactions:

(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.

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

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

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

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

$= \dfrac{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}]}$

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

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

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

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

Q.5.Find out the value of Kc for each of the following equilibria from the value of Kp:

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

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

Ans.

The relation between K_p and K_c is given as:

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

(i) Given,

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

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

T = 500 K

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

Now,

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

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

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

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

(ii) 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, $K_c = 6.3 \times 10^{14}$ $at\ 1000K$

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

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is 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 the 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 the density of the solid and pure liquid is fixed and molar mass is also fixed.

∴ Molar concentration are constant.

Q.8.

The reaction between N_2 and O_2 takes place as follows:

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

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 $K_c = 2.0 \times 10^{-37}$, determine the composition of the 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,

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

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 Br_2 and gives nitrosyl bromide as per reaction given below:

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

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 the equilibrium amount of NO and Br_2.

Ans.

The given reaction is:

$2NO_{(g)}+Br_{2(g)} \rightleftharpoons 2NOBr_{(g)}$

2mol 1mol 2mol

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

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

Therefore, 0.0518 mol of NOBr is 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:

$[Br_2]$ = 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.

$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ 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,

$$K_p = \ K_c(RT)\Delta n$$

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

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

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

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

$$= \ 7.48 \times \ 10^{11} L\, mol^{-1}$$

$$= \ 7.48 \times \ 10^{11} \ M^{-1}$$

Q.11. A sample of $HI_{(g)}$ is placed in a 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?

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

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:

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

Initial conc. 0.2 atm 0 0

At equilibrium 0.4 atm 0.16/2 0.16/2

=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

$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ is $1.7\times\ 10^2$

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

Ans.

The given reaction is:

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

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:

$4NO_{(g)}+6H_2O_{(g)} \rightleftharpoons 4NH_{3(g)}+5O_{2(g)}$

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,

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

Calculate the equilibrium constant for the reaction.

Ans.

The given reaction is:

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

Compound	H_2O	CO	H_2	CO_2
Initial Conc.	0.1M	0.1M	0	0
Equilibrium Conc.	0.06M	0.06M	0.04M	0.04M

Therefore, the equilibrium constant for the reaction,

$K_c = ([H_2][CO_2])/([H_2O][CO]) = (0.4*0.4)/(0.6*0.6) = 0.444$

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

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

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

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

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

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

$[HI]=0.5\ molL^{-1}$ 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?

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

Ans.

The given reaction is:

$2ICl_{(g)}$	$\rightleftharpoons$	$I_{2(g)}$	+ $Cl_{2(g)}$
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]= $(0.78 - 2 \times 0.167)M$

$$= 0.446M$$

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?

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

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,

$$p = \frac{-0.04\pm\sqrt{(0.04)^2-4\times1\times(-0.16)}}{2\times1}$$

$$= \frac{-0.04\pm0.80}{2}$$

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

$$= 0.38$$

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) $\rightleftharpoons$ $CH_3COOC_2H_5$ (l) + H_2O(l)

(i) Write the concentration ratio (reaction quotient), Qc, 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:

$CH_3COOH(l)+C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l)+H_2O(l)$

Initial conc. 1/V M 0.18/V M 0 0

At equilibrium (1-0.171)/V (0.18 – 0.171)/V 0.171/V M 0.171/V M

= 0.829/V M = 0.009/V M

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.

$CH_3COOH(l)+C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l)+H_2O(l)$

Initial conc. 1.0/V M 0.5/V M 0 0

At equilibrium (10-0.214)/V (0.5-0.214)/V 0.214/V M 0.214/V M

= 0.786/V M = 0.286/V M

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, the concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

PCl_5 (g) ⇌ 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) ⇌ 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 take 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) + CO_2 (g); K_p= 0.265 at 1050 K.

What is 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,

$FeO_{(g)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$

Initially, pCO = 1.4 atm and pCO_2= 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. The equilibrium constant, K_c for the reaction

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

At a specific time, from the analysis, we can conclude that the composition of the reaction mixture is 3.0 mol L $^{-1}$ N_2, 2.0 mol L^{-1} H_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.

