CBSE NCERT Solutions for Class 11 Chemistry Chapter 7

Back of Chapter Questions

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

(a) What is the initial effect of the change on vapour pressure?

(b) How do rates of evaporation and condensation change initially?

(c) What happens when equilibrium is restored finally, and what will be the final vapour pressure?

Solution:

(a) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.
(b) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.
(c) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

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

$2SO_2(g) + O_2(g) \longrightarrow 2SO_2(g)$

Solution:

Given: $[SO_2] = 0.60M,$

$[O_2] = 0.82M$

$[SO_3] = 1.90M$

Formula : The equilibrium constant (K_c) = $= \frac{[product]}{[reactant]}$

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

$$= \frac{(1.90)^2 M^2}{(0.60)^2(0.821)M^3}$$

$$= 12.239\ M^{-1}$$

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

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

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

Calculate K_p for the equilibrium.

Solution:

Given: total pressure of 10^5Pa

I atoms =40% by volume

Partial pressure=mole fraction × total pressure

Partial pressure of I atoms $(p_{1)} = \frac{40}{100} \times p_{\text{total}}$ $(\therefore volume\ \propto mole\ )$

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

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

Partial pressure of I_2 molecules,

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

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

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

Formula : $K_p = \frac{(\text{partial pressure of product})}{(\text{partial pressure of reactant})}$

$$K_p = \frac{(p_I)^2}{(P_{I_2})}$$

$$= \frac{(4 \times 10^4)^2 \mathrm{Pa}^2}{6 \times 10^4 \mathrm{Pa}}$$

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

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

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

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

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

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

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

Solution:

Formula : The equilibrium constant (K_c) = $= \frac{[product]}{[reactant]}$

For a heterogeneous equilibrium active mass of pure liquid and solid is taken to be 1

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

$$K_c = \frac{[NO\ (g)]^2[Cl_2\ (g)]}{[NOCl\ (g)]^2}$$

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

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

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

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

$$K_c = \frac{[CH_3COOH\ (aq)]^2[CH_3COOH\ (aq)]^4}{[CH_3COOC_2H_5(aq)][H_2O(l)]}$$

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

$$K_c = \frac{[Fe(OH)_3\ (s)]}{[Fe^{+3}(aq)][OH^-\ (aq)]^3} = \frac{1}{[Fe^{+3}(aq)][OH^-\ (aq)]^3}$$

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

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

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

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

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

Solution:

Formula : The relation between K_p and K_c is given as:$K_p = K_c(RT)^{\Delta n}$

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

$\Delta n = 3 - 2 = 1$

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

$T = 500\ K$

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

Put all values in the formula of $K_P = K_c(RT)^{\Delta n}$

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

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

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

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

$\Delta n = 2 - 1 = 1$

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

$T = 1073\ K$

$K_p = 167$

Now,put all values in a formula $K_p = K_c(RT)^{\Delta n}$

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

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

$= 1.87$ (approximately)

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

$NO\ (g) + O_3\ (g) \rightleftharpoons NO_2\ (g) + O_2\ (g)$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c' for the reverse reaction?

Solution:

formula :The equilibrium constant $(K_c) = = \frac{[product]}{[reactant]}$

$$NO\ (g) + O_3\ (g) \rightleftharpoons NO_2\ (g) + O_2\ (g)$$

It is given that Kc for the forward reaction is $K_c = \frac{[NO_2\ (g)]^2[O_2\ (g)]}{[NO\ (g)][O_3\ (g)]} = 6.3 \times 10^{14}$

Then, K_c' for the reverse reaction $= \frac{[NO\ (g)][O_3\ (g)]}{[NO_2\ (g)]^2[O_2\ (g)]}$

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

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

$= 1.59 \times 10^{-15}$

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

Solution:

For a pure substance (both solids and liquids),

Active mass of [Pure substance] $= \frac{\text{Number of moles}}{\text{Volume}} = \frac{\text{Mass/molecular moles}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}\times\text{Molecular mass}}$

$= \frac{\text{Density}}{\text{Molecular mass}}$

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

8. Reaction between N_2 and O_2 takes place as follows:

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

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

Solution:

Given: *initial* mol $N_2 = 0.482$

initial mol $O_2 =$ and 0.933

the volume of container =10 L

Let the concentration of N_2O at equilibrium be x.

The given reaction is:

	$2N_2(g) +$	$O_2(g)\ \rightleftharpoons$	$2N_2O(g)$
Initial conc.	0.482 mol	0.933 mol	0
At equilibrium	$(0.482 - x)$ mol	$(1.933 - x)$ mol	x mol

Therefore, at equilibrium, in the 10 L vessel:

$[N_2] = \frac{0.482}{10} = 0.0482\ mol\ L^{-1}$and $[O_2] = \frac{0.933}{10} = 0.0933 molL^{-1}$ $[N_2O] = \frac{x}{10} molL^{-1}$

Formula: The equilibrium constant $(K_c) = = \frac{[product]}{[reactant]}$

$$K_c = \frac{[N_2O(g)]^2}{[N_2(g)]^2[O_2(g)]}$$

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

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

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

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

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

9. Nitric oxide reacts with Br2 and gives nitrosyl bromide as per reaction is 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 equilibrium amount of NO and Br_2.

Solution:

Given: initial mol of NO =0.087

Initial mol of Br_2 =0.0437

mol of NOBr is obtained at equilibrium=0.0518

The given reaction is:

$$\underset{2\ mol}{2NO\ (g)} + \underset{1\ mol}{Br_2\ (g)} \leftrightharpoons \underset{2\ mol}{2NOBr\ (g)}$$

According to stoichiometry , 2 mol of NOBr are formed from 2 mol of NO and 1 mole of Br_2 react
, 2 mol of NOBr is formed

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

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

$[NO]\ =\ 0.087\ mol\ [Br_2]\ =\ 0.0437\ mol$
Therefore, the amount of NO present at equilibrium $=\ 0.087 - 0.0518\ =\ 0.0352$ mol
And, the amount of Br_2 present at equilibrium $=\ 0.0437 - 0.0259\ =\ 0.0178$ mol

10. At 450K, $Kp = 2.0 \times 10^{10}\ bar^{-1}$ for the given reaction at equilibrium.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3\ (g)$ What is K_c at this temperature?

Solution:

given :

$T = 450\ K$

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

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

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

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

Put all values in the above formula

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

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

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

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

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

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

11. A sample of HI(g) is placed in the 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?

$$2\text{HI (g)} \rightleftharpoons \text{H}_2\text{ (g)} + \text{I}_2\text{ (g)}$$

Solution:

Given: pressure = 0.2 atm

equilibrium the partial pressure of HI(g) = 0.04 atm

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)	$\rightleftharpoons$ $\text{H}_2\text{ (g)}$	+ $\text{I}_2\text{ (g)}$
Initial conc.	0.2 atm,	0	0
At equilibrium	0.04atm	$\frac{0.16}{2}$ $= 0.08$ atm	$\frac{2.15}{2}$ $= 0.08$atm

$$\text{formula for } K_p = \frac{\textit{partial pressure of peroduct}}{\textit{partial pressure of reactant}}$$

$$K_p = \frac{p_{H_2} \times p_{I_2}}{(P_{HI})^2}$$

$$= \frac{0.08 \times 0.08}{(0.04)^2}$$

$$= \frac{0.0064}{0.0016}$$

$$= 4.0$$

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

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 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Solution:

Given: mol of $N_2 = 1.57$

mol of $H_2 = 1.92$

mol of NH_3=8.13

the volume of vessel =20 Liter

temperature = 500 K

$K_c = 1.7 \times 10^2$

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

Now, reaction quotient Q_c is:

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

$$= \frac{\left(\frac{(8.13)}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3}$$

$$= 2.4 \times 10^3$$

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.

