NCERT Solutions for Class-XI Chemistry

Chapter-7

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?

1. (a) When volume is suddenly increased, the vapour pressure decreases.

Explanation: When volume is increased suddenly there is no sudden increase in number of vapour substance. Thus same number of particle occupies larger volume and thus have lower pressure. (After some time, the number of vapour molecules increases and vapour pressure slowly rises from the decreased value)

(b) At equilibrium state,

Rate of evaporation = Rate of condensation

When volume is increased, the vapour pressure decreases and so, the rate of evaporation will be greater than rate of condensation.

This can be understood by the Le Chatelier's principle, which states that, when an equilibrium state experiences a disturbance (here pressure decrease) the system will try to cancel the effect of change in the system.

(c) When equilibrium is finally restored, the system will have initial vapour pressure. Vapour pressure does not depend on volume of container, it only depends on nature of substance and temperature. Thus the sudden decrease in partial pressure is slowly raised so that a new equilibrium is obtained. Partial pressure of the vapour will be same as the initial.

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?

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

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

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

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

$$= 12.239\ M^{-1} \text{ (approximately)}$$

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

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

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

Calculate K_p for the equilibrium.

3. K_p value at equilibrium for reaction,

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

is given as,

$$K_p = \frac{[P(I)]^2}{[P(I_2)]}$$

Given, 40% volume is occupied by I atoms.

∴ 60 % volume is occupied by I_2.

Let V be total volume, then volume occupied by I and I_2 are 0.4V and 0.6V respectively.

Partial pressure of $I_2 = (60/100) \times 10^5 = 60$ kPa

Partial pressure of $I = (40/100) \times 10^5 = 40$ kPa

Substituting in equation for K_p,

$$K_p = \frac{(40 \times 10^3 \text{ KPa})^2}{(60 \times 10^3 \text{ KPa})} = 2.67 \times 10^4 \text{ KPa}$$

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

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

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

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

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

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

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

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

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

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

5. We know that,

$$K_p = K_c[RT]^{\Delta n}$$

Where Δn is number of gas molecule in products minus number of gas molecule in reactant in balanced chemical equation.

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

Number of gaseous species on product side is 3 (2 NO and 1 Cl_2) and on reactant side is 2 (2 NOCl)

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

$T = 500$ K

$R = 0.0821$ L atm K^{-1}

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

$$\therefore \quad K_c = \frac{K_P}{[RT]^{\Delta n}}$$

$$= \frac{(1.8\times10^{-2})\text{atm}}{(0.0821 \text{ L atm K}^{-1}\times 500 \text{ K})^1}$$

$= 4.4 \times 10^{-4}$ mol L^{-1}

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

Number of gaseous species on product side is 1 (1 CO_2) and on reactant side is 0.

Thus, $\Delta n = 1 - 0 = 1$

$T = 1073$ K

$K_p = 167$ atm

$$K_c = \frac{K_P}{[RT]^1}$$

$$= \frac{167 \text{ atm}}{0.0821 \text{ L atm K}^{-1}\times 1073 \text{ K}}$$

$= 1.9$ mol L^{-1}

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?

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

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

$$= \frac{1}{6.3\times10^{14}}$$

$$= 1.59\times10^{-15}$$

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

7. Concentration of solid or pure liquid,

$$[\text{substance}] = \frac{\text{number of mole of substance}}{\text{volume}}$$

$$= \frac{\text{amount of substance}}{\text{Molar mass} \times \text{Volume}}$$

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

Since density and molar mass doesn't vary, concentration of the substance remain constant.

Pure liquids and solid have a constant concentration. Composition of solids remain same throughout a reaction even though amount may change.

Similarly, pure liquids have same composition (since it has only one substance).

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 equilibrium mixture.

8. 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:

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

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,

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

$$\text{Now, } K_C = \frac{[N_2O(g)]^2}{[N_2(g)]^2[O_2(g)]}$$

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

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

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

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

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

$$= 6.6 \times 10^{-21}$$

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

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

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

9. The chemical reaction is,

	$2NO(g)$	+	$Br_2(g)$	$\rightleftharpoons$	$2NOBr(g)$
Initial amount:	0.087 mol		0.0437		0

Let x amount of Br_2 be reacted to attain equilibrium. Then amount of substance left at equilibrium,

	$2NO(g)$	+	$Br_2(g)$	$\rightleftharpoons$	$2NOBr(g)$
Equilibrium amount:	0.087 – 2x		0.0437 – x		2x

Given, equilibrium concentration of NOBr is 0.0518,
i.e., 2x = 0.0518
x = 0.0259
Thus,
Amount of NO at equilibrium = 0.087 – 2 × 0.0259
= 0.0352 mole
Amount of Br_2 at equilibrium = 0.0437 – 0.0259
= 0.0178 mole

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

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

What is K_c at this temperature?

10. For the given reaction,

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

T = 450 K

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

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

We know that,

$K_P = K_C\ (RT)\Delta n$

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

$$\Rightarrow K_C = \frac{2.0\times10^{10}\,bar^{-1}}{\left(0.0831\,L\,bar\,K^{-1}\,mol^{-1}\times450\,K\right)^{-1}}$$

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

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

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

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

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?

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

11. Partial pressure of HI = 0.04 atm

sum of partial pressures = total pressure, thus,

$$P(H_2) + P(I_2) = P - P(HI)$$

where,

P is total pressure = 0.2 atm

$P(H_2)$ is Partial pressure of H_2 = x

$P(I_2)$ is Partial pressure of I_2 = x

P(HI) is Partial pressure of HI = 0.04 atm

$\therefore$ x + x = 0.2 – 0.04
= 0.16

i.e., x = 0.08 atm

$$K_p = \frac{\left[p(H_2)\times(p(I_2))\right]}{\left[p(HI)\right]^2}$$

$$=\frac{(0.08)atm\times(0.08)atm}{(0.04\,atm)^2}=4$$

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?

12. The given reaction is:

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

The given concentration of various species is

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

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

Now, reaction quotient Q_C is:

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

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

$$= 2.4 \times 10^3$$

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.

13. For a chemical change,

$$aA + bB \rightleftharpoons cC + dD$$

Equilibrium constant K_c for the reaction,

$$K_C = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

In question, expression for equilibrium constant is given as,

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

Comparing the power of each concentration term we can find the chemical reaction.

The reaction here is given by,

$$4NO + 6H_2O \rightleftharpoons 4NH_3 + 5O_2$$

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,

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

Calculate the equilibrium constant for the reaction.

14. The given reaction is:

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

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,

$$K_C = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

$$= \frac{0.04 \times 0.04}{0.06 \times 0.06}$$

$$= 0.444 \text{ (approximately)}$$

15. At 700 K, 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?

15. For the reaction,

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

Equilibrium constant is given to be 54.8.

i.e., $K_c = \frac{[HI]^2}{[H_2]\times[I_2]}$

Let x be equilibrium concentration of H_2 at equilibrium. Then equilibrium concentration of I_2 will also be x. Since, initially there was only HI present, equal amount of H_2 and I_2 will be produced.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
At equilibrium:	x		x		0.5

$$K_c = \frac{[HI]^2}{[H_2]\times[I_2]}$$

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

$$x = \sqrt{\frac{(0.5)^2}{54.8}}$$

$$= 0.0675$$

Therefore, concentration of H_2 and I_2 is 0.0675 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?

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

16. The given reaction is:

	$2ICl(g)$	$\rightleftharpoons$	$I_2(g)$	$Cl_2(g)$
Initial conc.	0.78 M		0	0
At equilibrium	(0.78 – 2x) M		x M	xM

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

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

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

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

$\Rightarrow x = 0.292 - 0.748x$

$\Rightarrow 1.748x = 0.292$

$\Rightarrow x = 0.167$

Hence, at equilibrium

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

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

$= 0.446\ M$

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?

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

17. For the given reaction, lets assume that p atm is the pressure exerted by ethene and hydrogen gas at equilibrium.

Therefore, the given reaction is:

	$C_2H_6(g)$	$\rightleftharpoons$	$C_2H_4(g)$	+	$H_2(g)$
Initial pressure	4.0 atm		0		0
Equilibrium pressure	(4 – p) atm		p		p

Equilibrium pressure constant (K_p) is defined as a number that expresses the relationship between the partial pressures of products and reactants present at equilibrium in a reversible chemical reaction at a given temperature.

Here. K_p= 0.04 atm

For the given reaction,

$$K_p = \frac{p_{C_2H_2} \times p_{H_2}}{p_{C_2H_6}}$$

Where $p_{C_2H_4}$ = partial pressure pf C_2H_4 in atm at equilibrium

p_{H_2} = partial pressure of H_2 in atm at equilibrium

$p_{C_2H_6}$ = partial pressure of C_2H_6 in atm at equilibrium

$$0.04 = \frac{p \times p}{(40 - p)}$$

$p^2 = 0.16 - 0.04p$

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

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

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

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

$p = 0.38$

Therefore, at equilibrium, $[C_2H_6] = 4 - p = 4 - 038 = 3.62$ atm.

