

CHAPTER 6

EQUILIBRIUM

VEDA
ACADEMY

CLASS 11TH

NCERT EXERCISE AND SOLUTIONS - CHEMISTRY



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

- What is the initial effect of the change on vapour pressure?
- How do rates of evaporation and condensation change initially?
- What happens when equilibrium is restored finally and what will be the final vapour pressure?

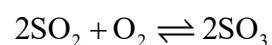
ANSWER:-

- 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.
- 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.
- 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.

Q. 2. What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[\text{SO}_2] = 0.60\text{M}$, $[\text{O}_2] = 0.82\text{M}$ and $[\text{SO}_3] = 1.90\text{M}$?



ANSWER:-



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(1.90)^2}{(0.60)^2 (0.82)} = 12.23$$



Q. 3. At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms $I_2(g) \rightarrow 2I(g)$ Calculate K_p for the equilibrium.

ANSWER:-

Partial pressure of I atoms,

$$P_I = \frac{40}{100} * P_{\text{total}} = \frac{40}{100} * 10^5$$

Partial pressure of I_2 molecules,

$$P_{I_2} = \frac{60}{100} * P_{\text{total}} \\ = \frac{60}{100} * 10^5$$

$$K_p = \frac{(P_I)^2}{P_{I_2}} \\ = \frac{(4 \times 10^4)^2 \text{ Pa}^2}{(6 \times 10^4) \text{ Pa}} \\ = 2.67 \times 10^4 \text{ pa}$$

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

- (i) $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$
- (ii) $2\text{Cu}(\text{NO}_3)_2(s) \rightleftharpoons 2\text{CuO}(s) + 4\text{NO}_2(g) + \text{O}_2(g)$
- (iii) $\text{CH}_3\text{COOC}_2\text{H}_5(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{C}_2\text{H}_5\text{OH}(aq)$
- (iv) $\text{Fe}^{3+}(aq) + 3\text{OH}^-(aq) \rightleftharpoons \text{Fe}(\text{OH})_3(s)$
- (v) $\text{I}_2(s) + 5\text{F}_2 \rightleftharpoons 2\text{IF}_5$

ANSWER:-

(a) The expression for the equilibrium constant is $K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$

(b) The expression for the equilibrium constant is $K_c = [\text{NO}_2]^4 [\text{O}_2]$.

(c) The expression for the equilibrium constant is

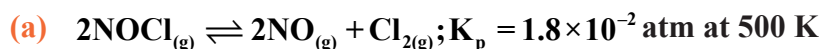
$$K_c = \frac{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5]}$$

(d) The expression for the equilibrium constant is $K_c = \frac{1}{[\text{Fe}^{3+}][\text{OH}^-]^3}$.

(e) The expression for the equilibrium constant is $K_c = \frac{[\text{IF}_5]^2}{[\text{F}_2]^5}$



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



ANSWER:-

(a) The relation between K_p and K_c is given as:

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

Here,

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

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

$$T = 500 \text{ K}$$

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

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

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

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

$$= 4.33 \times 10^{-4}$$

(b) $\Delta n = 2 - 1 = 1$

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

$$T = 1073 \text{ K}$$

$$K_p = 167$$

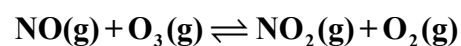
$$K_p = K_c (RT)^{\Delta n}$$

$$167 = K_c (0.0831 * 1073)^1$$

$$K_c = 167 / 0.0831 * 1073$$

$$K_c = 1.87$$

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



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

ANSWER:-

It is given that K_c for the forward reaction is 6.3×10^{14} Then, for the reverse reaction will be,

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



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

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

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

ANSWER:-

For pure substance (both solids & liquids),

$$[\text{Pure substance}] = \frac{\text{Number of moles}}{\text{Volume}}$$

$$= \frac{\text{Mass/molecular mass}}{\text{Volume}}$$

$$= \frac{\text{Mass}}{\text{Volume} \times \text{Molecular mass}}$$

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

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

Q. 8. A reaction between N_2 and O_2 takes place as follows:



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.