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

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

Write the balanced chemical equation corresponding to this expression.

Solution:

$$K_c = \frac{product\ of\ the\ molar\ concentation\ of\ produt}{product\ of\ the\ molar\ concentation\ of\ reactant}$$

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

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

14. One mole of H_2O and one mole of CO is taken in 10 L vessel and heated to 725 K. At equilibrium, 40% 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.

Solution:

The given reaction is:

	H_2O (g) +	$CO(g) \rightleftharpoons$	H_2 (g) +	CO_2 (g)
Initial conc	$\frac{1}{10}$ M	$\frac{1}{10}$ M	0	0
At equilibrium	$\frac{1-0.4}{10}$ M $= 0.06$ M	$\frac{1-0.4}{10}$ M $= 0.06$ M	$\frac{0.4}{10}$ M $= 0.04$ M	$\frac{0.4}{10}$ M $= 0.04$ M

Therefore, the equilibrium constant for the reaction $= \frac{product\ of\ the\ molar\ concentation\ of\ produt}{product\ of\ the\ molar\ concentation\ of\ reactant}$

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{[0.04][0.04]}{[0.06][0.06]} = 0.444 \text{ (approximately)}$$

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

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

is 54.8. If 0.5 mol L^{-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 700K?

Solution:

Given: equilibrium constant K_c for the reaction $H_2\ (g)\ +\ I_2\ (g) \rightleftharpoons\ 2HI\ (g)$ is 54.8.

temperature =700 K

equilibrium constant K_c for the reaction $\frac{[H_2(g)]\,[I_2(g)]}{[HI\ (g)]^2} = 54.8$

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

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

$$K'_c = \frac{[HI\ (g)]^2}{[H_2(g)]\,[I_2(g)]} = \frac{1}{54.8}$$

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

0.5 x x

moles of HI(g) is present at equilibrium =0.5 mol L^{-1}

[HI] = 0.5mol L^{-1} will be

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

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

$$K'_C = \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$$

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

$\Rightarrow x = 0.06754$

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

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

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

$2ICl\ (g) \rightleftharpoons I_2\ (g) + Cl_2(g);\ K_c = 0.14$

Solution:

The given reaction is:

	$2ICl\ (g)$	$\rightleftharpoons$	$I_2\ (g) +$	$Cl_2(g)$
Initial conc.	0.78 M		0	0
Conc. at equilibrium	$(0.78 - 2x)M$		xM	xM

Now, we can $\frac{[I_2][Cl_2]}{[ICl]^2} = K_c$

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

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

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

$\Rightarrow x = 0.292 - 0.748x$

$\Rightarrow 1.748x = 0.292$

$\Rightarrow x = 0.167$

Hence, at equilibrium,

$[H_2] = xM = 0.167M$

$[I_2] = xM = 0.167M$

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

$= 0.446\ M$

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?

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

Solution:

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

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

	C_2H_6	C_2H_4	H_2
Initial conc.	4.0 atm	0	0
At equilibrium	4.0 − p	p	p

Formula : $\frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} = K_p$

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

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

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

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

$$= \frac{-0.04 \pm 0.80}{2}$$

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

$$= 0.38$$

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), 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 some time. Has equilibrium been reached?

Solution:

(i) water is not in excess and is not a solvent in this reaction so all will be considered in the equilibrium expression

Reaction quotient (Q_c) $= \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$

(ii) given : temperature = 293 K,
initial mol of acetic acid= 1.00
initial mol of ethanol= 0.18
mol of ethyl acetate=0.171

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.	$\frac{1}{V}M$	$\frac{0.18}{V}M$	0	0
At equilibrium	$\frac{1-0.171}{V}$ $=\frac{0.829}{V}M$	$\frac{0.18-0.171}{V}$ $=\frac{0.009}{V}M$	$\frac{0.171}{V}M$	$\frac{0.171}{V}M$

Therefore, the equilibrium constant for the given reaction is:

$$K_c = \frac{[CH_3COOC_2H_3][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\frac{0.171}{V}\times\frac{0.171}{V}}{\frac{0.829}{V}\times\frac{0.009}{V}} = 3.919 \approx 3.92$$

(i) (ii) temperature = 293 K,
Initial mol of acetic acid = 1
initial mol of ethanol = 0. 5
mol of ethyl acetate formed = 0.214

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.	$\frac{1.0}{V}M$	$\frac{0.5}{V}M$	0	0
After some time	$\frac{10-0.214}{V}$ $=\frac{0.786}{V}M$	$\frac{0.5-0.214}{V}$ $=\frac{0.286}{V}M$	$\frac{0.214}{V}M$	$\frac{0.214}{V}M$

Therefore, the reaction quotient is,

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

$$= \frac{\frac{0.214}{V}\times\frac{0.214}{V}}{\frac{0.786}{V}\times\frac{0.286}{V}}$$

$= 0.2037$

$= 0204$ (approximately)

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

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?

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

Solution:

Given : temperature =473

After equilibrium concentration of PCl_5 = 0.5×10^{-1} mol L^{-1}

$K_c = 8.3 \times 10^{-3}$

Let the concentrations of both PCl_3 and Cl_2 at equilibrium be x molL^{-1}. The given reaction is:

	$PCl_5(g)$	$\leftrightarrow$	$PCl_3(g)$	$+ Cl_2(g)$
At equilibrium	0.5×10^{-1}mol L^{-1}		x mol L^{-1}	x mol L^{-1}

It if given that the value of the equilibrium constant, K_c is 8.3×10^{-3}.

Now we can write the expression for equilibrium as:

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

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

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

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

$$= 0.0204 \approx 0.02$$

Therefore, at equilibrium,

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

20. One of the reaction 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.

$FeO\,(s) + CO\,(g) \rightarrow Fe\,(s) + CO_2\,(g);\ Kp = 0.265$ atm 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 $= 0.80$ atm?

Solution:

Given: $Kp = 0.265$ atm

Temperature = 1050K

initial partial pressures of CO $(P_{CO}) = 1.4$ atm

initial partial pressures of CO_2 $(P_{CO_2}) = 0.80$ atm

For the given reaction,

$$\underset{\text{Initially,}}{FeO(s)} + \underset{1.4\text{ atm}}{CO\ (g)} \rightleftharpoons Fe\ (s) + \underset{0.80\text{ atm}}{CO_2(g)}$$

$$Q_p = \frac{p_{CO_2}}{P_{CO}}$$

$$= \frac{0.80}{1.4}$$

$$= 0.571$$

It is given that $K_p = 0.265$.