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

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

(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 sometime. Has equilibrium been reached?

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

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

The given reaction is:

	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ ⇌	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial conc.	$\frac{1}{V}$ M	$\frac{0.18}{V}$ M	0	0
At equilibrium	$\frac{1-0.171}{V}$	$\frac{0.18-0.171}{V}$	$\frac{0.171}{V}$ M	$\frac{0.171}{V}$ M
	$=\frac{0.829}{V}$ M	$=\frac{0.09}{V}$ M		

Therefore, equilibrium constant for the given reaction is:

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

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

= 3.92 (approximately)

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

	$CH_3COOH(l)$ +	$C_2H_5OH(l)$ ⇌	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial conc.	$\frac{1.0}{V}$ M	$\frac{0.5}{V}$ M	0	0
After some time	$\frac{10-0.214}{V}$	$\frac{0.5-0.214}{V}$	$\frac{0.214}{V}$ M	$\frac{0.214}{V}$ M

Therefore, the reaction quotient is,

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

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

= 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?

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

19. For the given reaction, lets assume that the initial molar concentration of PCl_5 is x mol/L.

The given reaction is:

	$PCl_5(g)$ ⇌	$PCl_3(g)$ +	$Cl_2(g)$
Initial concentration	x	0	0
Equilibrium concentration	0.05	(x – 0.05)	(x – 0.05)

Moles of PCl_5 decomposed during the reaction = Moles of PCl_3 formed = Moles of Cl_2 formed =

(x – 0.05) mol/L.

Equilibrium constant (K_c) is defined as a number that expresses the relationship between the amounts of products and reactants present at equilibrium in a reversible chemical reaction at a given temperature.

Here, $K_c = 0.0083$.

For the given reaction,

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

Where, $[PCl_3]$ = concentration of PCl_3 in mol/L at equilibrium

$[Cl_2]$ = concentration of Cl_2 in mol/L at equilibrium

$[PCl_5]$ = concentration of PCl_5 in mol/L at equilibrium

$$0.0083 = \frac{(x - 0.05) \times (x - 0.05)}{0.05}$$

$(x - 0.05)^2 = 0.000415$

$(x - 0.05) = 0.0203$

x = 0.07 mol/L

Therefore, $[PCl_3] = (x - 0.05) = 0.07 - 0.05 = 0.02$ mol/L

$[Cl_2] = (x - 0.05) = 0.07 - 0.05 = 0.02$ mol/L.

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.

$$FeO\ (s) + CO(g) \rightleftharpoons Fe\ (s) + CO_2(g);\ K_p = 0.265 \text{ atm at } 1050K$$

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are:

$$p_{CO} = 1.4 \text{ atm and } p_{CO_2} = 0.80 \text{ atm?}$$

20. For the given reaction,

FeO (s)	+ CO(g)	⇌	Fe (s) +	$CO_2(g)$
Initialy,	1.4 atm			0.80 atm

$$Q_P = \frac{pCO_2}{pCO}$$

$$= \frac{0.80}{1.4}$$
$$= 0.571$$

It is given that $K_P = 0.265$.

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

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

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

$$K_P = \frac{pCO_2}{pCO}$$
$$\Rightarrow 0.265 = \frac{0.80 - p}{1.4 + p}$$
$$\Rightarrow 0.371 + 0.265p = 0.80 - p$$
$$\Rightarrow 1.265p = 0.429$$
$$\Rightarrow p = 0.339 \text{ atm}$$

Therefore, equilibrium partial of CO_2, $pCO_2 = 0.80 – 0.339 = 0.461$ atm.

And, equilibrium partial pressure of CO, $pCO = 1.4 + 0.339 = 1.739$ atm.

21. Equilibrium constant, K_c for the reaction

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

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?

21. The given reaction is:

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

Given Concentration 3 mol/L 2 mol/L 0.5 mol/L

The reaction quotient (Q) measures the relative amounts of products and reactants present during a reaction at a particular point in time. It also indicates the direction in which the reaction is going to proceed.

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

Where, $[NH_3]$ = concentration of NH_3 in mol/L at a particular instant

$[N_2]$ = concentration of N_2 in mol/L at a particular instant

$[H_2]$ = concentration of H_2 in mol/L at a particular instant

Therefore, $Q_c = \frac{[0.50]^2}{[3.0][2.0]^3} = \frac{0.25}{24} = 0.0104$

And $K_c = 0.061$, where K_c is the equilibrium constant.

Since, $Q_c < K_c$, the reaction is not in equilibrium and will proceed in the forward direction in order to attain 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 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

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

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

Now, we can write,

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

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

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

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

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

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

Therefore, at equilibrium,

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

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

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

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

23. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with soild 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.

23. Let us assume that the total mass of the gaseous mixture is 100g.

Therefore, mass of CO = 90.55g

And mass of CO_2 = (100 – 90.55) = 9.45g

Number of moles of CO, $n_{CO} = \frac{\text{Mass of available CO}}{\text{Molar Mass of CO}} = \frac{90.55g}{28g} = 3.234$

Number of moles of CO_2, $n_{CO_2} = \frac{\text{Mass of available } CO_2}{\text{Molar Mass of } CO_2} = \frac{9.45g}{44g} = 0.215$

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

$$= \frac{3.234}{3.234 + 0.215} \times 1 = 0.938 \text{ atm}$$

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

$$= \frac{0.215}{3.234 + 0.215} \times 1 = 0.062 \text{ atm}$$

Equilibrium pressure constant (K_p) is defined as a number that expresses the relationship between the partial pressures of products and reactants present at equilibrium in a reversible chemical reaction at a given temperature.

Therefore, $K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(0.938 \text{ atm})^2}{(0.062 \text{ atm})} = 14.19 \text{ atm}$

Also we know that, $K_c = \frac{K_p}{(RT)^{\Delta ng}}$

Where K_c = Equilibrium constant

K_p = 14.19 atm

R = 0.081 L atm/K mol

T = 1127 K

Δng = Sum of stochiometric coefficients of products – Sum of stochiometric coefficients of reactants = 2 – 1 = 1.

$$K_c = \frac{(14.19\ \text{atm})}{\left(0.821\ \text{L}\frac{\text{atm}}{\text{K}}\text{mol}\right)\times(1127\ \text{K})^1} = 6.46$$

24. Calculate

(a) ΔG° and

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

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

Where:

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

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

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

24. (a) For the given reaction,

$\Delta G^\circ = \Delta G^\circ$ (Products) – ΔG° (Reactants)

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

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

(b) We know that,

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

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

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

$= 6.134$

$\therefore K_c$ = antilog (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) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

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

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

25. When the pressure on the system is increased, the volume decreases proportionately. According to Le Chatelier's principle, the equilibrium will shift in the direction in which there is a decrease in the number of moles, i.e., towards the direction in which there is a decrease in the volume. In general, an increase in pressure applied to the system at equilibrium favours the reaction in the direction which takes place with a decrease in a total number of moles and a decrease in the pressure favours the reaction in the direction which takes place with an increase in total number of moles. If there is no change in the number of moles of gases in a reaction, a pressure change does not affect the equilibrium.

Hence, according to Le Chatelier's principle, if the pressure on the system is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more.

(a) The number of moles of reaction products will increase. In the given reaction,

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

The number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward reaction. As a result, the number of moles of reaction products will increase.

(b) The number of moles of reaction products will decrease. In the given reaction,

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

The number of moles of gaseous products is less than that of gaseous reactants. Thus, the reaction will proceed in the backward reaction. As a result, the number of moles of reaction products will decrease.

(c) The number of moles of reaction products remains same.

In the given reaction,

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

The number of moles of gaseous products equal to gaseous reactants. Thus, the decreasing of pressure does not affect the equilibrium. As a result, the number of moles of reaction products will remain same.

Note: Le Chatelier's principle states that "if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in a direction that tends to undo the effect of the change".

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

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

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

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

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.