ANSWER:-

Given, given:

Initial moles of $\text{N}_2 = 0.482$ moles

Initial moles of $\text{O}_2 = 0.933$ moles

Volume of the reaction vessel = 10 L

Let x moles of $\text{N}_2(\text{g})$ take part in the reaction. According to the equation, $x/2$ moles of $\text{O}_2(\text{g})$ will react to form x moles of $\text{N}_2\text{O}(\text{g})$. The molar concentration per litre of different species before the reaction and at the equilibrium point is:

	$2\text{N}_{2(\text{g})}$	+	$\text{O}_{2(\text{g})}$	\leftrightarrow	$2\text{N}_2\text{O}(\text{g})$
Initial mole/litre:	$\frac{0.482}{10}$		$\frac{0.933}{10}$		Zero



Mole/litre at equation point:	$\frac{0.482 - x}{10}$	$\frac{0.933 - \frac{x}{2}}{10}$	$\frac{x}{10}$		
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The value of equilibrium constant (2.0×10^{-37}) is extremely small. This means that only small amounts of reactants have reacted.

“Applying Law of chemical Equilibrium” $K_c = \frac{[\text{N}_2\text{O}(\text{g})]^2}{[\text{N}_2(\text{g})]^2 [\text{O}_2(\text{g})]}$

$$2.0 \times 10^{-37} = \frac{\left(\frac{x}{10}\right)^2}{\left(\frac{0.482}{10}\right)^2 \times \left(\frac{0.933}{10}\right)}$$

$$= \frac{0.01x^2}{2.1676 \times 10^{-4}}$$

$$x^2 = 43.352 \times 10^{-40} \text{ or } x = 6.6 \times 10^{-20}$$

As x is extremely small it can be neglected

Thus in the equilibrium mixture

Molar conc. of $\text{N}_2 = 0.0482 \text{ mol L}^{-1}$

Molar conc. of $\text{O}_2 = 0.0933 \text{ mol L}^{-1}$

Molar conc. of $\text{N}_2\text{O} = 0.1 \times x$

$= 0.1 \times 6.6 \times 10^{-20} \text{ mol L}^{-1}$

$= 6.6 \times 10^{-21} \text{ mol L}^{-1}$

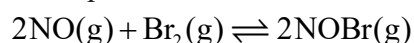
Q. 9. Nitric oxide reacts with and gives nitrosyl bromide as per reaction given below:



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

ANSWER:-

The equilibrium reaction is as shown below.



	NO	Br_2	NOBr
Initial	0.087	0.043	0
Change	-2x	-x	2x
Equilibrium	0.087-2x	0.043-x	2x

The number of moles of NOBr at equilibrium are 0.0518 .



Thus $2x = 0.0518$ mol or $x = 0.0259$ mol.

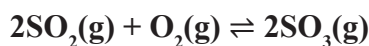
The number of moles of NO = $(0.087 - 0.0518)$ mol = 0.0352 mol.

The number of moles of Br₂ = $(0.043 - 0.0259)$ mol = 0.0178 mol.

Therefore, Equilibrium amount of NO = 0.0352 mol

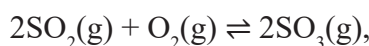
Equilibrium amount of Br₂ = 0.0178 mol

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



What is K_c , at this temperature?

ANSWER:-



For the given reaction,

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

$$T = 450\text{K}$$

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

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

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

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

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

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

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

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

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

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



ANSWER:-

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:

$$K_p = \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2}$$

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

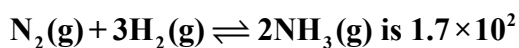


$$= \frac{0.0064}{0.0016}$$

$$= 4.0$$

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

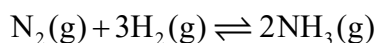
Q. 12. A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 and 8.13 mol of is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction



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

ANSWER:-

The given reaction is:



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

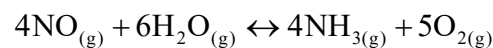
Q. 13. The equilibrium constant expression for a given reaction is

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

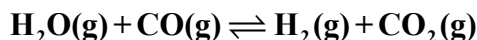
Write the balanced chemical equation corresponding to this expression.

