CBSE Class 11 Chemistry
NCERT Solutions
Chapter 7
EQUILIBRIUM

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) 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]= 0.60 M, [O_2] = 0.82 M and [SO_3] = 1.90 M ?

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

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

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$
$$= \frac{(1.90)^2}{(0.60)^2(0.821)M^3}$$
$$= 12.239M^{-1}$$

Hence, *Kc* for the equilibrium is $12.239M^{-1}$.

3. At a certain temperature and total pressure of 105 Pa, iodine vapour contains 40% by volume of I atoms $I_2(g) \leftrightarrow 2I(g)$ Calculate K_p for the equilibrium.

Ans. Partial pressure of I atoms,

$$p_I = \frac{40}{100} \times p_{total}$$
$$= \frac{40}{100} \times 10^5$$
$$= 4 \times 10^5 Pa$$

Partial pressure of I_2 molecules,

$$p_{I_2} = \frac{60}{100} \times p_{total}$$
$$= 6 \times 10^4 Pa$$

Now, for the given reaction,

$$Kp = \frac{(pI)^2}{p_{I_2}}$$
$$= \frac{(4 \times 10^4)^2 Pa^2}{6 \times 10^4 Pa}$$
$$= 2.67 \times 10^4 Pa$$

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

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

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

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

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

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

Ans.

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

$$(ii) K_c = \frac{[CuO_{(g)}]^2 [NO_{2(g)}]^4 [O_{2(g)}]}{[Cu(NO_3)_2]^2}$$

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

$$(iii) K_c = \frac{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]}{[CH_3COOH_{5(aq)}][H_2O_{(l)}]} = \frac{[CH_3COOH_{(aq)}][C_2COOH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}]}$$

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

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

$$(v) K_c = \frac{[IF_5]^2}{[1_{2(s)}][F_2]^5}$$

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

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

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

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

Ans. The relation between $K_p \, and \, K_c$ is given as:

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

(i) Here,

Δn = 3 - 2 = 1

R = 0.0831 bar $Lmol^{-1}K^{-1}$

T = 500 K

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

Now,

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

$$\Rightarrow 1.8\times10^{-2} = K_c(0.0831\times500)^1$$

$$\Rightarrow K_c = \frac{1.8\times10^{-2}}{0.0831\times500}$$

$$= 4.33\times10^{-4}$$

(ii) Here,

Δn = 2 - 1 = 1

R = 0.0831 bar $Lmol^{-1}K^{-1}$

T = 1073 K

K_p = 167

Now,

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

$$\Rightarrow 167 = K_c(0.0831\times1073)^{\Delta n}$$

$$\Rightarrow K_c = \frac{167}{0.0831\times1073}$$

$$= 1.87(approx)$$

6. For the following equilibrium, $K_c = 6.3\times10^{14}\ NO_{(g)} + O_3(g) \leftrightarrow NO_2(g) + O_2(g)$ **Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is** K_c **, for the reverse reaction?**

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

As we know that from the given information, the rate of backward reaction is the reciprocal of the rate of forward reaction:

Then, K_c for the reverse reaction will be

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

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

Ans. For a pure substance (both solids and liquids),

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

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 are not mentioned in the equilibrium constant expression.

8. Reaction between N_2 and O_2 takes place as follows: $2N_2(g) + O_2(g) \leftrightarrow 2N_2O(g)$

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

the composition of equilibrium mixture.

Ans. Let the concentration of N_2O at equilibrium be *x*.

The given reaction is:

$$\begin{array}{lll} & 2N_{2(g)} + O_{2(g)} & \leftrightarrow 2N_2O_{(g)} \\ Initial\ conc. & 0.482mol \quad 0.933mol & 0 \\ At\ equilibrium & (0.482-x) \quad (1.933-x) & xmol \end{array}$$

Therefore, at equilibrium, in the 10 L vessel:

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

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

Then,

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

Now,

$$K_c=\frac{[N_2O_{(g)}]}{[N_{2(g)}]^2[O_{2(g)}]}$$

$$\Rightarrow 2.0\times10^{-37}=\frac{\left(\frac{x}{10}\right)^2}{(0.0482)^2(0.0933)}$$

$$\Rightarrow \frac{x^2}{100} = 2.0\times10^{-37}\times(0.0482)^2\times(0.0933)$$
$$\Rightarrow x^2 = 43.35\times10^{-40}$$
$$\Rightarrow x = 6.6\times10^{-20}$$
$$[N_2O] = \frac{x}{10} = \frac{6.6\times10^{-20}}{10}$$
$$= 6.6\times10^{-21}$$

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

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

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

Ans. The given reaction is:

$$2NO(g) + Br_2(g) \leftrightarrow 2NOBr(g)$$
$$2mol \qquad 1mol \qquad 2mol$$

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

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

Therefore, 0.0518 mol of NOBr are formed from $\frac{0.0518}{2}$ mol 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 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

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

$$2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$$

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 $K^{-1}\ mol^{-1}$

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

We know that,

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

$$\Rightarrow 2.0\times10^{10}\,bar^{-1} = K_c(0.0831\,L\,bar\,K^{-1}mol^{-1}\times450K)^{-1}$$

$$\Rightarrow K_c = \frac{2.0\times10^{10}\,bar^{-1}}{(0.0831Lbar^{-1})(0.0831L\,bar\,K^{-1}mol^{-1}\times450K)^{-1}}$$

$$= (2.0\times10^{10}bar^{-1})(0.0831LbarK^{-1}mol^{-1}\times450K)$$

$$= 74.79\times10^{10}L\,mol^{-1}$$

$$= 7.48\times10^{11}L\,mol^{-1}$$

$$= 7.48\times10^{11}M^{-1}$$

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

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

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:

	$2HI(g) \leftrightarrow$	$H_2(g)$	$+ I_2(g)$
Initial conc.	$0.2 atm$	0	0
At equilibrium	$0.04 atm$	$\frac{0.16}{2} = 0.08 atm$	$\frac{2.15}{2} = 0.08 atm$

Therefore,

$$K_p = \frac{p_{H2} \times p_{I2}}{p^2_{HI}}$$

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

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

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 $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ is 1.7×10^2
Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Ans. The given reaction is:

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

The given concentrations of various species is

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

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

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.