	$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons$ $2NH_3$
At a particular time:	3.0 mol L^{-1}	2.0mol L^{-1}	0.5 mol L^{-1}

So,

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(0.5)^2}{(3.0)(2.0)^3}$$

$$= 0.0104$$

It is given that K_c=0.061

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

$\because \quad Qc < \quad K_c$,

the reaction preceeds in the forward direction to reach at equilibrium.

Q.22.Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

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

For which K_c= 32 at 500 K.

If initially pure BrCl is present at a concentration of 3.3 x 10^{-3} 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:

	$2BrCl(g)$ $\rightleftharpoons$	$Br_2(g)$ +	$Cl_2(g)$
Initial conc.	3.3×10^{-3}	0	0

At equilibrium $3.3 \times \ 10^{-3} - \ 2x$ x x

Now, we can write,

$$\frac{[Br_2][Cl_2]}{[BrCl]^2} = \ K_c$$

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

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

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

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

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

So , at equilibrium

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

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

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

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

Q.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

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

Calculate K_c for this reaction at the above temperature

Ans.

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

Given, mass of CO = 90.55 g

Now, the mass of CO_2 =(100 – 90.55)=9.45 g

Now, number of moles of CO, $n_{CO} = \frac{90.5}{28} = 3.234\, mol$

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

Partial pressure of CO,

$P_{CO}= \frac{n_{CO}}{n_{CO}+n_{CO_2}} \times p_{total} = \frac{3.234}{3.234+0.215} \times 1 = 0.938\, atm$

Partial pressure of CO_2, $P_{CO_2} = \frac{n_{CO_2}}{n_{CO}+n_{CO_2}} \times p_{total} = \frac{0.215}{3.234+0.215} \times 1 = 0.062, atm$

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. Calculate a) ΔG^0 and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K

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

Where;

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

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

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

Ans.

(a) For the given reaction, we have

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

$\Delta G^\circ = 52.0 - (87.0 + 0)$

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

(b) We know that,

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

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

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

$$= \ 6.134$$

$$\therefore \ K_c = \ antilog(6.134)$$

$$= \ 1.36 \times \ 10^6$$

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

Q.25. 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?

(a) $PCl_5(g) \rightleftharpoons PCl_3 + Cl_2\ (g)$

(b) $CaO(s) + CO_2\ (g) \rightleftharpoons CaCO_3(s)$

(c) $3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

Ans.

(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.

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

(I)$COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$

(II)$CH_4\ (g) + 2S_2\ (g) \rightleftharpoons CS_2\ (g) + 2H_2S\ (g)$

(III)$CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$

(IV)$2H_2\ (g) + CO\ (g) \rightleftharpoons CH_3OH(g)$

(V)$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

(VI)$4NH_3\ (g) + 5O_2\ (g) \rightleftharpoons 4NO\ (g) + 6H_2O\ (g)$

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 are 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.

$H_2\ (g) + Br_2\ (g) \rightleftharpoons 2HBr\ (g)$

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,

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

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

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

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) ⇌ CO (g) + $3H_2$ (g)

(a) Write as an expression for K_p for the above reaction.

(b) 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.

(a)For the given reaction,

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

(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.

Q.29. Describe the effect of:

a) Addition of H_2

b) Addition of CH_3OH

c) Removal of CO

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

$2H_2$ (g)+CO (g) ⇌ CH_3OH (g)

Ans.

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

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

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

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

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

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

$\Delta_rH° = 124.0$ kJ mol^{-1}

a) Write an expression for K_c for the reaction.

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

c) What would be the effect on K_c if

(i) more PCl_5 is added

(ii) pressure is increased?

(iii) The temperature is increased?

Ans.