27. Given:

For the given reaction,

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

The equilibrium constant (K_c) is 1.6×10^5

Initial pressure of HBr = 10bar

Temperature = 1024K

For equilibrium constant in terms of pressure, we apply the formula given below:

$$K_p = \left(\frac{p_X^x k.p_Y^y}{p_A^a \cdot p_A^b}\right)$$

Where P_x and P_Y are the partial pressures of x and y(products)

P_A and P_B are the partial pressures of a and b (reactants)

As we know that the relationship between K_p and K_c is $K_p = K_c\ (R/T)^{\Delta n}$

Where Δn = no. of moles of products – no. of moles of reactants
Hence for the given reaction,
$\Delta n = 0$
$\therefore K_p = K_c$
As the given reaction is a reversible reaction. Hence, we can write

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g), \qquad \therefore K_c = \frac{1}{1.6\times10^5}$$

Initial 10bar
At
Equilibrium 10–P P/2 P/2
Using the above formula,

$$K_p = \left(\frac{p_X^x \cdot p_Y^y}{p_A^a \cdot p_B^b}\right)$$

$$K_p = \left(\frac{\left(\frac{P}{2}\right)\left(\frac{P}{2}\right)}{(10-P)^2}\right) = K_c$$

$$\Rightarrow \left(\frac{\left(\frac{P}{2}\right)\left(\frac{P}{2}\right)}{(10-P)^2}\right) = \left(\frac{1}{1.6\times10^5}\right)$$

$$\Rightarrow \left(\frac{P^2}{4(10-P)^2}\right) = \left(\frac{1}{1.6\times10^5}\right)$$

Taking square root of both sides, we get

$$\Rightarrow \left(\frac{P}{2(10-P)}\right) = \left(\frac{1}{4.0\times10^2}\right)$$

$\Rightarrow 4.0 \times 10^2 = 2(10 - P)$
$\Rightarrow 402\ P = 20$

$$\Rightarrow P = \left(\frac{20}{402}\right)$$

$\Rightarrow P = 4.97 \times 10^{-2}$ bar
Hence, at equilibrium
$P_{H2} = P_{Br2} = P/2$

$$\Rightarrow \left(\frac{4.97\times10^{-2}\ \text{bar}}{2}\right) = 2.48\times10^{-2}\ \text{bar}$$

$P_{HBr} = 10 - P \approx 10$ bar
Thus, the equilibrium pressure of H_2 and Br_2 is 2.48×10^{-2} bar and HBr is 10 bar.

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

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

(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?

28. (a) For the given reaction,
(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 increase 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:

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

29. According to Le Chatelier's principle, if in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward reaction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the concentrations are decreased.
For the given reaction,

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

(a) If the addition of H_2 is taking place, it means the concentration of reactant is increasing. According to Le Chatelier's principle, the equilibrium shifts in the forward direction.
(b) If the addition of CH_3OH is taking place, it means the concentration of product is increasing. According to Le Chatelier's principle, the equilibrium shifts in the backward direction.
(c) If the removal of CO is taking place, it means the concentration of reactant is decreasing, the equilibrium shifts in the backward direction. According to Le Chatelier's principle, the equilibrium shifts in the backward direction.
(d) If the removal of CH_3OH is taking place, it means the concentration of product is decreasing, the equilibrium shifts in the forward direction. According to Le Chatelier's principle, the equilibrium shifts 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,

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

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

30. (a) $K_c \dfrac{\left[PCl_{3(g)}\right]\left[Cl_{2(g)}\right]}{\left[PCl_{5(g)}\right]}$

(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) Kc would remain the same because in this case, the temperature remains the same.
(ii) K_c is constant at constant temperature. Thus, in the case, K_c would not change.

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 the second stage, CO formed in the first stage is reacted with more steam in water gas shift reaction,

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

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? K_p= 10.1 at 400°C.

31. The given reaction is $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

Given: Temperature = 400° C

Partial pressure of CO (P_{CO}) = Partial pressure of H_2O (P_{H2O}) = 4.0 bar

K_p = 10.1 bar

Formula: $K_p = \left(\frac{p_X^x \cdot p_Y^y}{p_A^a \cdot p_B^b}\right)$

Let the partial pressure of H_2 (P_{H2}) at equilibrium = P bar

	CO (g) +	H_2O (g)	⇌ CO_2 (g) +	H_2 (g)
Initial pressure	4 bar	4 bar		
At equilibrium	(4 – P)	(4 – P)	P	P

By applying the formula given below:

$$K_p = \left(\frac{p_X^x \cdot p_Y^y}{p_A^a \cdot p_B^b}\right)$$

Where P_x and P_Y are the partial pressures of x and y (products)

P_A and P_B are the partial pressures of a and b (reactants)

Hence, $K_p = \left(\frac{P \times P}{(4-P)\times(4-P)}\right)$

As K_p = 10.1 bar (given)

$$\therefore 10.1 = \left(\frac{P \times P}{(4-P)\times(4-P)}\right)$$

$$\Rightarrow 10.1 = \left(\frac{P^2}{(4-P)^2}\right)$$

By taking square roots of both the sides, we get

$$\Rightarrow \sqrt{10.1} = \left(\frac{P}{4-P}\right)$$

$$\Rightarrow 0.3178 = \left(\frac{P}{4-P}\right)$$

$$\Rightarrow 12.712 - 0.3178P = P$$

$$\Rightarrow 4.178P = 12.712$$

$$\Rightarrow P = 3.042 \text{ bar}$$

Thus, the partial pressure of H_2 (P_{H2}) at equilibrium = P bar = 3.042 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) $Cl_2\ (g) + 2NO_2\ (g) \rightleftharpoons 2NO_2Cl\ (g)$; $K_c = 1.8$

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

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 the air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

33. Given:

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

The equilibrium constant of the given reaction = 2.0×10^{-50}

Temperature = 25° C

Equilibrium concentration of O_2 ($[O_2]$) = 1.6×10^{-2} M

To find out the equilibrium concentration of O_3, we will apply the

Law of Chemical Equilibrium, i.e., $K_c = \dfrac{[X][Y]}{[A][B]}$

Where X and Y are the products and A and B are the reactants.

Hence, equilibrium constant (K_c) of the given reaction,

$3O_2\,(g) \rightleftharpoons 2O_3\,(g)$

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

As $K_c = 2.0\times10^{-50}$ (given) and $[O_2] = 1.6 \times 10^{-2}$ M (given)

$$\therefore 2.0\times10^{-50} = \frac{\left([O_3]^2\right)}{\left(1.6\times10^{-2}\,M\right)^3}$$

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

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

$\Rightarrow\ [O_3] = \sqrt{8.192\times10^{-56}}$

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

Thus, the equilibrium concentration of O_3 is 2.86×10^{-28}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.

34. Let the concentration of methane at equilibrium be x.

	$CO(g)$	$+\ 3H_2(g)$	$\rightleftharpoons\ CH_4(g)$	$+\ H_2O(g)$
At equlibrium	$\frac{0.3}{1} = 0.3M$	$\frac{0.1}{1} = 0.1M$	x	$\frac{0.02}{1} = 0.02M$

It is given that $K_c = 3.90$.

Therefore,

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

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

$$\Rightarrow x = \frac{3.90\times0.3\times(0.1)^3}{0.02}$$

$$= \frac{0.00117}{0.02}$$
$$= 0.0585\ M$$
$$= 5.85 \times 10^{-2}\ M$$

Hence, the concentration of CH4 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-}

35. Consider the following acid-base reaction:

$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

HCl is an acid because it donates a proton to water (H_2O) and H_2O is a base because it accepts a proton from H_2O and hence is a base. Thus, there are two acid-base pairs in the reaction. These are HCl-Cl^- and H_3O^+ –H_2O. These acid-base pairs are called conjugate acid-base pairs.

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

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

36. Lewis acids are those acids which can accept a pair of electrons. For example, BF_3, H^+ and NH_4^+ are Lewis acids.

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

37. **Bronsted acid:** A bronsted acid is a substance that can donate a proton. A bronsted acid is proton-donor.

When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a conjugate base.

Conjugate base $\rightleftharpoons$ Conjugate acid – H^+ (loses proton)

Bronsted acids	**Loss of proton**	**Conjugate bases**
HF	HF – H^+	F^-
H_2SO_4	H_2SO_4 – H^+	HSO_4^-
HCO_3^-	HCO_3^- - H^+	CO_3^{2-}

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

38. 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.

39. **Bronsted acid:** A bronsted acid is a substance that can donate a proton. A bronsted acid is proton-donor.

Bronsted base: A bronsted base is a substance that can accept a proton from an acid. A bronsted base is proton-acceptor.

When a base gains a proton, the residual part of it has a tendency to accept the proton. Therefore, it behaves as conjugate acid.

When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a conjugate base.

Conjugate base $\rightleftharpoons$ Conjugate acid – H^+

Conjugate base $\rightleftharpoons$ Conjugate acid + H^+

Species	Conjugate acid (gain of proton)	Conjugate base (lose of proton)
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

40. (a) OH^- is a Lewis base since it can donate its lone pair of electrons.

(b) F^- is a Lewis base since it can donate a pair of electrons.

(c) H^+ is a Lewis acid since it can accept a pair of electrons.

(d) BCl_3 is a Lewis acid since it can accept a pair of electrons.