Ans. 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 are taken in 10 L vessel and heated to

725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

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

Calculate the equilibrium constant for the reaction.

Ans. The given reaction is:

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

Therefore, the equilibrium constant for the reaction,

We know that:

$$K_C = \frac{[H_2][CO_2]}{[H_2O][CO]}$$
$$= \frac{0.04 \times 0.04}{0.06 \times 0.06}$$
$$= 0.444(approx.)$$

15. At 700 K, equilibrium constant for the reaction $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ 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 700 K?

Ans. It is given that equilibrium constant K_C for the reaction

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

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

$2HI_{(g)} \leftrightarrow H_{2(g)} + I_{2(g)}$ will be $\frac{1}{54.8}$.

$[H_1] = 0.5 mol L^{-1}$

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

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

Therefore,

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

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

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

$$\Rightarrow x = 0.06754$$

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

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

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

$$2\ ICl_{(g)} \leftrightarrow I_{2(g)} + Cl_{2(g)}\ ;\ K_C = 0.14$$

Ans. The given reaction is:

$$2\ ICl_{(g)} \leftrightarrow I_{2(g)} + Cl_{2(g)}\ ;\ K_C = 0.14$$

Initial conc.	0.78 M	0	0
At equilibrium	(0.78 - 2x) M	x M	x M

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

$$\Rightarrow x = 0.292 - 0.748$$

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

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

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

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

Hence, at equilibrium,

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

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

$$= 0.446M$$

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?

$$C_2H_6 \leftrightarrow C_2H_{4(g)} + H_{2(g)}$$

Ans. Let *p* be the pressure exerted by ethene and hydrogen gas (each) at equilibrium.

Now, according to the reaction,

	C_2H_6	$\leftrightarrow$	$C_2H_{4(g)}$	+	$H_{2(g)}$
Initial conc.	$4.0 atm$		0		0
At equilibrium	$4.0 - p$		p		p

We can write,

$$\frac{p_{C2H6} \times p_{H2}}{p_{C2H6}} = K_p$$

$$\Rightarrow \frac{p \times p}{p_{C2H6}} = 0.04$$

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

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

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

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

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

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

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

$$= 0.38$$

Hence, at equilibrium,

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

$$= 3.62 atm$$

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

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

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

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

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293

K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

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

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

The given reaction is:

	$CH_3COOH(l)$ +	$C_2H_5OH(l) \leftrightarrow$	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
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, equilibrium constant for the given reaction is:

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

$$= \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.009}{V}} = 3.919$$

$$= 3.92 (approx)$$

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

	$CH_3COOH(l)$ +	$C_2H_5OH(l) \leftrightarrow$	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial conc.	$\frac{1.0}{V}M$	$\frac{0.5}{V}M$	0	0
At Equilibrium	$\frac{10-0.214}{V} = \frac{0.786}{V}M$	$\frac{0.5-0.214}{V} = \frac{0.286}{V}M$	$\frac{0.214}{V}M$	$\frac{0.214}{V}M$

Therefore, the reaction quotient is,

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$
$$= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}} = 0.2037$$
$$= 0204(approx)$$

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?

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

Ans. Let the concentrations of both PCl_3 and Cl_2 at equilibrium be $x\, mol^{-1}$. The given reaction is:

	$PCl_5(g)$	$\leftrightarrow PCl_3(g)$	$+ Cl_2(g)$
At equilibrium	$0.5\times10^{-1} molL^{-1}$	$xmolL^{-1}$	$xmolL^{-1}$

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

Now we can write the expression for equilibrium as:

$$\frac{[PCl_2][Cl_2]}{[PCl_5]} = K_c$$
$$\Rightarrow \frac{x\times x}{0.5\times10^{-1}} = 8.3\times10^{-3}$$
$$\Rightarrow x^2 = 4.15\times10^{-4}$$
$$\Rightarrow x = 2.04\times10^{-2}$$
$$= 0.0204$$
$$= 0.02(approx.)$$

Therefore, at equilibrium, $[PCl_3] = [Cl_2] = 0.02 mol L^{-1}$

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

FeO (s) + CO (g) $\leftrightarrow$ Fe (s) + CO_2 (g); *Kp*= 0.265 at 1050 K.

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

Ans. For the given reaction,

$$\mathbf{FeO}\ (s) + \mathbf{CO}\ (g) \leftrightarrow \mathbf{Fe}\ (s) + \mathbf{CO2}\ (g)$$

$$Initially, \quad 1.4 atm \qquad 0.80 atm$$

$$Q_V = \frac{p_{CO3}}{p_{CO}}$$

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

$$= 0.571$$

It is given that $Kp = 0.265$

Since $Q_p > K_P$, the reaction will proceed in the backward direction.

Therefore, we can say that the pressure of CO will increase while the pressure of CO_2 will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO_2 be *p*.

Then, we can write,

$$K_P = \frac{p_{CO2}}{p_{CO}}$$
$$\Rightarrow 0.265 = \frac{0.80 - p}{1.4 + p}$$
$$\Rightarrow 0.371 + 0.265p = 0.80 - p$$
$$\Rightarrow 1.265p = 0.429$$
$$\Rightarrow p = 0.339 atm$$

Therefore, equilibrium partial of CO_2, $p_{CO2} = 0.80 - 0.339 = 0.461 atm$

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

21. Equilibrium constant, K_c for the reaction

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

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

Ans. The given reaction is:

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

Now, we know that,

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
$$= \frac{(0.5)^2}{(3.0)(2.0)^3}$$
$$= 0.0104$$
$$It\ is\ given\ that\ K_c = 0.061$$

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:

$2BrCl(g) \leftrightarrow Br_2(g) + Cl_2(g)$ **for which *Kc*= 32 at 500 K. If initially pure BrCl is present at a concentration of $3.3 \times 10^{-3}\ \mathrm{mol L^{-1}}$, 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:

	$2BrCl(g)$	$\leftrightarrow$	$Br_2(g)+$	$Cl_2(g)$
Initial conc.	3.3×10^{-3}		0	0
At equilibrium	$3.3\times10^{-3}-2x$		x	x

Now, we can write,

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

$$\Rightarrow \frac{x\times x}{3.3\times10^{-3}-2x} = 5.66$$

$$\Rightarrow x = 18.678\times10^{-3} - 11.32x$$

$$\Rightarrow 12.32x = 18.678\times10^{-3}$$

$$\Rightarrow x = 1.5\times10^{-3}$$

Therefore, at equilibrium,

$$[BrCl] = 3.3\times10^{-3} - \left(2\times1.5\times10^{-3}\right)$$

$$= 3.3\times10^{-3} - 3.0\times10^{-3}$$

$$= 0.3\times10^{-3}$$

$$= 3.0\times10^{-4}\ mol L^{-1}$$

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 $C(s)+CO_2(g)\leftrightarrow 2CO(g)$. Calculate K_c for this reaction at the above temperature.