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

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

$$K_c^{'} = \frac{1}{K_c}$$

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

$$= 120.48$$

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

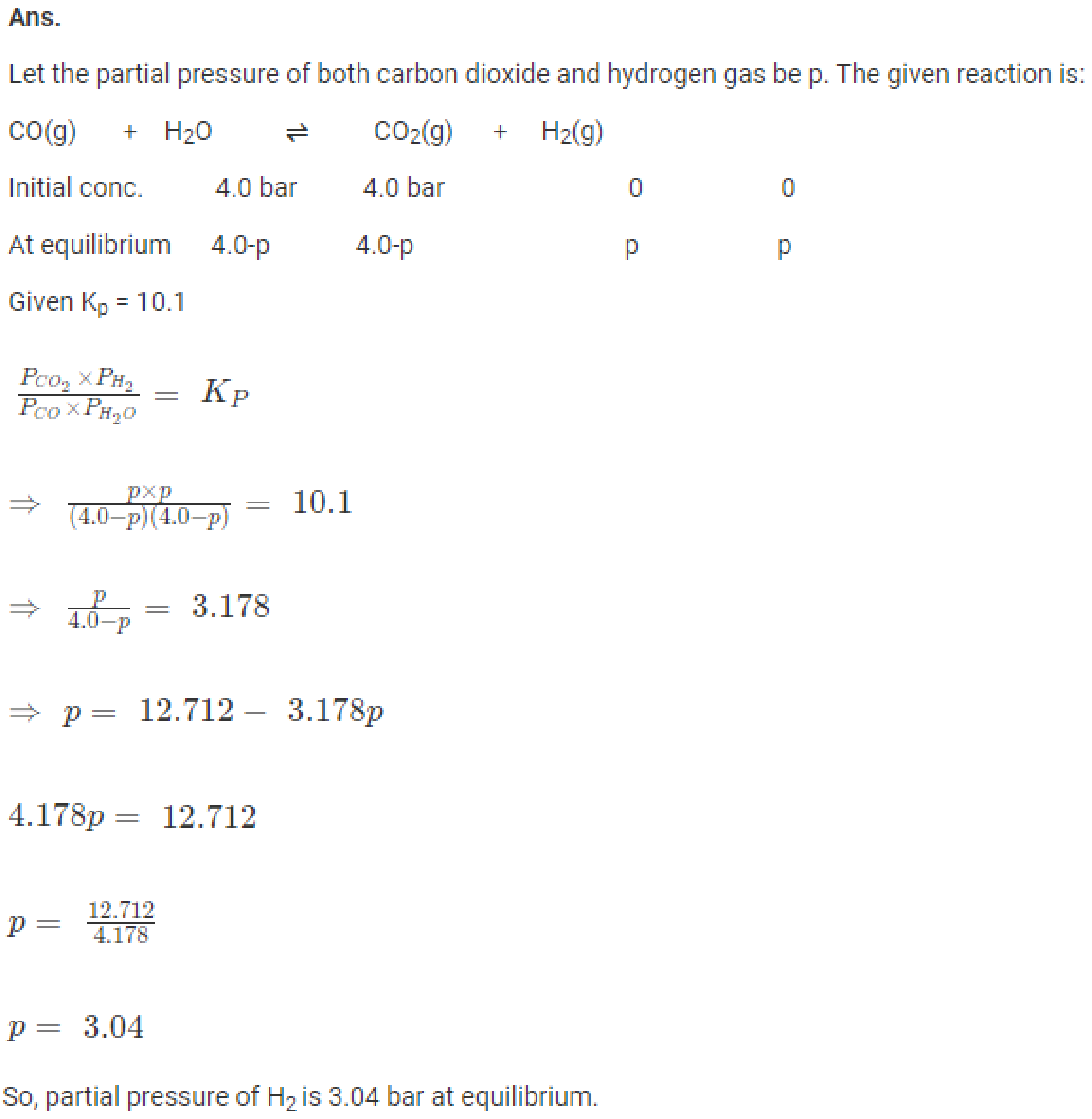
(ii) K_c is constant at a constant temperature. Thus, in this case, K_c would not change.

(iii)In an endothermic reaction, the value of K_c increases with an increase in temperature. Since the given reaction in an endothermic reaction, the value of K_c will increase if the temperature is increased.

Q.31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high-temperature steam. The first stage of two-stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

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

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 H_2 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 ⇌	$CO_2(g)$ +	$H_2(g)$
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 an appreciable concentration of reactants and products. Thus, the reaction given in (c) will have an appreciable concentration of reactants and products.