Since $Q_c > K_p$, 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,

$$\underset{\text{Initially,}}{FeO(s)} + \underset{1.4\text{ atm}}{CO\ (g)} \leftrightarrow Fe\ (s) + \underset{0.80\text{ atm}}{CO_2(g)}$$

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

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

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

$$\Rightarrow 1.265p = 0.429$$

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

Therefore, equilibrium partial pressure of $CO_2(P_{CO_2}) = 0.80 - 0.339 = 0.461$ atm

And, equilibrium partial pressure of $CO(P_{CO}) = 1.4 + 0.339 = 1.739$ atm

21. Equilibrium constant, K_c for the reaction

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

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

Solution:

given: $temperature = 500\ \text{K}$

K_c =0.061

composition of $N_2 = 3.0\ \text{mol L}^{-1}$

composition of $H_2 = 2.0\ \text{mol L}^{-1}$

composition of $NH_3 = 0.5\ \text{mol L}^{-1}$.

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

Formula: $Q_c = \frac{[\text{product}]}{[reactant]} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3}$

$= 0.0104$

It is given that $K_c = 0.061$

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

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

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 $3.3 \times 10^{-3}\ \text{mol L}^{-1}$, what is it's molar concentration in the mixture at equilibrium?

Solution:

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

	$2BrCl(g)$	$\leftrightarrow Br_2(g) +$	$Cl_2(g)$
Initial conc,	3.3×10^{-3}	0	0
At equilibrium	$3.3 \times 10^{-3} - 2x$	x	x

Now, we can write,

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

$$\Rightarrow 32 = \frac{x \times x}{(3.3 \times 10^{-3} - 2x)^2}$$ by taking root both side

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

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

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

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

Therefore, at equilibrium,

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

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.

Solution:

Given : CO by mass =90.55%

Temperature =1127 k

Pressure = 1 atm

We know $molecular\ weight\ of\ CO_2 = 44$

$molecular\ weight\ of\ CO = 28$

Let the total mass of the gaseous mixture is 100 g.
Mass of CO = 90.55 g
And, the mass of CO_2 = (100 – 90.55) = 9.45 g

Now, the number of moles of CO $(n_{CO}) = \frac{\text{weight of CO}}{molecular\ weight\ of\ Co} = \frac{90.55}{28} = 3.234$ mol

Number of moles of CO_2 $\left(n_{CO_2} \right) = \frac{\text{weight of } CO_2}{molecular\ weight\ of\ CO_2} = \frac{9.45}{44} = 0.215$ mol

The 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 $(p_{CO_2}) = \frac{\text{mole of } CO_2}{\text{total moles}} \times p_{total} = \frac{n_{CO_2}}{n_{CO}+n_{CO_2}} \times p_{total}$

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

$= 0.062$ atm

Therefore, $K_p = \frac{\text{the partial pressure of the product}}{\text{the partial pressure of reactant}} = \frac{[CO]^2}{[CO_2]} = \frac{(0.938)^2}{0.062} = 14.19$

For the given reaction,

$\Delta n = 2 - 1 = 1$

Formula : $K_p = K_c(RT)^{\Delta n}$ put the values in the formula

$\Rightarrow 14.19 = K_c(0.082 \times 1127)^{l}$

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

≈ 0.154

24. Calculate a) ΔG^e 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

$\Delta_1 G^o\ (NO_2) = 52.0$ kJ/mol

$\Delta G^o(NO) = 87.0 \frac{kJ}{mol}$

$\Delta G^o\ (O_2) = 0$ kJ/mol

Solution:

For the given reaction,

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

$$\Delta_1 G^o\ (NO_2) = 52.0\ kJ/mol$$
$$\Delta G^o (NO) = 87.0\ kJ/mol$$

$$\Delta G^o\ (O_2) = 0\ kJ/mol$$

Formula : $\Delta G^o\ = \Delta G^o$ (products) $-\Delta G^o$ (Reactants)

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

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

(b) formula : $\Delta G^o\ = -RT \ln K_c$

$\Delta G^o\ = -2.303\ RT \log K_c$

Put all values in above formula

$\log K_c = \frac{-35.0\times10^{-3}}{-2.303\times8.314\times298}$

$\log K_c = 6.134$

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

$K_c = 1.36 \times 10^6$

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

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

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

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

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

Solution:

(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.

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

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

Solution:

(i) $COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g) \qquad \Delta n_g = 1$

(ii) $CH_4\ (g) + 2S_2\ (g) \rightleftharpoons CS_2\ (g) + 2H_2S\ (g)\ \Delta n_g = 0$

(iii) $CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)\ \Delta n_g = 1$

(iv) $2H_2\ (g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)\ \Delta n_g = -2$

(v) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)\ \Delta n_g = 1$

(vi) $4\ NH_3\ (g) + 5O_2\ (g) \rightleftharpoons 4NO\ (g) + 6H_2O(g)\ \Delta n_g = 1$

The reaction is given in (ii) $\Delta n_g = 0$ no effect of pressure and no effect on equilibrium because of the number of moles of gaseous reactants is the same that of gaseous products.
(i), (iii), (iv), (v), and (vi) affected by pressure
The reaction is given in (iv) $\Delta n_g = -2$
will proceed in the forward direction because of the number of moles of gaseous reactants is more than that of gaseous products.
The reactions are given in (i), (iii), (v), and (vi) in $all\ \Delta n_g = +1$ will shift in the backward direction because the number of moles of gaseous reactants is less than that of gaseous products.

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.

Solution:

K_p for the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $= 1.6 \times 10^5$.

$$K_p = \frac{[HBr]^2}{[H_2[Br_2]}$$

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

$$K_p' = \frac{[H_2[Br_2]}{[HBr]^2} = \frac{1}{K_p} = \frac{1}{1.6\times10^5} = 6.25 \times 10^{-6}$$

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

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

Now, we can write,

$$\frac{p_{H_2} \times p_{Br_2}}{p_{HBr}} = K_p'$$

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

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

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

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

$$(10.5 \times 10^{-3})p = 2.5 \times 10^{-2}$$

$$p = 2.49 \times 10^{-2} \text{ bar} \approx 2.5 \times 10^{-2} \text{ bar}$$

Therefore, at equilibrium,

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

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

$$= 9.95 \text{ bar} \approx 10 \text{ bar}$$

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 the expression for Kp for the above reaction.

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

(i) increasing the pressure.

(ii) increasing the temperature.

(iii) using a catalyst?

Solution:

(a) For the given reaction,

$$K_p = \frac{p_{CO} \times [P_{H_2}]2}{p_{CH_4} \times p_{H_2O}}$$

(b)

(i)

CH_4 (g) + H_2O (g) ⇌ CO (g) + $3H_2$ (g) ; $\Delta n_g = 2$

$K_p \propto P^2$

According to Le Chatelier's principle,on increasing pressure, 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.

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)

Solution:

Given the reaction : $2H_2$(g) + CO (g) ⇌ CH_3OH (g) for this reaction $\Delta n_g = -2$

(a) According to Le Chatelier's principle, on the addition of H_2(reactant), the equilibrium of the given reaction will shift in the forward direction to maintain the equilibrium constant reactant has to decrease .
(b) On addition of CH_3OH, the equilibrium will shift in the backward direction to maintain the equilibrium constant reactant has to increase
(c) On removing CO, the equilibrium will shift in the backward direction to maintain the equilibrium constant reactant has to increase
(d) On removing CH_3OH, the equilibrium will shift in the forward direction to maintain the equilibrium constant reactant has to decrease

30. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride,

PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)\ \Delta_r H^e = 124.0\ \text{kJ mol}^{-1}$

(a) write an expression for K_c for the reaction.