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

Mass of CO = 90.55 g

And, mass of CO_2 = (100- 90.55) = 9.45 g

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

Number of moles of CO 2, $n_{CO2}=\frac{9.45}{44}=0.125mol$

Partial pressure of CO,

$$P_{CO}=\frac{n_{CO}}{n_{CO}+n_{CO2}}\times p_{total}$$
$$=\frac{3.234}{3.234+0.215}\times 1$$
$$=0.938atm$$

Partial pressure of CO_2,

$$p_{CO2}=\frac{n_{CO_2}}{n_{CO}+n_{CO_2}}\times p_{total}$$
$$=\frac{0.215}{3.234+0.215}\times 1$$
$$=0.062atm$$

$$Therefore, K_P=\frac{[CO]^2}{[CO_2]}$$

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

= 14.19

For the given reaction,

Δn = 2- 1 = 1

We know that,

$$K_P = K_C (RT)^{\Delta n}$$
$$\Rightarrow 14.19 = K_C (0.082 \times 1127)^1$$
$$\Rightarrow K_C = \frac{14.19}{0.082 \times 1127}$$
$$= 0.154 (approx)$$

24. Calculate a) Δ*G*°and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K $NO(g) + \frac{1}{2} O_{2(g)} \leftrightarrow NO_{2(g)}$ **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,

Δ*G*° = Δ*G*°(Products) - Δ*G*°(Reactants)

Δ*G*° = 52.0-{87.0 + 0}

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

(b) We know that,

Δ*G*° = RT log K_c

Δ*G*° = 2.303 RT log *Kc*

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

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 same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

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

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

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

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.

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

(ii) $CH_4(g) + 2S_2(g) \leftrightarrow CS_2 + 2H_2S(g)$

(iii) $CO_2(g)+C(s)\leftrightarrow 2CO(g)$

(iv) $2H_2(g)+CO(g)\leftrightarrow CH_3OH(g)$

(v) $CaCO_3(s)\leftrightarrow CaO(s)+CO2(g)$

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

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

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

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

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

$H_2(g)+Br(g)\leftrightarrow 2HBr(g)$

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., $H_2(g)+Br_{2(g)}\leftrightarrow 2HBr(g)\, is\, 1.6\times10^5$.

Therefore, for the reaction $2HBr(g)\leftrightarrow H_2(g)+Br_{2(g)}$ the equilibrium constant will be,

$$K'_P=\frac{1}{K^P}$$
$$=\frac{1}{1.6\times10^5}$$
$$=6.25\times10^{-6}$$

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,

$$\frac{p_{HBr} \times p}{p_{HBr}} = K'_p$$

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

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

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

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

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

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

Therefore, at equilibrium,

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

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

$$= 9.95 bar = 10 bar (approx)$$

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

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

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

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

(i) Increasing the pressure

(ii) Increasing the temperature

(iii) Using a catalyst?

Ans. (a) For the given reaction,

$$K_p = \frac{P_{CO} \times P^3{}_{H2}}{p_{CH_4} \times p_{H_2O}}$$

(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.

---

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:

$$2H_2(g) + CO(g) \leftrightarrow CH_3OH(g)$$

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

(b) On addition of CH_3OH, the equilibrium will shift in the backward direction.

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

(d) On removing CH_3OH, the equilibrium will shift in the forward direction.

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, $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$ $\Delta_r H^\circ = 124.0\ kJmol^{-1}$

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 K_c if (i) more PCl_5 is added (ii) pressure is increased? (iii) The temperature is increased?

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

(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 constant temperature. Thus, in this case, *Kc* 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.

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,

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

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO}=p_{H_2O}$ 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:

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

It is $given that\ K_P=10.1.$

Now,

$$\frac{p_{CO2}\times p_{H2}}{p_{COH}\times p}=K_p$$

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

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

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

$$\Rightarrow 4.178p=12.172$$

$$\Rightarrow p=3.04$$

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

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

a) $Cl_2(g)\leftrightarrow 2Cl(g);\ \ K_c=5\times10^{-39}$

b) $Cl_2(g)+2NO(g)\leftrightarrow 2NOCl(g);\ \ K_c=3.7\times10^{8}$

c) $Cl_2(g)+2NO(g)\leftrightarrow 2NOCl(g);\ \ K_c=1.8$

Ans. If the value of K_c lies between $10^{-3}\ and\ 10^{3}$, a reaction has appreciable

concentration of reactants and products. Thus, the reaction given in (c) will have appreciable concentration of reactants and products.

33. The value of K_c for the reaction $3O_2\ (g) \leftrightarrow 2O_3\ (g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O2 in air at 25°C is 1.6$\times 10^{-2}$, what is the concentration of O_3 ?

Ans. The given reaction is:

$$3O_{2(g)} \leftrightarrow 2O_{3(g)}$$

$$Then, K_C = \frac{\left[O_{3(g)}\right]^2}{\left[O_{2(g)}\right]^3}$$

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

Then, we have,

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

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

$$\Rightarrow \left[O_{3(g)}\right]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow \left[O_{3(g)}\right]^2 = 2.86 \times 10^{-28} M$$

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

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

Ans. Let the concentration of methane at equilibrium be *x*.

	$CO_{(g)}$	$+3H_{2(g)}$	$\leftrightarrow$	$CH_{4(g)}$ +	$H_2O_{(g)}$
At equilibrium	$\frac{0.3}{1}=0.3M$	$\frac{0.1}{1}=0.1M$		x	$\frac{0.02}{1}=0.02M$

It is given that K_c = 3.90.