Q.33. The value of Kc for the reaction $3O_2$ (g) ⇌ $2O_3$ (g) is 2.0 x 10^{-50} at 25^0 C. If the equilibrium concentration of O_2 in air at 25^0 C is 1.6 x 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,

$$2.0 \times\ 10^{-50} = \frac{[O_3(g)]^2}{[1.6\times10^{-2}]^3}$$

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

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

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

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

Q.34. The reaction, $CO_{(g)} \ + \ 3H_{2(g)} \ \rightleftharpoons \ CH_{4(g)} \ + \ H_2O_{(g)}$ 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 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 given temperature is 3.90.

Ans.

Let the concentration of CH_4 at equilibrium be y.

$$CO_{(g)} \ + \ 3H_{2(g)} \ \rightleftharpoons \ CH_{4(g)} \ + \ H_2O_{(g)}$$

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,

$$\frac{[CH_{4(g)}][H_2O_{(g)}]}{[CO_{(g)}][H_{2(g)}]^3} \ = \ K_c \ \frac{y\times0.02}{0.3\times(0.1)^3} \ = \ 3.9 \ y \ = \ \frac{3.9\times0.3\times(0.1)^3}{0.02} \ y \ = \ \frac{0.00117}{0.02} \ y \ = \ 0.0585M$$

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

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:

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-} **and** 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:

HNO_2 – NO_2^- (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)

Q.36. Which of the followings are Lewis acids?

H_2O, BF_3, H^+ **and** NH_4^+

Ans.

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

H_2O – Lewis base

BF_3 – Lewis acid

H^+ – Lewis acid

NH_4^+ – Lewis acid

Q.37. What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO_3

Ans.

The following shows the conjugate bases for the Bronsted acids:

HF – F^-

H_2SO_4 – HSO_4^-

HCO_3 – CO_3^{2-}

Q.38. Write the conjugate acids for the following Brönsted bases:

NH_2^- **, NH_3 and** $HCOO^-$

Ans.

The conjugate acids for the given Bronsted bases are:

NH_2^- → NH_3

NH_3 → NH_4^+

$HCOO^-$ → HCOOH

Q.39. The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

Ans.

The conjugate acids and conjugate bases for the given species are listed in the table below:

Species	Conjugate acid	Conjugate bases
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^-

Q.40. Classify the following species into Lewis acids and Lewis bases and show that these species act as Lewis base/acid:

(a) OH^-

(b) F^-

(c) H^+

(d) BCl_3

Ans.

(a) OH^-

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

(b) F^-

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

(c) H^+

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

(d) BCl_3:

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

Q.41.The concentration of hydrogen ion in a sample of soft drink is 3.8 × 10^{-3} M. what is its pH?

Ans.

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

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

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

$$= -log\,3.8 + 3$$

$$= -0.5798 + 3$$

$$= 2.423$$

Q.42. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Ans.

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

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

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

$$= antilog(-3.76)$$

$$= 0.000178$$

$= 1.78 \times 10^{-4} \therefore 1.78 \times 10^{-4}$ is the concentration of white vinegar sample.

Q.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.

Ans.

For F^-, $K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{(6.8 \times 10^{-4})} = 1.47 \times 10^{-11}$

For $HCOO^-$, $K_b = \frac{10^{-14}}{(1.8 \times 10^{-4})} = 5.6 \times 10^{-11}$

For CN^- = $K_b = \frac{10^{-14}}{(4.8 \times 10^{-9})} = 2.08 \times 10^{-6}$

Q.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?

Ans.

C_6H_5OH	⇌	$C_6H_5O^-$	$+ H^+$
Initial 0.05M		0	0
After dissociation 0.05-x		x	x

$$\therefore K\alpha = \frac{x^2}{0.05 - x}$$

Because the value of the ionization constant is very small, the value of x is very small. Accordingly, w e may ignore x in the denominator.

$$x = \sqrt{1 \times 10^{-10} \times 0.05}$$

$$x = \sqrt{5 \times 10^{-12}}$$

$\therefore$ x = 2.2×10^{-6}M

In presence of 0.01 sodium phenolate(C_6H_5Na), suppose y is the amount of phenol dissociated, then at equilibrium

$[C_6H_5OH]$ = 0.05 -y

$[C_6H_5OH]$ ≈ 0.05

$[C_6H_5O^-]$ = 0.01 + y ≈ 0.01M,

$[H^+] = y$ M

$$\therefore\ K_\alpha = \frac{(0.01)(y)}{0.05} = 1.0 \times\ 10^{-10}$$

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

$$\alpha = \frac{y}{c}\ \ \alpha = \frac{5\times10^{-10}}{5\times10^{-2}}$$

$\alpha = 10^{-8}$

Q.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.