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

41. Given:

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

To calculate of pH, we apply the formula

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

or $pH = \log\frac{1}{[H^+]}$

where pH is defined as the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contain or pH of the solution is the logarithm of the reciprocal of H^+ ion concentration.

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

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

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

$\Rightarrow$ $pH = -\log 3.8 - (-3 \log 10)$

$\Rightarrow$ $pH = -0.58 + 3$

$\Rightarrow$ $pH = 2.42$

Thus, pH value of soft drink is 2.42.

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

42. Given, pH
= 3.76
It is know 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 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.

43. Given:
The ionization constant of HF = 6.8×10^{-4}
The ionization constant of HCOOH = 1.8×10^{-4}
The ionization constant of HCN = 4.8×10^{-9}
$\Rightarrow$ Conjugate base of HF = F^-
$\Rightarrow$ Conjugate base of HCOOH = $HCOO^-$
$\Rightarrow$ Conjugate base of HCN = CN^-
To find out the ionization constants of the corresponding conjugate base, we apply the formula:
$K_w = K_a \times K_b$
Where K_w is the ionic product of water.
K_a is the ionization constant of acid.
K_b is the ionization constant of base.
To calculate the ionization constant of conjugate base of HF, i.e., F^-,
Using the formula, we write

$$K_b = \left(\frac{K_w}{K_a}\right)$$

As K_a of HF = 6.8×10^{-4} (given)
$K_w = 10^{-14}$ (same value for every acid or base)

$$\Rightarrow K_b = \left(\frac{10^{-14}}{6.8 \times 10^{-4}}\right)$$

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

To calculate the ionization constant of conjugate base of HCOOH, i.e., $HCOO^-$,
Using the formula, we write

$$K_b = \left(\frac{K_w}{K_a}\right)$$

As K_a of HCOOH = 1.8×10^{-4} (given)
$K_w = 10^{-14}$

$$\Rightarrow K_b = \frac{10^{-14}}{(1.8 \times 10^{-4})}$$

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

To calculate the ionization constant of conjugate base of HCN, i.e., CN^-,
Using the formula, we write

$$K_b = \left(\frac{K_w}{K_a}\right)$$

As K_a of HCN = 4.8×10^{-9} (given)
$K_w = 10^{-14}$

$$\Rightarrow K_b = \frac{10^{-14}}{(4.8\times10^{-9})}$$

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

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?

44. 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

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

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

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

$$\therefore x = \sqrt{1\times10^{-10}\times0.05}$$

$$= \sqrt{5\times10^{-12}}$$

$= 22 \times 10^{-6}$ M = $[H_3O^+]$

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

$[C_6H_5O^-] = 2.2 \times 10^{-6}$ 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. $0.05 - 0.05\alpha$ $\quad 0.05\alpha \quad 0.05\alpha$

$[C_6H_5OH] = 0.05 - 0.05\alpha$; 0.05 M

$[C_6H_5O^-] = 0.01 + 0.05\alpha$; 0.01 M

$[H_3O^+] = 0.05\alpha$

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

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

$$1.0\times10^{-10} = .01\alpha$$

$$\alpha = 1\times10^{-8}$$

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

45. **Given:**

First ionization constant of $H_2S = 9.1 \times 10^{-8}$
Second dissociation constant of $H_2S = 1.2 \times 10^{-13}$

$[H_2S] = 0.1M$

$[HCl] = 0.1M$

To calculate the $[HS^-]$

In the absence of 0.1M HCl

Let the concentration of HS^- ion be xM

	H_2S	$\leftrightarrow$	H^+ +	HS^-
Initial conc.	0.1 M (given)		0	0
After dissociation	0.1 – x		x	x

Then, Using the formula:

$$K_a = \left(\frac{\text{concentration of products}}{\text{concentration of reactants}}\right)$$

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

As $K_{a1} = 9.1 \times 10^{-8}$ (given)

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

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

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

Taking $0.1 - x \approx 0.1$

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

$$\Rightarrow x = \sqrt{9.1} \times 10^{-8}$$

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

Thus, in the absence of HCl, the concentration of HS^- ion is 9.54×10^{-5} M.
In the presence of 0.1 M HCl, let the concentration of HS^- ion be yM.
Then at equilibrium

	H_2S	$\leftrightarrow$	H^+ +	HS^-
Initial conc.	0.1 M (given)		0	0
After dissociation	0.1 – y		y	y

Then, using the formula:

$$K_{a1} = \left(\frac{\text{the concentration of products}}{\text{the concentration of reactants}}\right)$$

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

As $K_{a1} = 9.1 \times 10^{-8}$

$$\therefore 9.1 \times 10^{-8} = \frac{(y)(0.1 + y)}{0.1 - y}$$

$$\Rightarrow (9.1 \times 10^{-8})(0.1 - y) = (y)(0.1 + y)$$

Taking $0.1 - y \approx 0.1$

$0.1 + y \approx 0.1$

∴ $(9.1 \times 10^{-8})(0.1) = y(0.1)$
⇒ $y = 9.1 \times 10^{-8}$ M
Thus, in the presence of 0.1M HCl, the concentration of HS^- ion is 9.1×10^{-8} M.
To calculate $[S^{2-}]$
In the absence of HCl
Let the concentration of S^{2-} ion be x M

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

$[HS^-] = 9.54 \times 10^{-5}$M (from first ionization)
$[H^+] = 9.54 \times 10^{-5}$M (from first ionization)
$[S^{2-}]$ = xM
By applying the formula:

$$K_a = \left(\frac{\text{concentration of products}}{\text{concentration of reactants}}\right)$$

$$K_{a1} = \frac{\left[H^+\right]\left[S^2\right]}{\left[HS^-\right]}$$

As $K_{a2} = 1.2 \times 10^{-13}$ (given)

$$\therefore 1.2\times10^{-13} = \frac{\left(9.54\times10^{-5}\,M\right)\left(xM\right)}{9.54\times10^{-5}\,M}$$

$$\Rightarrow x = 1.2\times10^{-13}\,M$$

Thus, in the absence of HCl, the concentration of S^{2-} ion is 1.2×10^{-13} M.
Case 2: In the presence of 0.1 M HCl.
Let the concentration of S^{2-} ion be x M

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

$[HS^-] = 9.1 \times 10^{-8}$ (from first ionization, Case 2)
$[H^+] = 0.1$ M (from HCl, Case 2)
$[S^{2-}]$ = yM
By applying the formula:

$$K_a = \left(\frac{\text{concentration of products}}{\text{concentration of reactants}}\right)$$

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

As $K_{a2} = 1.2 \times 10^{-13}$ (given)

$$\therefore 1.2\times10^{-13} = \frac{\left(0.1M\right)\left(yM\right)}{9.1\times10^{-8}\,M}$$

⇒ $10.92 \times 10^{-21} = 0.1$ y
⇒ $y = 1.092 \times 10^{-19}$ M
Thus, in the presence of 0.1 M HCl, the concentration of S^{2-} ion is 1.092×10^{-19} M.

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.

46. Given:
Ionization constant of acetic acid = 1.74×10^{-5}
0.05 M solution
Ionization of CH_3COOH
$CH_3COOH \Rightarrow CH_3COO^- + H^+$
By applying the formula,

$$K_a = \left(\frac{\text{concentration of products}}{\text{concentration of reactants}}\right)$$

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

At equilibrium $[CH_3COO^-] = [H^+]$

Hence,

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

As $K_a = 1.74 \times 10^{-5}$ (given)

$[CH_3COOH] = 0.05$ M

$$\therefore 1.74 \times 10^{-5} = \frac{[H^+][H^+]}{5 \times 10^{-2} M}$$

$\Rightarrow [H^+]^2 = 1.74 \times 10^{-5} \times 5 \times 10^{-2}$M

$$\Rightarrow [H^+] = \sqrt{1.74 \times 10^{-5} \times 5 \times 10^{-2} M}$$

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

As, $[CH_3COO^-] = [H^+]$

Thus, the concentration of acetate ion is 9.33×10^{-4} M.

To calculate pH, we apply the formula,

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

$\Rightarrow$ pH = $-\log(9.33 \times 10^{-4})$

$\Rightarrow$ pH = $-\log 9.33 - \log 10^{-4}$

$\Rightarrow$ pH = $-\log 9.33 - (-4) \log 10$

$\Rightarrow$ pH = $4 - \log 9.33$

$\Rightarrow$ pH = $4 - 0.9699$

$\Rightarrow$ pH = 3.03

Thus, 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 pK_a.