Therefore,

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

$$\Rightarrow \frac{x\times 0.02}{0.3\times(0.1)^2}=3.90$$

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

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

$$=0.0585M$$

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

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

35. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: $HNO_2, CN^-, HClO_4, F^-.OH^-, CO_3^{2-}, and\ S^-$

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

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

Species	Conjugate acid-base
HNO_2	NO_2^- (base)
CN^-	HCN (acid)
$HClO_4$	ClO_2^- (base)
F^-	HF (acid)
OH^-	H_2O (acid) / O^{2-} (base)
CO_2^-	HCO_3^- (acid)
S^{2-}	HS^- (acid)

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

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

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

Ans. 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 Bronsted bases: NH_2^-, NH_3 and $HCOO^-$.

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

Bronsted base	Conjugate acid
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 Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

Ans. 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 .

Ans. (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?

Ans. Given,

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

∴ pH value of soft drink

$$= \log\left[H^+\right]$$
$$= -\log(3.8 \times 10^{-3})$$
$$= -\log 3.8 - \log 10^{-3}$$

=- 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.

Ans. Given,

pH = 3.76

It is known that,

$$pH = -\log\left[H^+\right]$$
$$\Rightarrow \log\left[H^+\right] = -pH$$
$$\Rightarrow \left[H^+\right] = anti\log(-pH)$$
$$= anti\log(-3.76)$$
$$= 1.74 \times 10^{-4} M$$

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

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.

Ans. It is known that,

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

Given,

K_a of HF = 6.8×10^{-4}

Hence, K_b of its conjugate base F^-

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

Given,

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

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

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

Given,

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

Hence, K_b of its conjugate base CN^-

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

$$= \frac{10^{-14}}{4.8 \times 10^{-9}}$$

$$= 2.08 \times 10^{-6}$$

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?

Ans. Ionization of phenol:

$$C_6H_5OH + H_2O \leftrightarrow C_6H_5O^- + H_3O$$

Initial conc.	0.05	0	0
At equilibrium	$0.05 - x$	x	x

$$K_{\Delta t} = \frac{x \times x}{0.05 - x}$$

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

$$\therefore x = \sqrt{1.5 \times 10^{-10}}$$
$$= \sqrt{5 \times 10^{-12}}$$
$$= 2.2 \times 10^{-6} M = \left[H_3O^+\right]$$
$$\text{Sin}\, ce \left[H_3O^+\right] = \left[C_6H_5O^-\right]$$
$$\left[C_6H_5O^-\right] = 2.2 \times 10^{-6} M.$$

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,

$$C_6H_5OH + H_2O \leftrightarrow C_6H_5O^- + H_3O^+$$

$$Conc.\ 0.05 - 0.05a \qquad 0.05a \qquad 0.05a$$

$$[C_6H_5OH] = 0.05 - 0.05a; 0.05M$$

$$[C_6H_5O^-] = 0.05a$$

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

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

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

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

45. The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS- ion in its 0.1 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. (i) To calculate the concentration of HS^- ion:

Case I (in the absence of HCl):

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

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

$$C_1 \quad 0.1 \quad 0 \quad 0$$

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

$$Then, K_{01} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$9.1\times10^{-8}=\frac{(x)(x)}{0.1-x}$$

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

$$Taking\ 0.1-xM;0.1M,\ we\ have\ (9.1\times10^{-8})(0.1)=x^2$$

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

$$x=\sqrt{9.1\times10^{-5}}$$

$$=9.54\times10^{-5}M$$

$$\Rightarrow\left[HS^-\right]=9.54\times10^{-5}M$$

Case II (in the presence of HCl):

In the presence of 0.1 M of HCl, let $\left[HS^-\right]$ be *y* M.

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

$$C_i \qquad 0.1 \qquad 0 \qquad 0$$

$$C_f \qquad 0.1-y \qquad y \qquad y$$

$$Also,\quad HCl\leftrightarrow H^++Cl^-$$

$$0.1 \quad 0.1$$

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

$$K_{a1}=\frac{[y](0.1+y)}{(0.1-y)}$$

$$9.1\times10^{-8}=\frac{y\times0.1}{0.1}\qquad(\because 0.1-y;0.1M)$$

$$(and\ 0.1+y;0.1M)$$

$$9.1\times10^{-8}=y$$

$$\Rightarrow\left[HS^-\right]=9.1\times10^{-8}$$

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

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

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

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

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

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

$$K_{a2} = \frac{\left[H^+\right]\left[S^{2-}\right]}{\left[HS^-\right]}$$

$$K_{a2} = \frac{(9.54 \times 10^{-5})(X)}{9.54 \times 10^{-5}}$$

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

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

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

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

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

$$\left[S^{2-}\right] = X'$$

$$Then, K_{a2} = \frac{\left[H^+\right]\left[S^{2-}\right]}{\left[HS^-\right]}$$

$$1.2\times10^{-13} = \frac{(0.1)(X')}{9.1\times10^{-8}}$$

$$10.92\times10^{-21} = 0.1X'$$

$$\frac{10.92\times10^{-21}}{0.1} = X'$$

$$X' = \frac{1.092\times10^{-20}}{0.1}$$

$$= 1.092\times10^{-19} M$$

$$\Rightarrow K_{a1} = 1.74\times10^{-5}$$

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.