ANSWER:-

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



- Q. 14.** One mole of H_2 and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium, H_2O of water (by mass) reacts with CO according to the equation,



Calculate the equilibrium constant for the reaction.

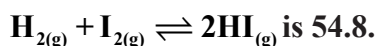
ANSWER:-

The equilibrium reaction is $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$.

	H_2O	CO	H_2	CO_2
Initial moles	1	1	0	0
change	-0.4	-0.4	0.4	0.4
Moles at equilibrium	0.6	0.6	0.4	0.4

The expression for the equilibrium constant is $K_c = \frac{0.4 \times 0.4}{0.6 \times 0.6} = \frac{4}{9} = 0.44$.

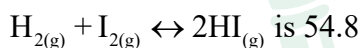
- Q. 15.** At 700 K, the equilibrium constant for the reaction;



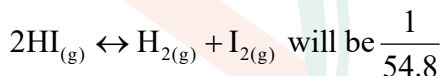
If 0.5 mol litre⁻¹ of $\text{HI}_{(\text{g})}$ is present at equilibrium at 700 K, what are the concentrations of $\text{H}_{2(\text{g})}$ and $\text{I}_{2(\text{g})}$ assuming that we initially started with $\text{HI}_{(\text{g})}$ and allowed it to reach equilibrium at 700 K.

ANSWER:-

It is given that equilibrium constant for the reaction



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



$$[\text{HI}] = 0.5 \text{ mol L}$$

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

$$[\text{H}_2] = [\text{I}_2] = x \text{ mol L}^{-1}$$

$$\text{Therefore, } \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = K'_c$$

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

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

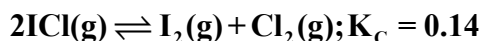
$$\Rightarrow x = 0.06754$$

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

Hence, at equilibrium, $[\text{H}_2] = [\text{I}_2] = 0.068 \text{ mol L}^{-1}$



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



ANSWER:-

The given reaction is:

	2ICl(g)	↔	I ₂ (g)	+Cl ₂ (g)
Initial conc.	0.78 M		0	0
At equilibrium	(0.78 - 2x)M		xM	xM

Now we can write, $\frac{[\text{I}_2][\text{Cl}_2]}{[\text{ICl}]^2} = K_c$

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

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

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

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

$$\Rightarrow x = 0.292 - 0.748x$$

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

Hence the equilibrium concentrations are,

$$[\text{I}_2] = 0.167\text{M}$$

$$[\text{Cl}_2] = 0.167\text{M}$$

$$[\text{ICl}] = 0.78 - 2(0.167) = 0.446\text{M}$$

- Q. 17.** $K_p = 0.04$ atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?



ANSWER:-

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

Now, according to the reaction,



$$\frac{P_{C_2H_4} \times P_{H_2}}{P_{C_2H_6}} = K_p$$

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

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

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

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

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

	$C_2H_{6(g)}$	\leftrightarrow	$C_2H_{4(g)}$	$+H_{2(g)}$
Initial conc.	4.0 atm		0	0
At equilibrium	4.0-p		p	p

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

$$= 0.38$$

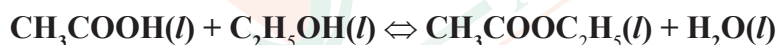
Hence, at equilibrium,

$$[C_2H_6] = 4 - p$$

$$= 4 - 0.38$$

$$= 3.62 \text{ atm}$$

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



- Write the concentration ratio (concentration quotient) Q for this reaction. Note that water is not in excess and is not a solvent in this reaction.
- At 293 K, if one starts with 1.000 mol of acetic acid 0.180 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- Starting with 0.50 mol of ethanol and 1.000 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

ANSWER:-

(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:

	$\text{CH}_3\text{COOH}(1)$	$+\text{C}_2\text{H}_5\text{OH}(1)$	\leftrightarrow	$\text{CH}_3\text{COOC}_2\text{H}_5(1)$	$+\text{H}_2\text{O}_{(1)}$
Initial conc.	$\frac{1}{V}\text{M}$	$\frac{0.18}{V}\text{M}$	0	0	
At equilibrium	$\frac{1-0.171}{V}$	$\frac{0.18-0.171}{V}$		$\frac{0.171}{V}\text{M}$	$\frac{0.171}{V}\text{M}$
	$=\frac{0.829}{V}\text{M}$	$=\frac{0.009}{V}\text{M}$			

Therefore, equilibrium constant for the given reaction is:

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$K_c = 3.92$$

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

	$\text{CH}_3\text{COOH}_{(1)}$	$\text{C}_2\text{H}_5\text{OH}_{(1)}$	\leftrightarrow	$\text{CH}_3\text{COOC}_2\text{H}_5(1)$	+	$\text{H}_2\text{O}_{(1)}$
Initial conc.	$\frac{1.0}{V}\text{M}$	$\frac{0.5}{V}\text{M}$		0		0
After some time	$\frac{1.0-0.214}{V}$	$\frac{0.5-0.214}{V}$		$\frac{0.214}{V}\text{M}$		$\frac{0.214}{V}\text{M}$
	$=\frac{0.786}{V}\text{M}$	$=\frac{0.286}{V}\text{M}$				

Therefore, the reaction quotient is,

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

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

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

$$= 0.2037$$

$$= 0.204$$

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

Q. 19. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, the concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If the value of K_c is 8.3×10^{-3} , what are the concentrations of PCl_3 and Cl_2 at equilibrium?



ANSWER:-

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



	$\text{PCl}_{5(g)}$	\leftrightarrow	$\text{PCl}_{3(g)}$	$\text{Cl}_{2(g)}$
At equilibrium	$0.5 \times 10^{-1} \text{ mol L}^{-1}$		$x \text{ mol L}^{-1}$	$x \text{ mol L}^{-1}$

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:

$$\frac{[\text{PCl}_2][\text{Cl}_2]}{\text{PCl}_5} = K_c$$

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

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

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

$$= 0.0204$$

$$= 0.02$$

Therefore, at equilibrium

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.02$$

<https://t.me/vedalland12>

Q. 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 . $\text{FeO}_{(s)} + \text{CO}_{(g)} \leftrightarrow \text{Fe}(s) + \text{CO}_2(g)$, $K_p = 0.265$ atm at 1050 K What are the equilibrium partial pressure of CO and at 1050 K if the partial pressure are: $p_{\text{CO}} = 1.4$ atm and $P_{(\text{CO}_2)} = 0.80$ atm?

ANSWER:-

For the given reaction,

$\text{FeO}(g)$	+	$\text{CO}(g)$	\leftrightarrow	$\text{Fe}(s)$	+	$\text{CO}_2(g)$
Initially		1.4 atm				0.80 atm

$$Q_p = P_{\text{CO}_2} / P_{\text{CO}}$$

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

$$= 0.571$$

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,

$$Q_p = \frac{P_{(\text{CO}_2)}}{P_{(\text{CO})}}$$

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



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

$$\Rightarrow 1.265p = 0.429$$

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

Therefore, equilibrium partial of CO_2 , $P_{(\text{CO}_2)} = 0.80 - 0.339 = 0.461 \text{ atm}$

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

Q. 21. Equilibrium constant, K_c for the reaction



At a particular time, the analysis shows that composition of the reaction mixture is $3.0 \text{ mol L}^{-1} \text{ N}_2$, $2.0 \text{ mol L}^{-1} \text{ H}_2$ and $0.5 \text{ mol L}^{-1} \text{ NH}_3$. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

ANSWER:-

The given reaction is:

	$\text{N}_2(\text{g})$	$3\text{H}_{2(\text{g})}$	\leftrightarrow	$2\text{NH}_{3(\text{g})}$
At a particular time	3.0 mol L^{-1}	2.0 mol L^{-1}		0.5 mol L^{-1}

Now, we know that,

$$\begin{aligned} Q_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\ &= \frac{(0.5)^2}{(3.0)(2.0)^3} \\ &= 0.0104 \end{aligned}$$

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.