Ans.

To calculate $[HS^-]$

To find $[HS^-]$:

Case 1 – HCl is absent.

Now

$K_a = ([H^+][HS^-])/[H_2S] = 9.1\times10^{-8}$ (given)

$\therefore\ x^2/(0.1-x) = 9.1\times10^{-8}$

But 0.1-x is approximately equal to 0.1. Substituting this value in the equation:

$x^2/0.1 = 9.1\times10^{-8}$

$x^2 = 9.1\times10^{-9}$

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

$\therefore$ concentration of HS^- is 9.54×10^{-5} M.

Case 2 – HCl is present

Now,

$K_a = ([H^+][HS^-])/[H_2S] = (y\times (0.1+y))/(0.1-y) = 9.1\times10^{-8}$ (given)

But (0.1 + y) and (0.1 – y) can be approximated to 0.1.

$9.1\times 10^{-8} = (0.1*y)/0.1$

∴ y = $[HS^-] = 9.1\times 10^{-8}$ M

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

Case 1 – HCl is absent.

The dissociation of HS^- is given by the equation:

$HS^- \rightleftharpoons H^+ + S^{2-}[HS^-] = 9.1\times10^{-5}$ M

$[H^+] = 9.54\times10^{-5}$ M

$K_a = ([H^+][S^{2-}])/[HS^-] = 1.2\times10^{-13}$ (given)

$K_a = (9.1\times 10^{-5} \times [S^{2-}])/9.1\times10^{-5}$

∴ $[S^{2-}] = 1.2\times10^{-13}$ M

Case 2 – HCl is present

$[HS^-] = 9.1\times10^{-8}$ M

$[H^+] = 0.1$ M

$K_a = 1.2\times10^{-13}$ M

$= (0.1\times[S^{2-}])/ 9.1\times10^{-8}$

Therefore, $[S^{2-}] = 1.092\times10^{-19}$ M

Q.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

Ans.

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

$$\Rightarrow [H^+] = \sqrt{K_a[CH3COOH]} = \sqrt{(1.74\times10^{-5})(5\times10^{-2})} = 9.33\times 10^{-4}M$$

$$[CH3COO^-] = [H^+] = 9.33\times 10^{-4}M$$

$$pH = -log(9.33\times 1.0^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$$

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.

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

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. Assuming complete dissociation, calculate the pH of the following solutions: (a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

Ans.

(a) $HCl + aq \rightarrow H^+ + Cl^-$

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

$$pH = -log(3 \times 10^{-3}) = 2.52$$

(b) $NaOH + aq \rightarrow Na^+ + OH^-$

[OH^-] = 5×10^{-3}

[H^+] = $10^{-14}/5 \times 10^{-3}$

[H^+] = 2×10^{-12}M

pH = -log (2×10^{-12})

pH = 11.70

(c) $HBr + aq \rightarrow H^+ + Br^-$

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

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

$pH = 2.70$

(d) $KOH + aq \rightarrow K^+ + OH^-$

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

$[H^+] = 10^{-14}/2 \times 10^{-3}$

$[H^+] = 5 \times 10^{-12} M$

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

$pH = 11.30$

Q.49. Calculate the pH of the following solutions:

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

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

(III)0.3g of NaOH dissolved in water to give 200 mL 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. 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 = 0.001MpH =?α =? $K_b = c\alpha^2$

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

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

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

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

$10^{-5})$

$= 6.187$

$pH = 7.813$

$Now,$

$$K_a\times\ K_b = K_w$$

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

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

Q.52. 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) $K_a = 1.82 \times 10^{-5}$

$$K_a = c\alpha^2$$

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

$$\alpha = \sqrt{\frac{1.82\times10^{-5}}{5\times10^{-2}}} = 1.908 \times 10^{-2}$$

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.

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

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.