Ans. Method 1

$$1)\, CH_3COOH \leftrightarrow CH_3COO^- + H^+ \quad K_a = 1.74\times10^{-5}$$

$$2)\, H_2O + H_2O \leftrightarrow H_3O^+ + OH^- \qquad K = 1.0\times10^{-14}$$

Since $K_a >> K_w$,:

$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$

$$C_f = \quad 0.05 \qquad\qquad 0 \qquad 0$$

$$0.0.05a \qquad\qquad 0.05a \qquad 0.05a$$

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

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

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

$$1.74\times10^{-5} = \frac{0.05a^2}{1-a}$$

$$1.74\times10^{-5} - 1.74\times10^{-5}a = 0.05a^2$$

$$0.05a^2 + 1.74\times10^{-5}a - 1.74\times10^{-5}$$

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

$$= (1.74\times10^{-5})^2 - 4(.05)(1.74\times10^{-5})$$

$$= 3.02\times10^{-25} + .348\times10^{-5}$$

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

$$a = \sqrt{\frac{1.74\times10^{-5}}{.05}}$$

$$= \sqrt{\frac{34.8\times10^{-6}\times10}{10}}$$

$$= \sqrt{3.48\times10^{-6}}$$

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

$$\overset{a1.86\times10^{-3}}{\left[CH_3COO^-\right]} = 0.05\times1.86\times10^{-3}$$

$$= \frac{0.93\times10^{-3}}{1000}$$

$$= .000093$$

Degree of dissociation,

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

$$c = 0.05M$$

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

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

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

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

$$a = 1.8610^{-2}$$

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

$$Thus, concentration\ of\ CH_3COO- = c.a$$

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

$$= 0.93 \times 10^{-2}$$

$$= .00093M$$

$$\text{Sin}\ ce\left[oAc^-\right] = \left[H\right]^+$$

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

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

$$= -\log(0.93 \times 10^{-2})$$

$$\therefore pH = 3.03$$

Method 2: Degree of dissociation,

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

c = 0.05 M

K_a = 1.74×10^{-5}

$$Then,\ a = \sqrt{\frac{1.74\times10^{-5}}{.05}}$$

$$a = \sqrt{34.8\times10^{-5}}$$

$$a = \sqrt{3.48}\times10^{-4}$$

$$a = 1.8610^{-2}$$

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

Thus, concentration of CH_3COO^- = c.α

$$= .05\times1.86\times10^{-2}$$

$$= .093\times10^{-2}$$

$$= .00093M$$

$$\text{Sin}\ ce\left[oAc^-\right] = \left[H^+\right]$$

$$\left[H^+\right] = .00093 = .093\times10^{-2}$$

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

$$= -\log(.093\times10^{-2})$$

$$\therefore pH = 3.03$$

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 p*K*a.

Ans. Let the organic acid be HA.

$$\Rightarrow HA \leftrightarrow H^+ + A^-$$

Concentration of HA = 0.01 M

pH = 4.15

$$-\log\left[H^+\right]=4.15$$
$$\left[H^+\right]=7.08\times10^{-5}$$

Now, $K_a=\dfrac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$

$$\left[H^+\right]=\left[A^-\right]=7.08\times10^{-5}$$
$$\left[HA\right]=0.01$$

Then,

$$K_a=\frac{(7.08\times10^{-5})(7.08\times10^{-5})}{0.01}$$
$$K_a=5.01\times10^{-7}$$
$$pK_a=-\log K_a$$
$$=-\log(5.01\times10^{-7})$$
$$pK_a=6.3001$$

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

Ans. (i) 0.003MHCl:

$$H_2O+Hcl\leftrightarrow H_3O^++Cl^-$$

Since HCl is completely ionized,

$$\left[H_2O^+\right]=\left[HCl\right]$$
$$\Rightarrow\left[H_3O^+\right]=0.003$$

Now,

$$pH=-\log\left[H_3O^+\right]=-\log(.003)$$
$$=2.52$$

Hence, the pH of the solution is 2.52**.**

(ii) 0.005MNaOH:

$$NaOH_{(aq)}\leftrightarrow Na^+{}_{(aq)}+HO^-{}_{(aq)}$$

$$\left[HO^-\right]=\left[NaOH\right]$$
$$\Rightarrow\left[HO^-\right]=.005$$
$$pOH=-\log\left[HO^-\right]=-\log(.005)$$
$$pOH=2.30$$
$$\therefore pH=14-2.30$$
$$=11.70$$

Hence, the pH of the solution is 11.70.

(iii) 0.002 HBr:

$$HBr+H_2O\leftrightarrow H_3O^++Br^-$$
$$\left[H_3O^+\right]=.002$$
$$\therefore pH=-\log\left[H_3O^+\right]$$
$$=-\log(0.002)$$
$$=2.69$$

Hence, the pH of the solution is 2.69.

(iv) 0.002 M KOH:

$$KOH_{(aq)} \leftrightarrow K^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$
$$\left[OH^{-}\right] = \left[KOH\right]$$
$$Now, pOH = -\log\left[OH^{-}\right]$$
$$= 2.69$$
$$\therefore pH = 14 - 2.69$$
$$= 11.31$$

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.

Ans. (a) For 2g of TlOH dissolved in water to give 2 L of solution:

$$\left[TlOH_{(aq)}\right] = \frac{2}{2} g / L$$
$$= \frac{2}{2} \times \frac{1}{221} M$$
$$= \frac{1}{221} M$$
$$TlOH_{(aq)} \rightarrow Tl^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$
$$\left[OH^{-}{}_{(aq)}\right] = \left[TlOH_{(aq)}\right] = \frac{1}{221} M$$
$$K = \left[H^{+}\right]\left(\frac{1}{221}\right)$$
$$221 \times 10^{-14} = \left[H^{+}\right]$$
$$\Rightarrow pH = -\log\left[H^{+}\right] = -\log(221 \times 10^{-14})$$
$$= -\log(2.21 \times 10^{-21})$$
$$= 11.65$$

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

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

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

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

$$= 1.2M$$

$$\left[H^+\right] = \frac{K}{\left[OH^-{}_{(aq)}\right]}$$

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

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

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

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

$$= (-0.0902 + 13)$$

$$= 12.098$$

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

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

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

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

$$Then, \left[H^+\right] = \frac{10^{-14}}{1.5}$$

$$= 6.66 \times 10^{-13}$$

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

$$= 12.18$$

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

13.6 × 1 mL = M_2 × 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 pK_a of bromoacetic acid.

Ans. Degree of ionization, α = 0.132

Concentration, *c* = 0.1 M

Thus, the concentration of H_3O^+ = *c*.α

= 0.1 × 0.132

= 0.0132

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

Now,

$$\begin{aligned} K_a &= Ca^2 \\ &= 0.1 \times (0.132)^2 \\ K_a &= .00017 \\ pK_a &= 2.75 \end{aligned}$$

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

Ans. *c* = 0.005M

pH = 9.95

pOH = 4.05

pH = -log (4.105)

$$4.05 = -\log\left[OH^-\right]$$
$$\left[OH^-\right] = 8.91\times10^{-5}$$
$$ca = 8.91\times10^{-5}$$
$$a = \frac{8.91\times10^{-5}}{5\times10^{-3}} = 1.782\times10^{-2}$$
$$Thus, K_b = ca^2$$
$$= 0.005\times(1.782)^2\times10^{-4}$$
$$= 0.005\times3.1755\times10^{-4}$$
$$= 0.0158\times10^{-4}$$
$$K_b = 1.58\times10^{-6}$$
$$Pk_b = -\log K_b$$
$$= -\log(1.58\times10^{-6})$$
$$= 5.80$$

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

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

c = 0.001M

pH =?