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

(c) what would be the effect on Kc if

(i) more PCl_5 is added

(ii) pressure is increased

(iii) the temperature is increased?

Solution:

(a) for the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

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

(a) Value of K_c for the reverse reaction at the same temperature is
$PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$

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

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

(b) **(i)** $K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

more PCl_5 is added then K_c *will not change* because of the equilibrium constant does not change by change mole , concentration , pressure. It depends only on temperature and stoichiometry of the reaction .

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

(iii)

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)\ \Delta_rH^o = 124.0\ kJ\ mol^{-1}$

The reaction is endothermic , 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.

Or $ln\frac{k_2}{k1} = \Delta H[\frac{1}{T_1} - \frac{1}{T_2}]$

As for endothermic reaction $\Delta H = +ve\ ; T_2 > T_1; K_2 > K_1$

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^oC is charged with an equimolar mixture of CO and steam such that $pco\ = pH_2O = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 10.1$ at $400°C$

Solution:

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

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

It is given that $K_p = 10.1$

Now,

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

$\Rightarrow \frac{p \times p}{(4.0-p)(4.0-p)} = 10.1$ by talking root both side we get

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

$\Rightarrow p = 12.712 - 3.178p$

$\Rightarrow 4.178p = 12.712$

$\Rightarrow p = 3.04$

Hence, at equilibrium, the partial pressure of H_2 =P= 3.04 bar.

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

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

b) $Cl_2\ (g) + 2NO\ (g) \rightleftharpoons 2NOCl\ (g)$ $K_c = 3.7 \times 10^{8}$

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

Solution:

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

b) $Cl_2\ (g) + 2NO\ (g) \rightleftharpoons 2NOCl\ (g)$ $K_c = 3.7 \times 10^{8}$

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

for (a) the values of$K_c = 5 \times 10^{-39}$ is very less, i.e. reactant is very more
b) $Cl_2\ (g) + 2NO\ (g) \rightleftharpoons 2NOCl\ (g)$ $K_c = 3.7 \times 10^{8}$ is very high i.e. product is very more

(c) $Cl_2\ (g) + 2NO_2\ (g) \rightleftharpoons 2NO_2Cl\ (g)$ $K_c = 1.8$
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.

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

Solution:

Given: $K_c = 2.0 \times 10^{-50}$

$[O_2(g)] = 1.6 \times 10^{-2}$.

The given reaction $3O_2(g) \rightleftharpoons 2O_3(g)$

$$K_c = \frac{\text{product of the molar concentration of product}}{\text{product of the molar concentration of reactant}} = \frac{[O_3(g)]^2}{[O_2(g)]^3}$$

Put all the given values in the expression of K_c

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

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

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

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

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

34. The reaction, $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1L flask. It also contains 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Solution:

Given :Temperature = 1300 K

mol of CO = 0.30

mol of H_2 = 0.10

mol of H_2O = 0.02

amount of CH_4= unknown

Let the concentration of methane at equilibrium be x.

$$\begin{array}{lcccc} & CO(g) & + \; 3H_2(g) & \rightleftharpoons CH_4(g) & + H_2O(g) \\ \text{At equilibrium} & \frac{0.3}{1} = 0.3\text{M} & \frac{0.1}{1} = 0.1\text{M} & x & \frac{0.02}{1} = 0.02\text{M} \end{array}$$

It is given that $K_c = 3.90$.

Therefore,

$$\frac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3} = K_c$$

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

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

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

$$= 0.0585\ M$$

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

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

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

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

Solution:

A conjugate acid-base pair is a pair that differs only by one proton.

$$Acid\ (HA) \rightarrow conjugate\ base(A^-) + H^+$$

$$base + H^+ \rightarrow conjugate\ acid$$

The conjugate acid-base for the given species is mentioned in the table below.

Species	**Conjugate acid-base**
HNO_2	NO_2^-(Conjugate - base)
CN^-	HCN (Conjugate - acid)
$HClO_4$	ClO_4^- (Conjugate - base)
F^-	HF (Conjugate - acid)
OH^-	H_2O (Conjugate - acid)
OH^-	O^{2-}(Conjugate - base)
CO_3^{2-}	HCO_3^- (Conjugate - acid)
S^{2-}	HS^- (Conjugate - acid)

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

Solution:

Lewis acids are those species which can accept a pair of electrons. They are electron-deficient species and having vacant orbital . For example, BF_3, H^+, And NH_4^+ are Lewis acids.

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

Solution:

$Acid\ (HA) \rightarrow conjugate\ base(A^-)\ +\ H^+$

Proton (H^+) donors are acid

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

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

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

Solution:
A conjugate acid of the base formed when base gains proton.

$$base\ +\ H^+ \rightarrow conjugate\ acid$$

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

Species	**Conjugate acid fo base**
NH_2^-	NH_3
NH_3	NH_4^+
$HCOO^-$	$HCOOH$

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.

Solution:

A conjugate acid-base pair is a pair that differs only by one proton.

$Acid\ (HA) \rightarrow conjugate\ base(A^-) + H^+$

$base + H^+ \rightarrow conjugate\ acid$

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

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

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

(a) OH^-

(b) F^-

(c) H^+

(d) BCl_3

Solution:

Lewis acids: species which can accept a pair of electrons. They are electron-deficient species and having vacant orbital

Lewis base: species which can donate a pair of electrons. They are electron-efficient species

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

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

Solution:

Given,

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

$\therefore$ pH value of soft drink $= -\log[H^+]$

$= -\log(3.8 \times 10^{-3})$ $\quad (\therefore logM \times N = logM + logN)$

$= -\log(3.8 - \log10^3)$ $\quad (\therefore logM^N = NlogM)$

$= -\log(3.8 + 3)$

$= -0.58 + 3$

$= 2.42$

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

Solution:

Given, pH $= 3.76$

It is known that,

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

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

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

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

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

Hence, the concentration of hydrogen ion $[H^+]$ in the given sample of vinegar is 1.74×10^{-4}M.

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

Solution:

Given : The ionization constant of HFat 298K is 6.8×10^{-4}

The ionization constant of HCOOH at 298K is 1.8×10^{-4}

The ionization constant of HCN at 298K is 4.8×10^{-9}

Formula : $K_bK_a=K_w$

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

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

Hence, K_b of its conjugate base $F^- = \frac{K_w}{K_a} = \frac{10^{-14}}{6.8\times10^{-4}} = 1.5 \times 10^{-11}$

K_a of HCOOH $= 1.8 \times 10^{-4}$ Hence, K_b of its conjugate base $HCOO^- = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8\times10^{-4}} = 5.6 \times 10^{-11}$

K_a of HCN $= 4.8 \times 10^{-9}$Hence, K_b of its conjugate base $CN^- = \frac{K_w}{K_a} = \frac{10^{-14}}{4.8\times10^{-9}} = 2.08 \times 10^{-6}$

44. The ionization constant of phenol is 1.0×10^{10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

Solution:

Given : Ionization of phenol $=1.0 \times 10^{10}$

	C_6H_5OH + $H_2O \rightleftharpoons$	$C_6H_5O^-$ +	H_3O^+
Initial conc.	0.05	0	0
At equilibrium	$0.05 - x$	x	x

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

$K_a = \frac{x\times x}{0.05-x} =1.0 \times 10^{10}$

As the value of the ionization constant is very less, x will be very small.