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

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

$$x = \frac{1.82\times10^{-5}\times0.05}{0.01}$$

$x = 1.82 \times 10^{-3} \times 0.05M$ Now, $\alpha = \frac{Amount\ of\ acid\ dissociation}{Amount\ of\ acid\ taken}$

$$= \frac{1.82\times10^{-3}\times0.05}{0.05}$$

$$= 1.82 \times 10^{-3}$$

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

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

$$x = \frac{1.82\times10^{-5}\times0.05}{0.1}$$

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

Now, $\alpha = \frac{Amount\ of\ acid\ dissociation}{Amount\ of\ acid\ taken}$

$$= \frac{1.82\times10^{-4}\times0.05}{0.05}$$

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

Q.53. The ionization constant of dimethylamine is 5.4 x 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.

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

$$c = 0.02M$$

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

$$= \sqrt{\frac{5.4\times10^{-4}}{0.02}} = 0.1643$$

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,

$(CH_3)_2NH$ + H_2O ↔ $(CH_3)_2NH_2^+$ + OH

(0.02-x) x x

0.02M 0.1M

Then,[$(CH_3)_2NH^+_2$]=x

[OH^-]=x+0.1;0.1

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

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

$$x = 0.0054$$

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

Q.54. 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 x 10^{-7}

(II) Human stomach fluid, 1.2

pH =1.2

1.2 = – log [H^+]

∴[H^+] = 0.063

(III) Human muscle fluid 6.83

pH = 6.83

pH = – log [H^+]

∴6.83 = – log [H^+] [H^+] =1.48 x 10^{-7} M

(IV) Human blood, 7.38

pH = 7.38 = – log [H^+]

∴ [H^+] = 4.17 x 10^{-8} M

Q.55. 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.56. 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.

[$KOH_{(aq)}$] = 0.561 / (1/5)g/L

= 2.805 g/L

= 2.805 x (1/56.11)

= 0.05M

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

[OH^-] = 0.05M = [K^+] [H^+][OH^-] = K_w

[H+] = Kw/[OH^-] [H+] = 10^{-14}/0.05

[H+] = 2 × 10^{-13}M

pH = -log[H^+]

pH = -log[2 × 10^{-13}]

pH = 12.70

Q.57. 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 $Sr(OH)_2$= $\frac{19.23}{121.63}M$

$$= 0.1581M$$

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

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

$[OH^-]$= 2 × 0.1581M

=0.3126

Now,

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

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

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

∴ pH = 13.50

Q.58. The ionization constant of propanoic acid is 1.32 x 10^{-5}. Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01 M in HCl also?

Ans.

Let the degree of ionization of propanoic acid be α.

Then, representing propionic acid as HA, we have:

$HA + H_2O \leftrightarrow H_3O^+ + A^-$

$(0.05-0.0\alpha) \approx 0.05 \quad 0.05\alpha \quad 0.05\alpha$

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

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

$= 0.05\alpha^2$

$\alpha = \sqrt{\frac{K_a}{0.05}}$

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

Then,[H_3O^+]= $0.05\alpha = 0.05 \times 1.63\times 10^{-2} = K_b. 15\times10^{-4}M$

∴ pH=3.09

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

Then, $[H_3O^+]$ = 0.01

$[A^-]$ = 0.05α'

[HA] = 0.05

Ka = 0.01 x 0.05α' / 0.05

⇒ 1.32×10^{-5} = 0. 01 α'

α' = 1.32×10^{-3}

Q.59. The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Ans.

c = 0.1 M

pH = 2.34

-log $[H^+]$ = pH

-log $[H^+]$ = 2.34

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

Also,

$[H^+]=c\alpha$

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

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

α = 0.045

$K_a = c\alpha^2$

$K_a = 0.1 \times (0.045)^2$

$K_a = 0.0002025$

$K_a = 2.025 \times 10^{-4}$

Q.60. 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.

Ans.

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

$$NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$$

$$K_h = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5 \times 10^{-4}} = 0.22 \times 10^{-10}$$

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

$$[NO_2^-] = 0.04 – y; 0.04$$

$$[HNO_2] = y$$

$$[OH^-] = y$$

$$K_h = \frac{y^2}{0.04} = 0.22 \times 10^{-10}$$

$$y^2 = 0.0088 \times 10^{-10}$$

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

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

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

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.61. A 0.02M solution of pyridinium hydrochloride (C_5H_6ClN) is having pH = 3.44. Calculate the ionization constant of C_5H_5N (pyridine).