α =?

$$k_b = ca^2$$
$$4.27\times10^{-10} = 0.001\times a^2$$
$$4270\times10^{-10} = a^2$$
$$65.34\times10^{-5} = a = 6.53\times10^{-4}$$
$$Then, [anion] = ca = .001\times65.34\times10^{-5}$$
$$= .065\times10^{-5}$$
$$pOH = -\log(0.65\times10^{-5})$$
$$= 6.187$$
$$pH = 7.813$$
$$Now,$$
$$K_a\times K_b = K_w$$
$$\therefore 4.27\times10^{-10}\times K_a = K_w$$
$$K_a = \frac{10^{-14}}{4.27\times10^{-10}}$$
$$= 2.34\times10^{-5}$$

$K_W=10^{-14.}$

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 p*K*a value is 4.74.

How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M in HCl?

Ans. c = 0.05 M

$$pK_a = 4.74$$
$$pK_a = -\log(K_a)$$
$$K_a = 1.82 \times 10^{-5}$$
$$K_a = ca^2 \quad a = \sqrt{\frac{K_a}{c}}$$
$$a = \sqrt{\frac{1.82 \times 10^{-5}}{5 \times 10^{-2}}} = 1.908 \times 10^{-2}$$

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 i.e., $0.05 - x$ and $0.01 + x$ can be taken as 0.05 and 0.01 respectively.

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

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

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

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

$Now,$

$$a = \frac{Amount\ of\ acid\ dissociated}{Amount\ of\ acid\ taken}$$

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

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

Case II: When 0.1 M HCl is taken.

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

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

$$[CH_3COO^-] = X$$

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

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

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

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

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

Now,

$$a = \frac{Amount\ of\ acid\ dissociated}{Amount\ of\ acid\ taken}$$

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

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

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

Ans.

$K_b = ca^2$

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

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

$$NaOH_{(aq)} \leftrightarrow Na^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$
$$0.1M \quad 0.1M$$

And,

$$(CH_3)_2NH + H_2O \leftrightarrow (CH_3)_2NH^{+}{}_2 + \bar{O}H$$
$$(0.02 - x) \qquad x \qquad x$$
$$;0.02M \qquad ;0.1M$$

$$Then, \left[(CH_3)_2NH_2^{+}\right] = x$$
$$\left[OH^{-}\right] = x + 0.1; 0.1$$
$$\Rightarrow K_b = \frac{\left[(CH_3)_2NH_2^{+}\right]\left[OH^{-}\right]}{\left[(CH_3)_2NH\right]}$$ x from $[OH^-]$= x + 0.1 can be neglected.
$$5.4 \times 10^{-4} = \frac{x \times 0.1}{0.02}$$
$$x = 0.0054$$

Percentage of dimethyamine is equal to 0.0054 * 100=0.54%.

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.

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

(a) Human muscle fluid 6.83:

pH = 6.83

pH = - log [H^+]

∴6.83 = - log [H^+]

[H^+] = 1.48×10^{-7} M

(b) Human stomach fluid, 1.2:

pH =1.2

1.2 = - log [H^+]

∴[H^+] = 0.063

(c) Human blood, 7.38:

pH = 7.38 = - log [H^+]

∴ [H^+] = 4.17×10^{-8} M

(d) Human saliva, 6.4:

pH = 6.4

6.4 = - log [H^+]

[H^+] = 3.98 x 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.

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 of black 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 juice = 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)

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

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

Ans.

$$\left[KOH_{aq}\right] = \frac{0.561}{1} g/L$$
$$= 2.805 g/L$$
$$= 2.805 \times \frac{1}{56.11} M$$

= **0.05 M**

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

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

$=(10^{-14}/0.05)=2x10^{-13}M$

pH = - log$[2x10^{-13}]$

= 12.70

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

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

Then, concentration of Sr $(OH)_2$

$$= \frac{19.23}{121.63} M$$
$$= 0.1581M$$
$$Sr(OH)_{2(aq)} \rightarrow Sr^{2+}{}_{(aq)} + 2(OH^-)_{(aq)}$$
$$\therefore \left[Sr^{2+}\right] = 0.1581M$$
$$\left[OH^-\right] = 2 \times 0.1581M = 0.3126M$$
$$Now,$$
$$K = \left[OH^-\right]\left[H^+\right]$$
$$\frac{10^{-14}}{0.3126} = \left[H^+\right]$$
$$\Rightarrow \left[H^+\right] = 3.2 \times 10^{-14}$$
$$\therefore pH = 13.495; 13.50$$

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

Ans. Let the degree of ionization of propanoic acid be α.

Then, representing propionic acid as HA, we have:

$$HA \quad + H_2O \leftrightarrow H_3O^+ + A^-$$
$$(.05 = 0.0a) \approx .05 \qquad .05a \qquad .05a$$
$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$
$$= \frac{(.05a)(.05a)}{0.05} = .05a^2$$

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

$$Then, \left[H_3O^+\right] = .05a = .05 \times 1.63 \times 10^{-2} = K_b.1.5 \times 10^{-4} M$$

$$\therefore pH = 3.09$$

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

$$Then, \left[H_3O^+\right] = 0.01$$

$$\left[A^-\right] = 005a'$$

$$\left[HA\right] = .05$$

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

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

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

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.

Ans. c = 0.1 M

pH = 2.34

$$-\log\left[H^+\right] = pH$$
$$-\log\left[H^+\right] = 2.34$$
$$\left[H^+\right] = 4.5\times10^{-3}$$
$$Also,$$
$$\left[H^+\right] = ca$$
$$4.5\times10^{-3} = 0.1\times a$$
$$\frac{4.5\times10^{-3}}{0.1} = a$$
$$a = 45\times10^{-3} = .045$$
$$Then,$$
$$K_a = ca^2$$
$$= 0.1\times(45\times10^{-3})^2$$
$$= 202.5\times10^{-6}$$
$$= 2.02\times10^{-4}$$

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.