47. Given:

pH of = 4.15

Concentration of HA = 0.01M

To calculate the concentration of the anion, we apply the formula:

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

To calculate the ionization constant of the acid, we apply the formula:

$$K_a = \left(\frac{\text{concentration of products}}{\text{concentration of reactants}}\right)$$

To calculate the pK_a of an organic acid, we apply the formula:

$pK_a = -\log k_a$

where K_a is the ionization constant of the acid

Let the HA be the acid

The ionization of organic acid HA is $HA \rightleftharpoons H^+ + A^-$

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

We can also write,

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

As pH = 4.15 (given)

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

By taking antilog of both the sides, we get

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

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

Thus, the concentration of anion is 7.08×10^{-5} M.

$$K_a = \left(\frac{\text{concentration of products}}{\text{concentration of reactants}}\right)$$

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

As $[A^-] = [H^+] = 7.08 \times 10^{-5}$ (calculated above)

$[HA] = 10^{-2}$ (given)

$$\therefore K_a = \frac{[7.08\times10^{-5}\,M][7.08\times10^{-5}\,M]}{10^{-2}\,M}$$

$\Rightarrow K_a = 5.0 \times 10^{-7}$

Thus, the ionization constant of the acid is 5.0×10^{-7}.

$pK_a = -\log k_a$

As $K_a = 5.0 \times 10^{-7}$

$\therefore pK_a = -\log(5.0 \times 10^{-7})$

$\Rightarrow pK_a = -\log 5 - (-7) \log 10$

$\Rightarrow pK_a = 7 - \log 5$

$\Rightarrow pK_a = 7 - 0.699$

$\Rightarrow pK_a = 6.301$

Thus pk_a is 6.301.

Note: pK_a is a measure of acid strength. It depends on the identity and chemical properties of the acid. pH is a measure of $[H^+]$ in a solution. For acids, the smaller the pK_a, the more acidic the substance is (the more easily a proton is lost, thus the lower the pH).

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

(i) 0.003 M HCl (ii) 0.005 M NaOH

(iii) 0.002 M HBr (iv) 0.002 M KOH

48. (i) 0.003MHCl:

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

Since HCl is completely ionized,
$[H_3O^+] = [HCl]$
$\Rightarrow [H_3O^+] = 0.003$
Now,
$pH = -\log [H_3O^+] = -\log (.003)$
$= 2.52$
Hence, the pH of the solution is 2.52.
(ii) 0.005MNaOH:
$$NaOH_{(aq)} \leftrightarrow Na^+_{(aq)} + HO^-_{(aq)}$$
$[HO^-] = [NaOH]$
$\Rightarrow [HO^-] = .005$
$pOH = -\log [HO^-] = -\log (.005)$
$pOH = 2.30$
$\therefore pH = 14 - 2.30$
$= 11.70$
Hence, the pH of the solution is 11.70.
(iii) 0.002 HBr:
$$HBr + H_2O \leftrightarrow H_3O^+ + Br^-$$
$[H_3O^+] = [HBr]$
$\Rightarrow [H_3O^+] = .002$
$\therefore pH = -\log [H_3O^+]$
$= -\log (0.002)$
$= 2.69$
Hence, the pH of the solution is 2.69.
(iv) 0.002 M KOH:
$$KOH_{(aq)} \leftrightarrow K^+_{(aq)} + OH^-_{(aq)}$$
$[OH^-] = [KOH]$
$\Rightarrow [OH^-] = .002$
Now, $pOH = -\log [OH^-]$
$= 2.69$
$\therefore pH = 14 - 2.69$
$= 11.31$
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.

49. To find out the concentration, we apply the formula:
$$\text{Concentration} = \frac{n}{V}$$
Where n = No. of moles, V= Volume
As we know that $n = \left(\frac{\text{Mass}(m)}{\text{Molar mass}(M)}\right)$

$\therefore$ Concentration $= \left(\frac{m}{V \times M}\right)$

To calculate $[H^+]$, we apply the formula:

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

Where K_w is the ionic product of water which is defined as the product of molar concentration of H^+ and OH^- ions.

To calculate pH, we apply the formula:

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

(a) For 2g of TiOH dissolved in water to give 2L of solution,

Given:

Mass of TiOH(m) = 2g

Volume(V) = 2l

Molar mass of TiOH(M) = 221 g/mol

To calculate concentration of TiOH, we apply the formula,

$$\text{Concentration} = \left(\frac{m}{V \times M}\right)$$

$$[\text{TiOH}] = \left(\frac{2g}{21 \times 221 g/mol}\right)$$

$\Rightarrow$ [TiOH] $= 4.52 \times 10^{-3}$ M

Now, the ionisation of TiOH

$\Rightarrow TiOH \leftrightarrow Ti^+ + OH^-$

TiOH is completely ionized

$\therefore$ [TiOH] = $[OH^-] = 4.52 \times 10^{-3}$ M

To calculate $[H^+]$, we apply the formula

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

As the value of K_w is taken as 10^{-14}

$$\therefore [H^+] = \left(\frac{10^{-14}}{4.52 \times 10^{-3} M}\right)$$

$$\Rightarrow [H^+] = 2.21 \times 10^{-12} M$$

To calculate pH, we apply the formula:

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

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

$\Rightarrow pH = -\log 2.21 - (-12)\log 10$

$\Rightarrow pH = 12 - \log 2.21$

$\Rightarrow pH = 12 - 0.3424$

$\Rightarrow pH = 11.65$

Thus, the pH of the given solution is 11.65.

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

Given:

Mass of $Ca(OH)_2$ (m) = 0.3g

Volume (V) = 500 ml $= \frac{500}{1000} L = 0.5L$

Molar mass of $Ca(OH)_2$ (M) = 40 × 2(16 + 1) = 74 g/mol

To calculate concentration of $Ca(OH)_2$, we apply the formula,

$$\text{Concentration} = \left(\frac{m}{V \times M}\right)$$

$$\Rightarrow [Ca(OH)_2] = \left(\frac{0.3g}{0.51 \times 74\, g/mol}\right)$$

$$\Rightarrow [Ca(OH)_2] = 8.1 \times 10^{-3} M$$

Now, the ionisation of $Ca(OH)_2$
$\Rightarrow Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-$
$Ca(OH)_2$ is completely ionized
$\therefore [Ca(OH)_2] = 2[OH^-]$
$\Rightarrow 2[OH^-] = 2 \times 8.1 \times 10^{-3}$ M
$\Rightarrow 16 \times 10^{-3}$ M
To calculate pOH, we apply the formula:
$pOH = -\log[OH^-]$
$\Rightarrow pOH = -\log(16 \times 10^{-3})$
$\Rightarrow pOH = -\log 16 - (-3)\log 10$
$\Rightarrow pOH = 3 - 1.201$
$\Rightarrow pOH = 1.79$
As we know that pH + pOH = 14
$\therefore pH = 14 - 1.79$
pH = 12.21
Thus, the pH of the given solution is 12.21
(c) for 0.3g of NaOH dissolved in water to give 500 mL of solution,
Given:
Mass of NaOH (m) = 0.3g
$\text{Volume(V)} = 200\text{ ml} = \frac{200}{1000}\text{L} = 0.2\text{L}$
Molar mass of NaOH (M) = 40 g/mol
To calculate concentration of NaOH, we apply the formula,
$$\text{Concentration} = \left(\frac{m}{V \times M}\right)$$
$$\Rightarrow [NaOH] = \left(\frac{0.3g}{0.21 \times 40g/mol}\right)$$
$$\Rightarrow [NaOH] = 3.75 \times 10^{-2} M$$
Now, the ionisation of NaOH
$\Rightarrow NaOH \leftrightarrow Na + OH^-$
NaOH is completely ionized
$\therefore [NaOH] = [OH^-]$
$\Rightarrow [OH^-] = 3.75 \times 10^{-2}$ M
To calculate pOH, we apply the formula:
$pOH = -\log[OH^-]$
$\Rightarrow pOH = -\log(3.75 \times 10^{-2})$ M
$\Rightarrow pOH = -\log 3.75 - (-2)\log 10$
$\Rightarrow pOH = 2 - \log 3.75$
$\Rightarrow pOH = 1.42$
As we know that pH + pOH = 14
$\therefore pH = 14 - 1.42$
$\Rightarrow pH = 12.57$
Thus, the pH of the given solution is 12.57.
(d) For 1mL of 13.6 M HCl diluted with water to give 1 L of solution:
Given:
$M_1 = 13.6$ M
$V_1 = 1$ ml ,
$V_2 = 1L = 1000$ ml
As we know that, $M_1 V_1 = M_2 V_2$
(Before dilution) (After dilution)
$\therefore 13.6 \times 1\text{ mL} = M_2 \times 1000\text{ mL}$
$\Rightarrow M_2 = 1.36 \times 10^{-2}$

Ionization of HCl

$HCl \rightleftharpoons H^+ + Cl^-$

As it is completely ionized

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

$\Rightarrow 1.36 \times 10^{-2}$

To calculate pH, we apply the formula:

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

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

$\Rightarrow pH = -\log 1.36 - (-2) \log 10$

$\Rightarrow pH = 2 - \log 1.36$

$\Rightarrow pH = 2 - 0.1335$

$\Rightarrow pH = 1.8665$

Thus, the pH of the solution is 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.