We can ignore x in the denominator $0.05 - x \approx 0.05$

$\frac{x\times x}{0.05} =1.0 \times 10^{10}$

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

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

$= 2.2 \times 10^{-6}\text{M} = [H_3O^+]$

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

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

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

$$C_6H_5ONa \rightarrow C_6H_5O^- + Na^+$$

Conc. 0.01

Also, $C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3^+O$

Conc. $0.05 - 0.05\alpha$ $\quad 0.01 + 0.05\alpha \quad 0.05\alpha$

$[C_6H_5OH] = 0.05 - 0.05\alpha \approx 0.05\text{M} \; (\therefore \alpha \approx 0)$

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

$[H_3O^+] = 0.05\alpha$

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

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

$1.0 \times 10^{-10} = 0.01\alpha$

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

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

Solution:

Given: first ionization constant of $H_2S = 9.1 \times 10^{-8}$

the second dissociation constant of H_2S is 1.2×10^{-13}

(i) To calculate the concentration of HS^- ion:
Case a: (in the absence of HCl): concentration of H_2S solution = 0.1 M

Let the concentration of HS^- = x M.

$$\begin{array}{llll} & H_2S & \rightleftharpoons H^+ & + HS^- \\ C_i & 0.1 & 0 & 0 \\ C_f & 0.1-x & x & x \end{array}$$

Then, $K_{a1} = \frac{[H^+][HS^-]}{[H_2S]}$

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

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

$\therefore$ $first\ ionization\ constant\ of\ H_2S = 9.1 \times 10^{-8}$ so x can be ignored and $0.1 - x\ M \approx 0.1\ M$, we have $(9.1 \times 10^{-8})(0.1) = x^2$.

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

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

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

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

Case b : (in the presence of HCl): concentration of H_2S solution = 0.1 M

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

$$\begin{array}{lllll} \text{Then,} & H_2S & \rightleftharpoons & HS^- & + H^+ \\ C_i & 0.1 & & 0 & 0.1 \\ C_f & 0.1-y & & y & 0.1+y \end{array}$$

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

$$K_{a_j} = \frac{[y][0.1 + y]}{[0.1 - y]}$$

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

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

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

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

Case c (in the absence of 0.1 M HCl):

$HS^- \rightleftharpoons H^+ + S^{2-}$

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

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

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

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

$$K_{a_2} = \frac{[9.54 \times 10^{-5}][X]}{[9.54 \times 10^{-5}]}$$

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

Case d (in the presence of 0.1 M HCl):

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

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

$[H^+] = 0.1M$ (From HCl, case II)

$[S^-] = X'$

HS^-	$\rightleftharpoons$	H^+	$+$	S^{2-}
$9.1 \times 10^{-8}M$		0.1		X'

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

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

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

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

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

$= 1.092 \times 10^{-19}M$

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

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

Solution:

Given: The ionization constant of acetic acid = 1.74×10^{-5}

Concentration of acetic acid solution = 0.05 M solution

Method 1

1) $\mathrm{CH_3COOH \rightleftharpoons CH_3COO^- + H^+} \quad K_a = 1.74 \times 10^{-5}$
2) $\mathrm{H_2O + H_2O \rightleftharpoons H_3O^- + OH^-} \quad K_w = 1.0 \times 10^{-14}$

Since $K_a >> K_w$,:

$$\begin{array}{lllll} & \mathrm{CH_3COOH + H_2O} & \rightleftharpoons & \mathrm{CH_3COO^- } & \mathrm{+ H_3O^+} \\ C_i = & 0.05 & & 0 & 0 \\ & 0.05 - .05\alpha & & 0.05\alpha & 0.05\alpha \end{array}$$

$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.74\times10^{-5}}{0.05}}$= 0.018 or 18 % so α can not be neglected so quadratic equation have to solve

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

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

$$= \frac{0.05\alpha^2}{1-\alpha}$$

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

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

$$0.05\alpha^2 + 1.74 \times 10^{-5}\alpha - 1.74 \times 10^{-5} = 0$$

$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} =$$

$$= \frac{-1.74\times10^{-5} \pm \sqrt{(1.74\times10^{-5})^2 - 4(0.05)(-1.74\times10^{-5})}}{2\times0.05}$$

$$\alpha = \frac{-1.74\times10^{-5} \pm \sqrt{(1.74\times10^{-5})^2 + (0.348\times10^{-5})}}{2\times0.05}$$

$$\alpha = \frac{-1.74 \times 10^{-5} \pm (1.86 \times 10^{-3})}{2 \times 0.05}$$

$$\alpha = \frac{-1.74 \times 10^{-5} + 1.86 \times 10^{-3})}{2\ \times 0.05}$$

$$\alpha = \frac{1.84 \times 10^{-3}}{0.1} = 1.84 \times 10^{-2}$$

$$[H^+]\ = c\alpha = 0.05 \times 1.86 \times 10^{-3}$$

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

$$= .000093$$

Method 2

Degree of dissociation,

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

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

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

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

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

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

$$\alpha = 1.86 \times 10^{-2}$$

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

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

$$= 0.05 \times 1.86 \times 10^{-2}$$

$$= 0.093 \times 10^{-2}$$

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

Since $[OAc^-] = [H^+]$,

$$[H^+] = 0.00093 = 0.093 \times 10^{-2}$$

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

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

$$\therefore pH = 3.03$$

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

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 pKa.

Solution:

given: $pH = 4.15$

Let the organic acid be HA (weak acid)

Concentration of $HA = 0.01\ M$

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

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

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

Now, $dissociation\ of\ waek\ acid:\ HA \rightleftharpoons H^+ + A^-$

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

$[HA] = 0.01$

Then,

$$K_a = \frac{[H^+][A^-]}{0.01} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{0.01} = 5.01 \times 10^{-7}$$

$pK_a = -\log K_a$

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

$pK_a = 6.3001$

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

Solution:

(i) $0.003 MHCl$:
$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$
Since HCl is completely ionized,

$[H_3O^+] = [HCl]$
$\Rightarrow [H_3O^+] = 0.003$
Now,
$pH = -\log[H_2O^+]$
$= -\log(0.003) = -\log(3 \times 10^3) = -[\log(3) + log(10^3)] = -[0.477 + 3] =$
$= 2.52$

Hence, the pH of the solution is 2.52.

(ii) $0.005MNaOH$

$NaOH(aq) \rightleftharpoons \mathrm{Na}^+(aq) + \mathrm{HO}^-(aq)$

$[HO^-] = [NaOH] \qquad (\therefore NaOH\ is\ strong\ base\ )$

$\Rightarrow [HO^-] = 0.005$

$pOH = -\log[HO^-] = -\log(0.005)$

$pOH = 2.30$

$\therefore\ pH + pOH = pK_W\ ;\ pH = 14 - pOH$

$pH = 14 - 2.30$

$= 11.70$

Hence, the pH of the solution is 11.70.