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



for which $K_c = 32$ at 500 K . If initially pure BrCl is present at a concentration of $3.3 \times 10^{-3} \text{ mol L}^{-1}$, what is its molar concentration in the mixture at equilibrium?

ANSWER:-

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

	$2\text{BrCl}_{(\text{g})}$	\leftrightarrow	$\text{Br}_{2(\text{g})} + \text{Cl}_{2(\text{g})}$
Initial conc.	3.3×10^{-3}		0 0
At equilibrium	$3.3 \times 10^{-3} - 2x$		x x



Now, we can write,

$$\frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]_2} = K_c$$

$$\Rightarrow \frac{x \times x}{(0.0033 - 2x)^2} = 32$$

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

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

$$\Rightarrow 12.32 \times 10^{-3}$$

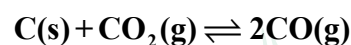
Therefore, at equilibrium,

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

Hence, the equilibrium concentration of BrCl is

$$3.30 \times 10^{-3} - 3.00 \times 10^{-3} = 0.30 \times 10^{-3} = 3.0 \times 10^{-4} \text{ M}$$

Q. 23. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO₂ in equilibrium with solid carbon has 90.55% CO by mass



Calculate K_c for this reaction at the above temperature.

ANSWER:-

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

Mass of CO = 90.55 g

And, mass of CO₂ = (100 - 90.55) = 9.45 g

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

number of moles of CO₂, $n_{\text{CO}_2} = \frac{9.45}{44} = 0.215 \text{ mol}$

Partial pressure of CO,

$$\begin{aligned} P_{\text{CO}} &= \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2}} \times P_{\text{total}} \\ &= \frac{3.234}{3.234 + 0.215} \times 1 \\ &= 0.938 \text{ atm} \end{aligned}$$

Partial pressure of CO₂,

$$\begin{aligned} P_{\text{CO}_2} &= \frac{n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \times P_{\text{total}} \\ &= \frac{0.215}{3.234 + 0.215} \times 1 \\ &= 0.062 \text{ atm} \end{aligned}$$



$$K_p = \frac{[\text{CO}]^2}{[\text{CO}_2]}$$

$$\begin{aligned}\text{Therefore } K_p &= \frac{[\text{CO}]^2}{[\text{CO}_2]} \\ &= \frac{(0.938)^2}{0.062} \\ &= 14.19\end{aligned}$$

For the given reaction,

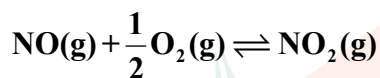
$$\Delta n = 2 - 1 = 1$$

We know that,

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

$$\begin{aligned}\Rightarrow 14.19 &= K_c (0.082 \times 1127)^1 \\ &= 0.154\end{aligned}$$

Q. 24. Calculate a) ΔG° and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K



where $\Delta_f G^\circ \text{NO}_2 = 52.0 \text{ kJ/mol}$

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

$\Delta_f G^\circ (\text{O}_2) = 0 \text{ kJ/mol}$

ANSWER:-

a) For the given reaction, $\Delta G^\circ = \Delta G^\circ (\text{Products}) - \Delta G^\circ (\text{Reactants})$

$$\Delta G^\circ = 52.0 - \{87.0 + 0\} = -35.0 \text{ kJ mol}^{-1}$$

b) We know that, $\Delta G^\circ = RT \log K_c$

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

$$K_c = \frac{-35.5 \times 10^{-3}}{-2.303 \times 8.314 \times 298}$$

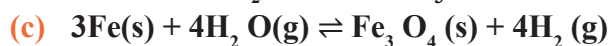
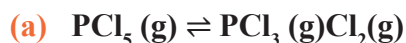
$$= 6.134$$

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

$$= 1.36 \times 10^6$$

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

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



ANSWER:-

- (a) The change in the number of moles of the gaseous species $\Delta n = 1 + 1 - 1 = 1 > 0$. Hence, the number moles of reaction product increase by decrease in pressure due to increase in volume.
- (b) The change in the number of moles of the gaseous species $\Delta n = 0 - 1 = -1 < 1$. Hence, the number moles of reaction product decrease by decrease in pressure due to increase in volume.
- (c) The change in the number of moles of the gaseous species $\Delta n = 4 - 4 = 0$. Hence, the number moles of reaction product remains same due to decrease in pressure due to increase in volume.