Ans.

pH = 3.44As

we know,

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

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

Now, $K_h = \ \frac{3.63 \times 10^{-4}}{0.02}$;

(Given that concentration = 0.02M)

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

As we know that,

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

= 1.51×10^{-9}

Q.62 Predict if the solutions of the following salts are neutral, acidic or basic:

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

Ans.

- KBr

KBr + H_2O $\leftrightarrow$ KOH (Strong base)+ HBr (Strong acid)Thus, it is a neutral solution.

- NH_4NO_3

NH_4NO_3 + H_2O $\leftrightarrow$ NH_4OH(Weak base) + HNO_2 (Strong acid)Thus, it is an acidic solution.

- KF

KF + H_2O $\leftrightarrow$ KOH (Strong base) + HF (weak acid)Thus, it is a basic solution.

- $NaNO_2$

$NaNO_2$ + H_2O $\leftrightarrow$ NH_4OH(Strong base) + HNO_2(Weak acid)Thus, it is a basic solution.

- NaCN

NaCN + H_2O $\leftrightarrow$ HCN (Weak acid) + NaOH (Strong base)Thus, it is a basic solution.

- NaCl

NaCl + H_2O $\leftrightarrow$ NaOH (Strong base) + HCL (Strong acid)Thus, it is a neutral solution.

Q.63. 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?

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

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

- 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, $K_h = \frac{y^2}{0.1} \Rightarrow 0.740 \times 10^{-11} = \frac{y^2}{0.1} \Rightarrow 0.0740 \times 10^{-11} = y^2$

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

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

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

$[H^+] = 1.162 \times 10^{-3}$

pH = $-\log[H^+]$ = 7.94

Q.64. Ionic product of water at 310 K is 2.7 × 10^{-14}. What is the pH of neutral water at this temperature?

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

= $-\log[1.64 \times\ 10^{-7}]$ = 6.78Thus, the pH of neutral water at 310K temperature is 6.78.

Q.65. 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.

Ans.

$Ag_2CrO_4 \rightarrow 2Ag^{2+} + CrO_4^-$

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

Assuming the solubility of Ag_2CrO_4 is ‘x’.

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

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

Assuming the solubility of AgBr is y.

$AgBr_{(s)} \rightarrow Ag^{2+} + Br^-$

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

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

Ans.

Cupric chlorate and sodium iodate having equal volume are mixed together, then the molar concentration of cupric chlorate and sodium iodate will reduce to half. So, the molar concentration of cupric chlorate and sodium iodate in a mixture is 0.001M.

$Na(IO_3)_2 \rightarrow Na^+ + IO_3^-$

0.0001M 0.001M

$Cu(ClO_3)_2 \rightarrow$ 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, precipitation will not occur.

Q.67. 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?

Ans.

Here, pH = 3.19

[H3O+] = $6.46 \times \ 10^{-4} M$

$C_6H_5COOH + H_2O \rightarrow C6H5COO^{-}$ + H_3O

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

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

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

Now, $[Ag^+]$ = y

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

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

$[C6H5COO^{-}]$ = y/11

K_{sp}= $[Ag^+]$ $[C6H5COO^{-}]$ $2.5 \times \ 10^{-13} = \ y\frac{y}{11}$

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

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

For, water:Assuming the solubility of silver benzoate (C6H5COOAg) is x mol/L.

Now, $[Ag^+]$ = y' M and [CH3COO-] = y'M

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

K_{sp} = $(y')^2$ = $\sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} mol/L$

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

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

Q.68. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

Ans.

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

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

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

$$6.3 \times 10^{-18} = (\tfrac{y}{2})(\tfrac{y}{2})$$

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

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 $5.02 \times 10^{-9} M$, then there won't be precipitation of FeS.

Q.69. 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}).

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.70. 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?

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

$[S^{2-}]$ = $\frac{1.0\times10^{-19}\times10}{15} = 6.67\times 10^{-20}M$

$[M^{2+}]$ = $\frac{0.04\times5}{15} = 1.33\times 10^{-2}M$

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.