50. Degree of ionization, $\alpha = 0.132$

Concentration, c = 0.1 M

Thus, the concentration of H_3O^+ = c.a

= 0.1 × 0.132

= 0.0132

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

$= -\log (0.0132)$

= 1.879 : 1.88

Now,

$K_a = C\alpha^2$

$= 0.1 \times (0.132)^2$

$K_a = .0017$

$pK_a = 2.75$

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

51. Given:

pH of Codeine ($C_{18}H_{21}NO_3$) solution = 9.95

[Cod] = 0.005 M

Ionisation of Cod:

$Cod + H_2O \leftrightarrow CodH^+ + OH^{-1}$

As we know that pH + pOH = 14

$\therefore$ 9.95 + pOH =14

$\Rightarrow$ pOH = 14 – 9.95

$\Rightarrow$ pOH = 4.05

As we know that, $pOH = -\log[OH^-]$

$\therefore 4.05 = -\log[OH]$

By taking antilog of both the sides, we get

Antilog $4.05 = -[OH^-]$

$\Rightarrow [OH^-] = 8.913 \times 10^{-5}$

As we know that, K_b (ionization constant)

$$\Rightarrow K_b = \left(\frac{\text{the concentration of products}}{\text{the concentration of reactants}}\right)$$

Hence, for the reaction, Cod + $H_2O \leftrightarrow CodH^+ + OH^{-1}$

$$K_b = \frac{[CodH^+][OH^-]}{[Cod]}$$

As the reaction is completely ionized,

$\therefore [CodH^+] = [OH^-]$

Hence, $K_b = \frac{[OH^-]^2}{[Cod]}$

As $[OH^-] = 8.913 \times 10^{-5}$ (calculated)

[Cod] = 0.005M

$$K_b = \frac{[8.913 \times 10^{-5}]^2}{[5 \times 10^{-3}]}$$

$\Rightarrow K_b = 1.588 \times 10^{-6}$

Thus, the ionization constant of codeine is 1.588×10^{-6}.

To calculate Pk_b we apply the formula:

$Pk_a = -\log K_b$

As $K_b = 1.74 \times 10^{-3}$

$\therefore pk_b = -\log(1.588 \times 10^{-6})$

$\Rightarrow Pk_b = -\log 1.588 - (-6) \log 10$

$\Rightarrow Pk_b = 5.80$

Thus, the Pk_b of codeine is 5.80.

52. What is the pH of 0.001M 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.

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

c = 0.001M pH

= ?

a = ?

$k_b = c\alpha^2$

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

$4.270 \times 10^{-10} = \alpha^2$

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

Then, [anion] $= c\alpha = .001 \times 65.34 \times 10^{-5}$

$= .065 \times 10^{-5}$

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

$= 6.187$

pH = 7.813

Now,

$K_a \times K_b = K_w$

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

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

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

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 pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01M (b) 0.1M in HCl?

53. Given:
Concentration of acetic acid = 0.05M
$pK_a = 4.74$
As we know that, $pk_a = -\log K_a$
We can also write,
$\therefore pK_a = -\log K_a$
$\Rightarrow 4.74 = -\log K_a$
By taking antilog of both the sides, we get
Antilog $-4.74 = K_a$
$K_a = 1.82 \times 10^{-5}$
By applying the formula, $k_a = c\alpha^2$
Where c is the concentration and α is the degree of ionization
We can also write,

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

$K_a = 1.82 \times 10^{-5}$ (given)
C = 0.05M (given)

$$\therefore \alpha = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}}$$

$$\Rightarrow \alpha = 1.908 \times 10^{-2}$$

In the presence of HCl due to the high concentration of H^+, the dissociation equilibrium will shift in the backward direction i.e., dissociation of acetic acid will decrease.

(a) In the presence of HCl, let x be the amount of acetic acid dissociated after the addition of HCl.

Ionization of acetic acid

	CH_3COOH ↔	CH_3COO^- +	H^+
Initial conc.	0.05	0	0
At equilibrium	0.05 – x	x	0.01 + x

We can assume, $0.05 - x \approx 0.05$
$0.01 + x \approx 0.01$
To calculate the degree of ionization, we apply the formula

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

Where $\alpha = \left(\frac{\text{Amount dissociated}}{\text{the amount is taken}}\right)$

K_a is the ionization constant
c is the concentration
$K_a = 1.82 \times 10^{-5}$ (given)
C = 0.01M (given)

$$\therefore \alpha = \sqrt{\left(\frac{1.82 \times 10^{-5}}{0.01M}\right)}$$

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

Thus, the degree of ionization in the presence of 0.01M HCl is 1.82×10^{-3}.

(b) In the presence of 0.1 M HCl, let y be the amount of acetic acid dissociated after the addition of HCl.

Ionization of acetic acid

	$CH_3COOH \leftrightarrow$	CH_3COO^- +	H^+
Initial conc.	0.05	0	0
At equilibrium	0.05 – y	y	0.1 + y

We can assume, $0.05 - x \approx 0.05$

$0.1 + x \approx 0.1$

To calculate the degree of ionization, we apply the formula

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

Where $\alpha = \left(\frac{\text{Amount dissociated}}{\text{the amount is taken}}\right)$

K_a is the ionization constant

c is the concentration

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

C = 0.1M (given)

$$\therefore \alpha = \sqrt{\left(\frac{1.82 \times 10^{+-5}}{0.1}\right)}$$

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

Thus, the degree of ionization in the presence of 0.1M HCl is 1.82×10^{-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?

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

c = 0.02 M

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

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

= 0.1643

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

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

And,

$$(CH_3)_2NH + H_2O \leftrightarrow (CH_3)_2NH_2^+ + \bar{O}H$$
$$(0.02 - x) \qquad\qquad x \qquad\qquad x$$
$$;0.02M \qquad\qquad\qquad ;0.1\,M$$

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

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

$$\Rightarrow K_b = \frac{\left[(CH_3)_2 NH_2^+\right]\left[OH^-\right]}{\left[(CH_3)_2 NH\right]}$$

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

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

55. (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

⇒ pH = log $[H^+]$

⇒ $[H^+]$ = 4.17 × 10^{-8} M

(d)Human saliva, 6.4:

⇒ pH = 6.4

⇒ 6.4 = – log $[H^+]$

⇒ $[H^+]$ = 3.98 × 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.

56. The hydrogen ion concentration in the given substances can be calculated by using the given reaction: pH = –log$[H^+]$

(i) pH of milk = 6.8

Since, pH = –log $[H^+]$

6.8 = – log $[H^+]$ log

$[H^+]$ = –6.8

$[H^+]$ = antilog (–6.8)

= 1.5 × 19^{-7} M

(ii) pH of black coffee = 5.0

Since, pH = –log $[H^+]$

5.0 = –log $[H^+]$ log

$[H^+]$ = –5.0

$[H^+]$ = antilog (–5.0)

= 10^{-5} M

(iii) pH of tomato juice = 4.2
Since, pH = –log $[H^+]$
4.2 = –log $[H^+]$ log
$[H^+]$ = –4.2
$[H^+]$ = antilog (–4.2)
= 6.31×10^{-5} M
(iv) pH of lemon juice = 2.2
Since, pH = –log $[H^+]$
2.2 = –log $[H^+]$ log
$[H^+]$ = –2.2
$[H^+]$ = antilog (–2.2)
= 6.31×10^{-3} M
(v) pH of egg white = 7.8
Since, pH = –log $[H^+]$
7.8 = –log $[H^+]$ log
$[H^+]$ = –7.8
$[H^+]$ = antilog (–7.8)
= 1.58×10^{-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?

57. Given:
Mass of KOH (m) = 0.561g
Volume (V) $= 200\text{ ml} = \frac{200}{1000}\text{L} = 0.2\text{L}$
Molar mass of KOH (M) = 56 g/mol
To calculate concentration of KOH, we apply the formula,

$$\text{Concentration} = \left(\frac{m}{V \times M}\right)$$

$$\Rightarrow [\text{KOH}] = \left(\frac{0.561\text{g}}{0.2\text{L} \times 56\text{ g/mol}}\right)$$

⇒ [KOH] = 0.05 M
Now, the ionisation of KOH
⇒ KOH ↔ K + OH^-
At equilibrium
∴ [K] = $[OH^-]$ = 0.05 M
To calculate $[H^+]$, we apply the formula:
$K_w = [H^+][OH^-]$
Where K_w is the ionic product of water which is defined as the product of molar concentration of H^+ and OH^- ions.
Using the formula, we write

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

As the value of K_w is taken as 10^{-14}
$[OH^-]$ = 0.05 M (calculated)

$$\therefore [H^+] = \frac{10^{-14}}{0.05M}$$

$\Rightarrow [H^+] = 2.0 \times 10^{-13}$

Thus, the concentration of potassium, hydrogen, and hydroxyl ions are 0.05, 0.05 and 2.0×10^{-13} respectively

To calculate pH, we apply the formula:

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

$pH = -\log (2.0 \times 10^{-13})$

$\Rightarrow pH = 13 - \log 2$

$\Rightarrow pH = 12.69$

Thus, the pH is 12.69.