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

$$NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$$
$$K_h = \frac{\left[HNO_2\right]\left[OH^-\right]}{\left[NO_2^-\right]}$$
$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5\times10^{-4}} = .22\times10^{-10}$$

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

$$\left[NO_2^-\right] = .04 - x; 0.04$$
$$\left[HNO_2\right] = x$$
$$\left[OH^-\right] = x$$
$$K_b = \frac{x^2}{0.04} = 0.22 \times 10^{-10}$$
$$x^2 = .0088 \times 10^{-10}$$
$$x = .093 \times 10^{-5}$$
$$\therefore \left[OH^-\right] = 0.093 \times 10^{-5} M$$
$$\left[H_3O^+\right] = \frac{10^{-14}}{.093 \times 10^{-5}} = 10.75 \times 10^{-9} M$$
$$\Rightarrow pH = -\log(10.75 \times 10^{-9})$$
$$= 7.96$$

Therefore, degree of hydrolysis

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

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

Ans. pH = 3.44

We know that,

pH = -log [H^+]

$$\therefore \left[H^+\right] = 3.63\times10^{-4}$$

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

$$\Rightarrow K_a = 6.6\times10^{-5}$$

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

$$\Rightarrow K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6\times10^{-5}}$$

$$= 1.51\times10^{-9}$$

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

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

Ans. (i) NaCl:

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

Therefore, it is a neutral solution.

(ii) KBr:

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

Therefore, it is a neutral solution.

(iii) NaCN:

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

Therefore, it is a basic solution.

(iv) NH_4NO_3

$$NH_4NO_3 + H_2O \leftrightarrow \underset{Weak\ base}{NH_4OH} + \underset{Strong\ acid}{HNO_3}$$

Therefore, it is an acidic solution.

(v) $NaNO_2$

$$NaNO_2 + H_2O \leftrightarrow \underset{Strong\ base}{NaOH} + \underset{Weak\ acid}{HNO_3}$$

Therefore, it is a basic solution.

(vi) KF

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

Therefore, it is a basic solution.

---

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?

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

$\Rightarrow K_a = ca^2$

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

$= \sqrt{\frac{1.35\times10^{-3}}{0.1}}$ $(\because concentration\, of\, acid = 0.1m)$

$a = \sqrt{1.35\times10^{-2}}$

$= 0.116$

$\therefore \left[H^+\right] = ca = 0.1\times0.116$

$= .0116$

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

$ClCH_2$ COONa is the salt of a weak acid i.e., $ClCH_2COOH$ and a strong base i.e., NaOH.

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

$K_b = \frac{\left[ClCH_2COOH\right]\left[OH^-\right]}{\left[ClCH_2COO^-\right]}$

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

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

$= 0.740\times10^{-11}$

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

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

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

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

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

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

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

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

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

$$= 7.94$$

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

Ans. Ionic product,

$$K_w = \left[H^+\right]\left[OH^-\right]$$

$$Let \left[H^+\right] = x$$

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

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

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

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

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

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

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

$$= 6.78$$

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

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

$$Moles\ of\ OH^- = \frac{10 \times 0.2 \times 2}{1000} = .0040 mol$$
$$Thus, excess\ of\ OH^- = .0015 mol$$
$$[OH^-] = \frac{.0015}{35 \times 10^{-3}} mol / L = .0428$$
$$pOH = -\log[OH]$$
$$= 1.36$$
$$pH = 14 - 1.36$$
$$= 12.64$$

(b) $Moles\ of\ H_3O^+ = \frac{2 \times 10 \times 0.01}{1000} = .002 mol$

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

Since there is neither an excess of $H_3O^+\ or\ OH^-$, the solution is neutral.

Hence, pH=7.

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

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

Excess of H_3O^+ = .001 mol

$$Thus, \left[H_3O^+\right] = \frac{.001}{20 \times 10^{-3}} = 0.5$$
$$\therefore pH = -\log(0.05)$$
$$= 1.30$$

= 1.30

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

Ans. (1) Silver chromate:

$$Ag_2CrO_4 \rightarrow 2Ag^+CrO_4^{2-}$$
$$Then,$$
$$K_{xp} = \left[Ag^+\right]^2 \left[CrO_4^{2-}\right]$$

Let the solubility of $Ag_2CrO_4^{2-}$ be s.

$$\Rightarrow \left[Ag^+\right] 2s\ and \left[CrO_4^{2-}\right] = s$$
$$Then,$$
$$K_{xp} = (2s)^2 .s = 4s^3$$
$$\Rightarrow 1.1 \times 10^{-12} = 4s^3$$
$$.275 \times 10^{-12} = s^3$$
$$s = 0.65 \times 10^{-4} M$$

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

Molarity of CrO_4^{2-} = s = 0.65×10^{-4} M

(2) Barium chromate:

$$BaCrO_4 \rightarrow Ba^{2+} + CrO_4^{2-}$$
$$Then, K_{sp} = \left[Ba^{2+}\right]\left[CrO_4^{2-}\right]$$

Let *s* be the solubility of $BaCrO_4$

Thus, $\left[Ba^{2+}\right]$ = *s* and $\left[CrO_4^{2-}\right]$ = *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^{2+} = Molarity of $CrO_4^{2-} = s = 1.09 \times 10^{-5} M$

(3) Ferric hydroxide:

$$Fe(OH)_3 \rightarrow Fe^{2+} + 3OH^-$$
$$K_{sp} = \left[Fe^{2+}\right]\left[OH^-\right]^3$$

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

$$Thus, \left[Fe^{3+}\right] = s \; and \left[OH^-\right] = 3s$$
$$\Rightarrow K_{sp} = s.(3s)^2$$
$$= s.27s^3$$
$$K_{sp} = 27s^4$$
$$1.0 \times 10^{-38} = 27s^4$$
$$0.37 \times 10^{-38} = s^4$$
$$.00037 \times 10^{-36} = s^4 \Rightarrow 1.39 \times 10^{-10} M = S$$