(iii) 0.002 HBr:

$HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$

$[H_3O^+] = [HBr]$

$\Rightarrow [H_3O^+] = 0.002$

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

$= -\log(0.002) = -\log(2 \times 10^3) = -[\log(2) + \log(10^3)] = -[\log(2) + 3\log(10)]$

$= 2.69$

Hence, the pH of the solution is 2.69.

(iv) 0.002 $M\ KOH$:

$KOH(aq) \rightleftharpoons K^+(aq) + OH^-(aq)$

$[OH^-] = [KOH]$

$\Rightarrow [OH^-] = 0.002$

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

$= 2.69$

$\therefore\ pH + pOH = pK_W\ ;\ pH = 14 - pOH$

$pH = 14 - 2.69$

$= 11.31$

Hence, the pH of the solution is 11.31.

49. Calculate the pH of the following solutions:

(A) 2 g of TlOH dissolved in water to give 2 litre of solution.

(B) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

(C) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

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

Solution:

(a) For $2g$ of $TlOH$ dissolved in water to give 2 L of solution:
Moles of $TlOH = \frac{weight}{molecular\ weight} = \frac{2}{221}$

$$[TlOH(aq)] = \frac{\frac{2}{221}}{2} mole/L$$

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

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

$$TIOH(aq) \rightarrow TI^{+}(aq) + OH^{-}(aq)$$

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

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

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

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

$\Rightarrow pH = -\log[H^{+}] = -[\log(221 \times 10^{-14})] = -[\log(2.21 \times 10^{-12})] = -[\log(2.21 - 12\ log 10\ )]$

$= 11.65$

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

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

Molar mass of $Ca(OH)_2 = 40 + 2(17) = 74$

$$[Ca(OH)_2] = \frac{0.3}{34} \times \frac{1000}{500} = 0.0176M$$

$[OH^-(aq)] = 2 \times [Ca(OH)_2] = 2 \times 0.0176M$

$= 0.035\ M$

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

$$= \frac{10^{-14}}{0.035} M$$

$= 28.33 \times 10^{-14}$

$pH = -[\log(28.33 \times 10^{-14})]$

$= -[\log(0.2833 \times 10^{-12})]$
$= -\ [\log(0.2833 \times 10^{-12})]$

$= -[\log(0.2833) \times (-12 log 10)\ )$

$= -(-0.5477 - 12)$

$= 12.54$

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

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

Molecular weight of NaOH

$$[NaOH] = \frac{mole}{volume(liter)} = \frac{0.3}{40} \times \frac{1000}{200} = 0.0375M$$

$[OH^-(aq)] = 0.0375M$

$[H^+]\ [OH^-] = Kw$

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

$$[H^+] = \frac{10^{-14}}{0.0375}$$

$= 26.66 \times 10^{-14}$
$= 0.2666 \times 10^{-12}$

$$pH = -[\log(0.2666 \times 10^{-12})] = -[\log(0.2666) \times \log(10^{-12})] =$$
$$= -[\log(0.2666) \times (-12\log(10\,)] =$$

$= 12 - \log\,(0.2666)$ =12+0.57=12.574

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

$13.6\ \times\ 1\,mL\ =\ M_2 \times\ 1000\,mL$

(Before dilution) (After dilution)

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

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

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

$pH\ = -\ log\,(1.36\ \times\ 10^{-2})$

$=\ (-\ 0.1335 + 2)$

$=\ 1.866\ 1.87$

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

Solution:

Degree of ionization $(a)\ =\ 0.132$
Concentration($c)\ =\ 0.1\ M$
Thus, the concentration of $H_3O^+\ =\ c.a$
$=\ 0.1\ \times\ 0.132$

$=\ 0.0132$

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

$= -\log(0.0132)$

$= 1.879 = 1.88$

Now,

$K_a = C\alpha^2$

$= 0.1 \times (0.132)^2$

$K_a = 0.00174$

$pK_a = 2.75$

51. The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pKb.

Solution:

pH of solution $=$ 9.95
Concentration (c) $=$ 0.005 M
Thus, the concentration of $H_3O^+ = c.a$

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

$9.95 = -\log[H^+]$

$[H^+] = 3.162 \times 10^{-10}$

$K_a = C\alpha^2$

$C\ K_a = C^2\alpha^2$

$K_a = \frac{[H^+]^2}{C} =$

$pK_a = 2.75$

52. What is the pH of 0.001M aniline solution? The ionization constant of aniline is 4.27×10^{-10}. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

Solution:

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

$c = 0.001M$

$\alpha = ?$

$k_b = c\alpha^2$

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

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

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

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

$= 0.065 \times 10^{-5}$

$pOH = -\log(.065 \times 10^5)$

$= 6.187$

$pH = 7.813$

the ionization constant of the conjugate acid of aniline
$K_a \times K_b = K_w$

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

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

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

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

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

(a) 0.01M*in HCl*

(b) 0.1M in HCl?

Solution:

$c = 0.05\ M$

$pK_a = 4.74$

$pK_a = -\log(K_a)$

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

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

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

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

Case I: When 0.01 $M\ HCl$ is taken.
Let x be the amount of acetic acid dissociated after the addition of HCl.

	$CH_3COOH \leftrightarrow$	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 $0.05 - x \approx 0.05$

$0.01 + x \approx 0.01$ taken

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

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

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

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

Now,

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

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

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

Case II: When 0.1 $M\ HCl$ is taken.
Let the amount of acetic acid dissociated in this case be X. As we have done in the first case, the concentrations of various species involved in the reaction are:

$$[CH_3COOH] = 0.05 - X \approx 0.05M$$

$$[CH_3COO^-] = X$$

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

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

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

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

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

Now,

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

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

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

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

Solution:

$K_b = 5{,}4 \times 10^{-4}$

$c = 0.02$ M

Then, $\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{5.4\times10^{-4}}{0.02}} = 0.643$

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

$$\text{NaOH(aq)} \leftrightarrow \underset{0.1\text{ M}}{\text{Na}^+\text{(aq)}} + \underset{0.1\text{ M}}{\text{OH}^-\text{(aq)}}$$

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + HO^-$$

At equi. (0.02-x) x x+0.1

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

$(CH_3)_2NH = 0.02 - x \approx 0.02$

$[OH^-] = x + 0.1 \approx 0.1$

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

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

$x = 0.0054$

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

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

(A) Human muscle-fluid, 6.83

(B) Human stomach fluid, 1.2

(c) Human blood, 7.38

(D) Human saliva, 6.4.