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.

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

Then, concentration of $Sr(OH)_2$

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

= 0.1581 M

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

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

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

Now,

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

$$\frac{10^{-11}}{0.3126} = [H^+]$$

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

$\therefore$ 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 1.32×10^{-5} solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

59. Given:

$K_a = 1.32 \times 10^{-5}$

C = 0.005 M

Assuming α to be very small, applying formula directly, we have

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

$$\Rightarrow \alpha = \sqrt{\frac{1.32 \times 10^{-5}}{0.005 \text{ M}}}$$

$\Rightarrow \alpha = 1.62 \times 10^{-2}$

Thus, the degree of ionization in 0.05M solution is 1.62×10^{-2}.

Let the degree of ionization of propanoic acid be x.

Ionization of propanoic acid

	CH_3CH_2COOH	$\leftrightarrow$	$CH_3CH_2COO^- \;+$	H^+
Initial conc.	C		0	0
At equilibrium	$C - x \approx C$		$0.01M + x \approx 0.01M$	x

By applying the formula

$$K_a = \left(\frac{\text{the concentration of products}}{\text{the concentration of reactants}}\right)$$

$$\Rightarrow K_a = \frac{(x)(0.01)}{C - x}$$

$$\Rightarrow K_a = \left(\frac{0.01x}{C}\right)$$

As $K_a = 1.32 \times 10^{-5}$, C = 0.1 M (given)

Hence,

$x = 1.32 \times 10^{-3}$

Thus, the degree of ionization in 0.01M solution is 1.32×10^{-3}.

60. The pH of a 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.

60. c = 0.01 M

pH = 2.34

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

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

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

Also,

$[H^+] = c\alpha$

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

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

$\alpha = 45 \times 10^{-3} = .045$

Then,

$K_a = c\alpha^2$

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

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

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

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.

61. Given:

K_a of nitrous acid is 4.5×10^{-4}

$[NO_2] = 0.04$ M

To calculate the degree of hydrolysis, we apply the formula:

$K_h = K_w / K_a$

Where K_h is a degree of hydrolysis of a salt which is defined as the fraction of one mole of the salt which is hydrolyzed, when the equilibrium is attained. Hence for a salt (acid and base),

$K_h = K_w / K_a$

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

Using the formula, we write

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

As $K_w = 10^{-14}$ (same value)

$K_a = 4.5 \times 10^{-4}$ (given)

$$\therefore K_h = \left(\frac{10^{-14}}{4.5 \times 10^{-4}}\right)$$

$\Rightarrow K_h = 0.22 \times 10^{-10}$

Thus, the degree of hydrolysis is 0.22×10^{-10}.

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

$[NO_2] = 0.04$ M (given)

Now, if x moles of the salt undergo hydrolysis, then the concentration of the various species will be:

$[NO_2] = 0.04\text{ M} - x \approx 0.04\text{ M}$

$[HNO_2] = x$

$[OH] = x$

Using the formula,

$$K_h = \left(\frac{\text{the concentration of products}}{\text{concentration of reactants}}\right)$$

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

$$\Rightarrow K_h = \frac{[x]^2}{0.04\text{ M}}$$

As $K_h = 0.22 \times 10^{-10}$ (calculated)

$\therefore 0.22 \times 10^{-10}\text{ M} \times 0.04\text{ M} = x^2$

$$\Rightarrow X = \sqrt{0.22 \times 10^{-10} \times 0.04}$$

$$\Rightarrow X = 0.93 \times 10^{-5}$$

As $[OH] = x$

$\Rightarrow [OH^-] = 0.93 \times 10^{-5}$

Now,

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

Using the formula, we write

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

As the value of K_w is taken as 10^{-14}

$\Rightarrow [\,OH^-] = 0.93 \times 10^{-5}$ (calculated)

$$\therefore \left[H^+\right] = \left(\frac{10^{-14}}{0.93 \times 10^{-5}}\right)$$

$\Rightarrow [H^+] = 10.75 \times 10^{-9}$

To calculate pH of the solution, we apply the formula,

$pH = -\log (H^+)$

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

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

➡ $pH = 7.96$

Thus, the pH of the solution is 7.96.

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

62. pH = 3.44

We know that,

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

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

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

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

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

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

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

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

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

63. (i) NaCl is neutral as it is salt of strong acid (HCl) and strong base (NaOH).

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

(ii)KBr is neutral as it is salt of strong acid (HBr) and strong base (KOH).

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

(iii) NaCN is basic as it is a salt of strong base (NaOH) and weak acid (HCN).

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

(iv) NH_4NO_3 is acidic as it a salt of strong acid (HNO_3) and weak base (NH_4OH).

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

(v) $NaNO_2$ is basic as it a salt of strong base (NaOH) and weak acid (HNO_2).

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

(vi) KF is basic as it is salt of strong base (KOH) and weak acid (HF).

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

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?

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

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

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

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

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

$= 0.116$

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

$= .0116$

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

$ClCH_2COONa$ is the salt of a weak acid i.e., $ClCH_2COOH$ and a strong base i.e., NaOH.

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

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

$$K_b = \frac{K_w}{K_\alpha}$$

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

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

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

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

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

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

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

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

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

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

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

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

$= 7.94$

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

65. Given:

Ionic product of water (K_w) = 2.7×10^{-14}

As we know that $K_w = [H^+] [OH^-]$

For neutral water $[H^+] = [OH^-]$

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

$\Rightarrow [H^+]^2 = 2.7 \times 10^{-14}$

$$\Rightarrow [H^+] = \sqrt{2.7 \times 10^{-14}}$$

$\Rightarrow [H^+] = 1.643 \times 10^{-7}$

Since, pH = –log [H^+]

⇒ pH = –log (1.643×10^{-7})

⇒ pH = –log 1.643 + 7 log 10

⇒ pH = 7 – 0.1256

⇒ pH = 6.78

Thus, the pH of the 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

66. (a) $\text{Molas of } H_2O^+ = \frac{25 \times 0.1}{1000} = .0025 \text{ mol}$

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

Thus, excess of OH^- = .0015 mol

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

pOH = –log [OH]

= 1.36

pH = 14 – 1.36

= 12.63 (not matched)

(b) $\text{Moles of } H_3O^+ = \frac{2 \times 10 \times 0.01}{1000} = .0002 \text{ mol}$

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

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

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

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

Excess of H_3O^+ = .001 mol

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

∴ pH = –log (0.05)

= 1.30

The solution is neutral. Hence, pH = 7.

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. Determine also the molarities of individual ions.

67. To determine the solubility, we apply the formula

$K_{sp} = [A^+] [B^-]$

Where K_{sp} is the solubility product which is equal to the product of ionic concentrations in a saturated solution.

(a) Silver chromate ionization of silver chromate:

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

As we know that,

$K_{sp} = [A^+]\,[B^-]$
Where A and B are the ions dissolved
In the above reaction,
$\Rightarrow [A^+] = [Ag^+]$
$\Rightarrow [B^-] = [CrO_4^{2-}]$
$\therefore K_{sp} = [Ag^+]^2 + [CrO_4^{2-}]$
As K_{sp} of Ag_2CrO_4 $=1.1 \times 10^{-12}$ (given)
Let 's' be the solubility of Ag_2CrO_4
$[Ag^+] = 2s$
$[CrO_4^{2-}] = s$
$\therefore 1.1 \times 10^{-12} = (2s)^2\, s$
$\Rightarrow 1.1 \times 10^{-12} = 4(s)^3$
$\Rightarrow 0.275 \times 10^{-12} = s^3$
$\Rightarrow s = \sqrt[3]{0.275 \times 10^{-12}}$
$\Rightarrow s = 0.65 \times 10^{-4}$
Thus, 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
(b) Barium chromate ionization of barium chromate:
$BaCrO_4 \leftrightarrow Ba^{2+} + CrO_4^{2-}$
As we know that,
$K_{sp} = [A^+]\,[B^-]$
Where A and B are the ions dissolved
In the above reaction,
$\Rightarrow [A^+] = [Ba^{2+}]$
$[B^-] = [CrO_4^{2-}]$
$\therefore K_{sp} = [Ba^{2+}] + [CrO_4^{2-}]$
As K_{sp} of $BaCrO_4 = 1.2 \times 10^{-10}$ (given)
Let 's' be the solubility of $BaCrO_4$
$[Ba^{2+}] = s$
$[CrO_4^{2-}] = s$
$\therefore 1.2 \times 10^{-10} = (s \times s)$
$\Rightarrow 1.2 \times 10^{-10} = (s)^2$
$\Rightarrow s = \sqrt[2]{1.2 \times 10^{-10}}$
$\Rightarrow s = 1.09 \times 10^{-5}$
Thus, Molarity of Ba^{2+} and $CrO_4^{2-} = s = 1.09 \times 10^{-5}$ M
(c) Ferric hydroxide ionization of ferric hydroxide
$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$
As we know that,
$K_{sp} = [A^+]\,[B^-]$
Where A and B are the ions dissolved
In the above reaction,
$\Rightarrow [A^+] = [Fe^{3+}]$
$\Rightarrow [B^-] = [OH^-]$
$\therefore K_{sp} = [Fe^{3+}] + [OH^-]$
As K_{sp} of $Fe(OH)_3 = 1.0 \times 10^{-38}$ (given)
Let 's' be the solubility of $Fe(OH)_3$