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

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

(4) Lead chloride:

$$PbCl_2 \rightarrow Pb^{2+} + 2Cl^-$$
$$K_{SP} = \left[Pb^{2+}\right]\left[Cl^-\right]^2$$

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

$$\left[Pb^{2+}\right] = s \; and \left[Cl^-\right] = 2s$$
$$Thus, K_{sp} = s.(2s)^2$$
$$= 4s^3$$
$$\Rightarrow 1.6\times10^{-5} = 4s^3$$
$$\Rightarrow 0.4\times10^{-5} = s^3$$
$$4\times10^{-6} = s^3 \Rightarrow 1.58\times10^{-2}M = S.1$$
$$Molarity\ of\ \mathbf{P}B^{2+} = s = 1.58\times10^{-2}M$$
$$Molarity\ of\ chloride = 2s = 3.16\times10^{-2}M$$

(5) Mercurous iodide:-

$$Hg_2I_2 \rightarrow Hg^{2+} + 2I^-$$
$$K_{sp} = \left[Hg_2^{2+}\right]^2\left[I^-\right]^2$$
$$Let\ s\ be\ the\ solubility\ of\ Hg_2I_2$$
$$\Rightarrow \left[Hg_2^{2+}\right] = s \; and \left[I^-\right] = 2s$$
$$Thus, K_{sp} = s(2s)^2 \Rightarrow K_{sp} = 4s^3$$
$$4.5\times10^{-29} = 4s^3$$
$$1.125\times10^{-29} = s^3$$
$$\Rightarrow s = 2.24\times10^{-10}M$$
$$Molarity\ of\ Hg_2^{2+} = s = 2.24\times10^{-10}M$$
$$Molarity\ of\ I^- = 2s = 4.48\times10^{-10}M$$

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.

Ans. Let *s* be the solubility of Ag_2CrO_4 .

$$Then, Ag_2CrO_4 \leftrightarrow Ag^{2+} + 2CrO_4^-$$
$$K_{sp} = (2s)^2.s = 4s^3$$
$$1.1\times10^{-12} = 4s^3$$
$$s = 6.5\times10^{-5} M$$

Let *s* ´ be the solubility of AgBr.

$$AgBr_{(s)} \leftrightarrow Ag^+ + Br^-$$
$$K_{sp} = s'^2 = 5.0\times10^{-13}$$
$$\therefore s' = 7.07\times10^{-7} M$$

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

$$\frac{s}{s'} = \frac{6.5\times10^{-5} M}{7.07\times10^{-7} M} = 91.9$$

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 $K_{sp} = 7.4 \times 10^{-8}$).

Ans. 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,

$$Na10_3 \rightarrow Na^+ + 10_3^-$$
$$0.001M \qquad 0.001M$$
$$Cu(ClO_3)_2 \rightarrow Cu^{2+} + 2ClO_3^-$$
$$0.001M \qquad 0.001M$$

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

$$Cu(10_3)_2 \rightarrow Cu^{2+}{}_{(aq)} + 210_{3(aq)}^-$$

Ionic product of copper iodate:

$$= \left[Cu^{2+}\right]\left[10_3^-\right]^2$$
$$= (0.001)(0.001)^2$$
$$= 1 \times 10^{-9}$$

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

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?

Ans. Since pH = 3.19,

$$\left[H_3O^+\right] = 6.46 \times 10^{-4} M$$
$$C_6H_5OOH + H_2O \leftrightarrow C_6H_5COO^- + H_3O$$
$$K_a = \frac{\left[C_6H_5COO^-\right]\left[H_3O^+\right]}{\left[C_6H_5COOH\right]}$$
$$\frac{\left[C_6H_5COOH\right]}{\left[C_6H_5COO^-\right]} = \frac{\left[H_3O^+\right]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let the solubility of C_6H_5COOAg be *x* mol/L.

Then,

$$\left[Ag^{+}\right]=x$$
$$\left[C_6H_5COOH\right]+\left[C_6H_5COO^{-}\right]=x$$
$$10\left[C_6H_5COO^{-}\right]+\left[C_6H_5COO^{-}\right]=x$$
$$\left[C_6H_5COO^{-}\right]=\frac{x}{11}$$
$$K_{sp}\left[Ag^{+}\right]\left[C_6H_5COO^{-}\right]$$
$$2.5\times10^{-13}=x\left(\frac{x}{11}\right)$$
$$x=1.66\times10^{-6}mol/L$$

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_5COO Ag be *x'* mol/L.

$$Then, \left[Ag^{+}\right]=x'M \text{ and } \left[CH_3COO^{-}\right]=x'M$$
$$K_{sp}=\left[Ag^{+}\right]\left[CH_3COO^{-}\right]$$
$$K_{sp}=(x')^2$$
$$x'=\sqrt{K_{sp}}=\sqrt{2.5\times10^{-13}}=5\times10^{-7}mol/L$$
$$\therefore \frac{x}{x'}=\frac{1.66\times10^{-6}}{5\times10^{-7}}=3.32$$

Hence, C_6H_5COO Ag 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, $K_{sp}=6.3\times10^{-18}$).

Ans. 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., $\frac{x}{2}$.

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

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

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

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

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

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

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

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

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

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}).

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

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

Let the solubility of $CaSO_4$ be *s*.

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

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

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

Molecular mass of $CaSO_4$ = 136 g/mol

Solubility of $CaSO_4$ in gram/L = $3.02 \times 10^{-3} \times 136$

= 0.41 g/L

This means that we need 1L of water to dissolve 0.41g of $CaSO_4$

Therefore, to dissolve 1g of $CaSO_4$ we require $= \frac{1}{0.41} L = 2.44L$ 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: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

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

Ans. For precipitation to take place, it is required that the calculated ionic product exceeds the *Ksp* value.

Before mixing:

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

$$volume = 10mL \qquad volume = 5mL$$

After mixing:

$$\left[S^{2-}\right] = ? \qquad \left[M^{2+}\right] = ?$$

$$volume = (10+5) = 15mL \qquad volume = 15mL$$

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

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

$$Ionic\ product = \left[M^{2+}\right]\left[S^{2-}\right]$$

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

$$= 8.87 \times 10^{-22}$$

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