Solution:

(a) Human muscle fluid 6.83:

$$\mathrm{pH} = 6.83$$

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

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

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

(b) Human stomach fluid, 1.2:

$$\mathrm{pH} = 1.2$$

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

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

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

(c) Human Blood, 7.38

$$\mathrm{pH} = 7.38$$

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

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

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

(d) Human saliva, 6.4:

$$\mathrm{pH} = 6.4$$

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

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

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

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

Solution:

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

(i) the pH of milk $= 6.8$

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

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

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

$[\mathrm{H}^+] = 1.5 \times 19^{-7}\mathrm{M}$

(ii) the pH of black coffee $= 5.0$

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

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

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

$[\mathrm{H}^+] = \mathrm{antilog}(-5.0) = 10^{-5}\mathrm{M}$

(iii) the pH of tomato juice $= 4.2$

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

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

$[\mathrm{H}^+] = \mathrm{antilog}(-4.2) = 6.31 \times 10^{-5}\mathrm{M}$

(iv) the pH of lemon juice $= 2.2$

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

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

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

$[\mathrm{H}^+] = \mathrm{antilog}(-2.2) = 6.31 \times 10^{-3}\mathrm{M}$

(v) the pH of egg white $= 7.8$

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

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

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

$[\mathrm{H^+}] = \mathrm{antilog}(-7.8) = 1.58 \times 10^{-8}\mathrm{M}$

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

Solution:

We know : molecular weight of KOH=39+17=56

moles of KOH=0.561/56

molar concentration of $[\mathrm{KOH(aq)}] = \text{moles of} \frac{\text{solute}}{\text{volume of solution(liter)}} = \frac{\frac{0.561}{56}}{(200/1000)\mathrm{L}} M =$ 0.05 M

$\mathrm{KOH(aq)} \rightarrow \mathrm{K^+(aq)} + \mathrm{OH^-(aq)}$

$[\mathrm{OH^-}] = 0.05\ \mathrm{M} = [\mathrm{K^+}]$

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

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

$$[\mathrm{H^+}] = \frac{10^{-14}}{0.05} = 2 \times 10^{-13}\mathrm{M}$$

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

-$\log(2 \times 10^{-13})$

=-$[\log 2 + \log 10^{-13}$

$= -[log 2 - 13\log 10] = \ 12.70$

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

Solution:

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

Then, concentration of $\mathrm{Sr(OH)_2} = \frac{19.23}{121.63}\mathrm{M} = 0.1581\ \mathrm{M}$

$\mathrm{Sr(OH)_2(aq) \rightarrow Sr^2(aq) + 2(OH^-)(aq)}$

$\therefore [\mathrm{Sr^{2+}}] = 0.5181\ \mathrm{M}$

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

Now,

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

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

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

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

= - $[\log 0.32 + \log 10^{-14}]$

$= -[log 0.32 - 14\log 10]$

$\mathrm{pH} = 13.495 \approx 13.50$

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

Solution:

Let the degree of ionization of propanoic acid be α

. Then, representing propionic acid as HA, we have:

$$HA \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ \quad + \quad A^-$$

$0.05\text{-}0.05\alpha \approx 0.05 \qquad 0.05\alpha \qquad 0.05\alpha$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(0.05\alpha)(0.05\alpha)}{0.05} = 0.05\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{0.05}} = 1.63 \times 10^{-2}$$

Then, $[H_3O^+] = 0.05\alpha = 0.05 \times 1.63 \times 10^{-2} = 8.15 \times 10^{-4}M$

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

pH =-[log8.15 $\times 10^{-4}$]

$= -[log8.15 + log10^{-4}]$

$= -[log8.15 - 4log10]$

$= 4 - 0.911 = 3.09$

In the presence of 0.01M of HCl, let α' is a degree of ionisation.

Then, $[H_3O^+] = 0.01$

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

$[HA] = 0.05$

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

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

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

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

Solution:

$c = 0.1M$

$pH = 2.34$

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

$$-\log[\mathrm{H^+}] = 2.34$$

$$[\mathrm{H^+}] = \text{antilog}(-2.34)$$

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

Also,

$[\mathrm{H^+}] = \mathrm{c}\alpha$

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

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

$\alpha = 45 \times 10^{-3} = 0.045$

Then,

$\mathrm{K_a} = \mathrm{c}\alpha^2$

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

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

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

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

Solution:

$\mathrm{NaNO_2}$ is the salt of a strong base (NaOH) and a weak acid ($\mathrm{HNO_2}$).

$\mathrm{NO_2^-} + \mathrm{H_2O} \leftrightharpoons \mathrm{HNO_2} + \mathrm{OH^-}$

$\mathrm{K_h} = \dfrac{[\mathrm{HNO_2}][\mathrm{OH^-}]}{[\mathrm{NO_2^-}]} = \dfrac{[\mathrm{HNO_2}][\mathrm{OH^-}][H^+]}{[\mathrm{NO_2^-}][H^+]} \qquad \therefore k_w = [\mathrm{OH^-}][H^+] = 10^{-14}\,; K_a = \dfrac{[\mathrm{NO_2^-}][H^+]}{[\mathrm{HNO_2}]}$

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

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

$[\mathrm{NO_2^-}] = 0.04 - \mathrm{x} \approx 0.04$

$[\mathrm{HNO_2}] = \mathrm{x}$

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

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

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

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

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

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

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

$$pH = -[\log(10.75 + \log(10^{-9})]$$

$$pH = -[\log(10.75) - 9\log 10\ )$$

$$= 7.96$$

Therefore, degree of hydrolysis (h)= $\frac{x}{0.04} = \frac{0.093\times10^{-5}}{0.04} = 2.325 \times 10^{-5}$

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

Solution:

pyridinium hydrochloride ($C_5H_7ClN^+$) is salt of a weak base(C_5H_5N) and strong acid(HCl)

$$pH = 3.44$$

We know that,

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

$$-3.44 = \log [H^+]$$

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

$$pyridinium\ hydrochloride + H_2O \rightleftharpoons pyridinium + HO^-$$

Then, $K_h = \frac{(3.63\times10^{-4})^2}{0.02}$ ($\because$ concentration $= 0.02M$)

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

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

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

63. Predict if the solutions of the following salts are neutral, acidic or basic:
$NaCl, KBr, NaCN, NH_4NO_3, NaNO_2$ and KF

Solution:

(i) NaCl

$$NaCl + H_2O \rightleftharpoons \underset{\text{Strong base}}{NaOH} + \underset{\text{Strong acid}}{HCl}$$

It is a salt of strong acid and strong base .Therefore it is a neutral solution. And its pH=7

(ii) KBr

$$KBr + H_2O \rightleftharpoons \underset{\text{Strong base}}{KOH} + \underset{\text{Strong acid}}{HBr}$$

It is a salt of strong acid and strong base .Therefore it is a neutral solution. And its pH=7

(iii) NaCN:

$$NaCN + H_2O \rightleftharpoons \underset{\text{Weak acid}}{HCN} + \underset{\text{Strong base}}{NaOH}$$

It is a salt of a weak acid and strong base. Therefore, it is a basic solution.its pH > 7

(iv) NH_4NO_3

$$NH_4NO_3 + H_2O \rightleftharpoons \underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HNO}$$

It is a salt of a strong acid and weak base.Therefore, it is an acidic solution.its pH < 7

(v) $NaNO_2$

$$NaNO_2 + H_2O \rightleftharpoons \underset{\text{Strong base}}{NaOH} + \underset{\text{Weak acid}}{HNO_2}$$

It is a salt of a weak acid and strong base. Therefore, it is a basic solution.its pH > 7

(vi) KF

$$\underset{}{KF} + H_2O \rightleftharpoons \underset{\text{Strong base}}{KOH} + \underset{\text{Weak acid}}{HF}$$

It is a salt of a weak acid and strong base. Therefore, it is a basic solution.its pH > 7

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

Solution:

Given : Ka for $ClCH_2COOH = 1.35 \times 10^{-3}$.