$[Fe^{3+}] = s$

$[3OH^-] = 3s$

$\therefore 1.0\times 10^{-38} = (s)\,(3s)^3$

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

$\Rightarrow 0.37 \times 10^{-38} = s^3$

$\Rightarrow s = \sqrt[4]{0.37\times10^{-38}}$

$\Rightarrow s = 1.39 \times 10^{-10}$

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

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

(d) Lead chloride ionization of lead chloride:

$PbCl_2 \leftrightarrow Pb^{2+} + 2Cl^-$

As we know that,

$Ks_p = [A^+]\,[B^-]$

Where A and B are the ions dissolved

In the above reaction,

$\Rightarrow [A^+] = [Pb^{2+}]$

$\Rightarrow [B^-] = [Cl^-]$

$\therefore K_{sp} = [Pb^{2+}] + [Cl^-]^2$

As K_{sp} of $PbCl_2 = 1.6 \times 10^{-5}$ (given)

Let 's' be the solubility of $PbCl_2$

$[Pb^{2+}] = s$

$[Cl^-] = 2s$

$\therefore 1.6 \times 10^{-5} = (s)\,(2s)^2$

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

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

$\Rightarrow s = \sqrt[3]{0.4\times10^{-5}}$

$\Rightarrow s = 1.58 \times 10^{-2}$

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

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

(e) Mercurous Iodide ionization of mercurous iodide:

$Hg_2I_2 \leftrightarrow Hg_2^{2+} + 2I^-$

As we know that,

$Ks_p = [A^+]\,[B^-]$

Where A and B are the ions dissolved

In the above reaction,

$\Rightarrow [A^+] = [Hg_2^{2+}]$

$\Rightarrow [B^-] = [I^-]^2$

$\therefore K_{sp} = [Hg_2^{2+}] + [I^-]^2$

As K_{sp} of $Hg_2I_2 = 4.5 \times 10^{-29}$

Let 's' be the solubility of Hg_2I_2

$[Hg_2^{2+}] = s$

$[I^-]$ 2s

$\therefore 4.5 \times 10^{-29} = (s)(2s)^2$

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

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

$\Rightarrow s = \sqrt[3]{4.5\times10^{-29}}$

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

Thus, Molarity of $Hg_2^{2+} = s = 2.24 \times 10^{-10}$ M

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

Note: K_{sp} increases with increase in temperature.

$\Rightarrow$ In a saturated solution, $K_{sp} = [A^+]\,[B^-]$.

$\Rightarrow$ In an unsaturated solution of AB, $K_{sp} > [A^+]\,[B^-]$ means more solute can be dissolved.

$\Rightarrow$ ln a super saturated solution of AB, $K_{sp} < [A^+][B^-]$ means precipitation will start to occur.

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.

68. Let s be the solubility of Ag_2CrO_4.

Then, $Ag_2CrO_4 \leftrightarrow Ag^{2+} + 2CrO_4^-$

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

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

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

Let s' be the solubility of AgBr.

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

$K_{sp} = s'^2 = 5.0 \times 10^{-13}$

$\therefore s' = 7.07 \times 10^{-7}$ 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 $Ks_p = 7.4 \times 10^{-8}$).

69. Given:

Ks_p of cupric iodate $= 7.4 \times 10^{-8}$

Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together.

Ionization of sodium iodate:

$$2NaIO_3 + CuCrO_4 \leftrightarrow Na_2CrO_4 + Cu(IO_3)_2$$

After mixing, $[NaIO_3] = [IO_3^-] = \frac{0.002\ M}{2} = 10^{-3}M$

$$[CuCrO_4] = [Cu^{2+}] = \frac{0.002\ M}{2} = 10^{-3}M$$

For cupric iodate, the ionization is:

$Cu\,(IO_3)_2 \leftrightarrow [Cu^{2+}]\,[IO_3^-]$

As we know that,

$Ks_p = [A^+]\,[B^-]$

Where A and B are the ions dissolved

In the above reaction,

$\Rightarrow [A^+] = [Cu^{2+}]$

$\Rightarrow [B^-] = [IO_3^-]$

$\therefore K_{sp} = [Cu^{2+}]\,[IO_3^-]$

$\Rightarrow K_{sp} = (10^{-3})(10^{-3})$

➡ $K_{sp} = 10^{-9}$

As we know that precipitation only occur when $Ks_p < [A^+]\,[B^-]$.

70. The ionization constant of benzoic acid is 6.46×10^{-5} and Ks_p for silver benzoate are 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?

70. Since pH = 3.19,

$[H_3O^+] = 6.45 \times 10^{-4}$ M

$$C_6H_5COOH + H_2O \leftrightarrow C_6H_5COO^- + H_3O$$

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

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

Let the solubility of C_6H_5COOAg be x mol/L.

Then,

$[Ag^+] = x$

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

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

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

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

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

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

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

Now, let the solubility of C_6H_5COOAg be x' mol/L.

Then, $[Ag^+] = x'$ M and $[CH_3COO^-] = x'$ M.

$K_{sp} = [Ag^+]\ [CH_3COO^-]$

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

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

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

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

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

71. Given:

K_{sp} of FeS = 6.3×10^{-18}

Let the concentration of solution of $FeSO_4$ and Na_2S is x mol/L.

On mixing the equimolar (equal moles) solutions, the volume of the concentration become half

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

$$\therefore [Fe^{2+}] = [S^{2-}] = \frac{x}{2} \text{M}$$

Ionization of ferrous sulphide:
$FeS \leftrightarrow Fe^{2+} + S^{2-}$
As we know that,
$Ks_p = [A^+] [B^-]$
Where A and B are the ions
In the above reaction,
$\Rightarrow [A^+] = Fe^{2+}$
$\Rightarrow [B^-] = S^{2-}$
$\therefore K_{sp} = [Fe^{2+}][S^{2-}]$
As $K_{sp} = 6.3 \times 10^{-18}$ (given)

$$\Rightarrow 6.3\times10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right)$$

$$\Rightarrow \left(\frac{x^2}{4}\right) = 6.3\times10^{-18}$$

Thus, $x = 5.02 \times 10^{-9}$
As we know that precipitation only occur when $Ks_p < [A^+] [B^-]$.
Thus, if the concentration of ferrous sulphate and sodium sulhide are equal to or less than that of 5.02×10^{-9}, then there no precipitation of ferrous sulphide takes place.

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}).

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

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

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?

73. Given:
Concentration of sulphide ion $[S^{2-}] = 1.0 \times 10^{-19}$ M
Volume of solution containing S^{2-} ion = 10 ml
Volume of metals salt solution added = 5ml
As 10 ml of solution containing S^{2-} ion is mixed with 5ml of metals salt solution. Hence, after mixing volume will be 10 ml + 5 ml = 15 ml
Now the concentration of sulphide ion is:

$$\left[S^{2-}\right] = 1\times10^{-19}\,M\times\left(\frac{10}{15}\right)ml$$

$\Rightarrow 6.67 \times 10^{-20}$

The concentration of metals solution $[M^{2+}]$ is

$$\Rightarrow\left[Fe^{2+}\right]=\left[Mn^{2+}\right]=\left[Zn^{2+}\right]=\left[Cd^{2+}\right]=\frac{5}{15}\times0.04=1.33\times10^{-2}$$

As we know that precipitation will take place in the solution for which ionic product is greater than solubility product. $K_{sp} < [A^+] [B^-]$

Ionic product for each of these will be $[M^{2+}] [S^{2-}]$

$\Rightarrow 6.67 \times 10^{-20} \times 1.33 \times 10^{-2}$

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

As this is greater than solubility product of ZnS and CdS, therefore $ZnCl_2$ and $CdCl_2$ solutions will be precipitated.