$\Rightarrow K_a = c\alpha^2$

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

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

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

$= 0.116$

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

$= 0.0116$

$\Rightarrow pH = -\log[H^+] = -\log[0.0116] \approx 1.94$

$ClCH_2COONa$ is the salt of a weak acid ($ClCH_2COOH$) and a strong base (NaOH).

$$ClCH_2COO^- + H_2O \rightleftharpoons ClCH_2COOH + OH^-$$

At equi $\quad 0.1 \qquad\qquad x \qquad x$

$$K_b = \frac{[ClCH_2COOH][OH^-]}{[ClCH_2COO^-]} = \frac{[ClCH_2COOH][OH^-][H^+]}{[ClCH_2COO^-][H^+]} \quad \left(\because [OH^-][H^+] = K_w\, ; K_a = \frac{[ClCH_2COO^-][H^+]}{[ClCH_2COOH]}\right)$$

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

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

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

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

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

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

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

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

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

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

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

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

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

=-[log(1.162×10^{-8})]

=-[log1.162-(8log10)]

=log1.162+8log10

$= 7.94$

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

Solution:

Ionic product,

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

Let $[H^+] = x$

Since $[H^+] = [OH^-], K_w = x^2$.

$\Rightarrow K_w$ at 310K is 2.7×10^{-14}

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

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

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

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

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

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

= -log1.64+7log10

$= 6.78$

Hence, the pH of neutral water is 6.78.

66. Calculate the pH of the resultant mixtures:

(a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

(b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

(c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

Solution:

(a) Moles of $H_3O^+ = \text{molarity} \times \text{volume (litre)} = \frac{25\times0.1}{1000} = 0.0025$ mol

Moles of $OH^- = \text{molarity} \times \text{volume (litre)} = \frac{10\times0.2\times2}{1000} = 0.0040$ mol

Total volume= $\frac{10+25}{1000} liter = 35 \times 10^{-3}\ liter$

Thus, $[OH^-] > [H^+]$

$$[OH^-] = \frac{\text{Moles of } OH^- - \text{Moles of } H_3O^+}{\text{total volume}} = \frac{0.0040 - 0.1125}{35 \times 10^{-3}}$$

$$= \frac{0.0015}{35 \times 10^{-3}} \text{mol/L} = 0.0428$$

$pOH = -\log[OH^-] = -\log(0.0428)$

$= 1.36$

$pH = PK_w - pOH = 14 - 1.36$

$= 12.63$ (not matched)

(b) Moles of $H_3O^+ = \frac{2\times10\times0.01}{1000} = 0.0002$ mol

Moles of $OH^- = \frac{2\times10\times.01}{1000} = 0.0002$ mol

Since there is neither an excess of H_3O^+ or OH^- so the pH of the solution =7

(c) Moles of $H_3O^+ = \frac{2\times10\times0.1}{1000} = 0.002$ mol

Moles of $OH^- = \frac{10\times0.1}{1000} = 0.001$ mol

Total volume$=\frac{10+10}{1000} liter = 20 \times 10^{-3}\ liter$

$H_3O^+ > OH^-$

$$[H_3O^+] = \frac{\text{Moles of }(OH^-) - \text{Moles of }(H_3O^+)}{\text{total volume}} = \frac{0.002-0.001}{20\times10^{-3}} = \frac{0.001}{20\times10^{-3}} = \frac{10^{-3}}{20\times10^{-3}}$$
$$= 0.05$$

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

$= 1.30$

The solution is acidic.

67. Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constant are 1.1×10^{-12}, 1.2×10^{-10}, 1.0×10^{-38}, 1.6×10^{-5}, 4.5×10^{-29} *respectively* . Determine also the molarities of individual ions.

Solution:

(1) Silver chromate:

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

Then,

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

Let the solubility of Ag_2CrO_4 be s.

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

Then,

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

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

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

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

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

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

(2) Barium chromate:

$BaCrO_4 \rightarrow Ba^{2+} + CrO_4^{2-}$

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

Let solubility of $BaCrO_4$ be s.

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

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

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

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

(3) Ferric hydroxide:

$Fe(OH)_3 \rightarrow Fe^{3+} + 3OH^-$

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

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

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

$\Rightarrow K_{SP} = s \times (3s)^3$

$= s \times 27s^3$

$K_{SP} = 27s^4$

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

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

$0.037 \times 10^{-38} = s^4$

$0.00037 \times 10^{-36} = s^4 \Rightarrow 1.39 \times 10^{-10} M = S$

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

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

(4) Lead chloride:

$PbCl_2 \rightarrow Pb^{2+} + 2Cl^-$

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

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

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

Thus, $K_{xp} = s \times (2s)^2$

$= 4s^3$

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

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

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

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

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

(5) Mercurous iodide:

$Hg_2I_2 \rightarrow Hg_2^{2+} + 2I^-$

$K_{sp} = [Hg_2^{2+}]\,[I^-]^2$

Let s be the solubility of Hg_2I_2.

$\Rightarrow [Hg_2^{2+}] = s$ and $[I^-] = 2s$

Thus, $Hg_2I_2 = s(2s)^2 \Rightarrow K_{xy} = 4s^3$

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

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

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

Molarity of $Hg_2^{2+} = s = 2.24 \times 10^{-10}M$

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

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

Solution:

Let s be the solubility of Ag_2CrO_4.

Then,$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

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

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

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

Let s´ be the solubility of AgBr.

$AgBr \rightleftharpoons Ag^+ + Br^-$

$\qquad s'^2 \qquad s'$

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

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

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

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

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

Solution:

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

$NaIO_3 \rightarrow Na^+ + IO_3^-$

0.00IM 0.00IM

$Cu(ClO_3)_2 \rightarrow Cu^{2+} + 2ClO_3^-$

0.00lM 0.00IM

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

$Cu(IO_3)_2 \rightarrow Cu^{2+}(aq) + 2IO_3^-(aq)$

Ionic product of copper iodate:

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

$= (0.001)(0.001)^2$

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

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

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

Solution:

Since pH = 3.19,

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

$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

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

$$\frac{[C_6H_3COOH]}{[C_6H_5COO^-]} = \frac{[H_3O^+]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let the solubility of C_6H_5COOAg be x mol/L.

Then,

$[Ag^+] = x$

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

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

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

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

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

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

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

Now, let the solubility of C_6H_5COOAg be x' mol/L.

Then, $[Ag^+] = x'M$ and $[CH_3COO^-] = x'M$

$K_{sp} = [Ag^+][CH_3COO^-]$

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

$$x' = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7}\,\text{molL}$$

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

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

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

Solution:

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

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

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

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

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

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

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

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

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

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

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

Solution:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

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

Let the solubility of $CaSO_4$ be s.

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

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

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

The molecular mass of $CaSO_4 = 136\ \ g/mol$

The solubility of $CaSO_4$ in gram/L

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

$= 0.41\ \ g/L$

This means that need 1L of water to dissolve 0.41 g of $CaSO_4$

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

73. The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $\mathrm{FeSO_4, MnCl_2, ZnCl_2}$ and $\mathrm{CdCl_2}$. in which of these solutions precipitation will take place?

Solution:

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

Before mixing:

$[S^{2-}] = 1.0 \times 10^{-19} M\ ;\ volume_1\ = 10\ mL$

$[M^{2+}] = 0.04M;\ volume_2\ = 5\ mL$

After mixing:

$[S^{2-}] =?$

Total Volume $= (10mL + 5mL) = 15\ mL$

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

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

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

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

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