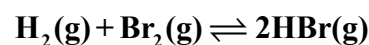
Q. 26. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

- i. $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$
- ii. $\text{CH}_4(\text{g}) + 2\text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g})$
- iii. $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$
- iv. $2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$
- v. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- vi. $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

ANSWER:-

- (i) The change in the number of moles of the gaseous species $\Delta n = 2 - 1 = 1$.
When pressure is increased, the equilibrium reaction is affected. The direction of reaction will shift into backward direction.
- (ii) The change in the number of moles of the gaseous species $\Delta n = 3 - 3 = 0$.
When the pressure is increased, the equilibrium reaction is not affected.
- (iii) The change in the number of moles of the gaseous species $\Delta n = 2 - 1 = 1$.
When pressure is increased, the equilibrium reaction is affected. The direction of reaction will shift into backward direction.
- (iv) The change in the number of moles of the gaseous species $\Delta n = 1 - 3 = -2$.
When pressure is increased, the equilibrium reaction is affected. The direction of reaction will shift into forward direction.
- (v) The change in the number of moles of the gaseous species $\Delta n = 1 - 0 = 1$.
When pressure is increased, the equilibrium reaction is affected. The direction of reaction will shift into backward direction.
- (vi) The change in the number of moles of the gaseous species $\Delta n = 10 - 9 = 1$.
When pressure is increased, the equilibrium reaction is affected. The direction of reaction will shift into backward direction.

Q. 27. The equilibrium constant for the following reaction is 1.6×10^5 at 10^{24} K

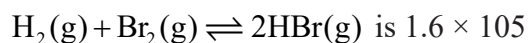


Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 10^{24} K.



ANSWER:-

Given, K_p for the reaction



Therefore, for the reaction $2\text{HBr}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{Br}_2(\text{g})$ the equilibrium constant will be, K_p'

$$\begin{aligned} K_p' &= \frac{1}{K_p} \\ &= \frac{1}{1.6 \times 10^5} \\ &= 6.25 \times 10^{-6} \end{aligned}$$

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,

$$\begin{aligned} \frac{P_{\text{H}_2} \times P_{\text{Br}_2}}{P_{\text{HBr}}^2} &= K_p' \\ \frac{P \times P'}{(10 - 2p)^2} &= 6.25 \times 10^{-6} \\ \frac{P}{10 - 2p} &= 2.5 \times 10^{-3} \end{aligned}$$

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

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

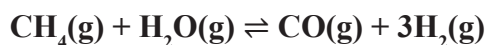
Therefore, at equilibrium,

$$[\text{H}_2] = [\text{Br}_2] = 2.49 \times 10^{-2} \text{ bar}$$

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

$$= 9.95 \text{ bar}$$

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



- Write an expression for K_p for the above reaction.
- How will the values of K_p and composition of equilibrium mixture be affected by
 - increasing the pressure,
 - Increasing the temperature and
 - Using a catalyst?



- (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, K_c would not change.
(iii) In an endothermic reaction, the value of K_c increases with an increase in temperature. Since the given reaction is an endothermic reaction, the value of K_c will increase if the temperature is increased.

Q. 31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of the 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 $O(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$. If a reaction vessel at 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 $400^\circ C$

ANSWER:-

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

	$CO_{(g)}$	$+H_2O_{(g)}$	\leftrightarrow	$CO_{2(g)} +$	$H_{2(g)}$
Initial conc.	4.0 bar	4.0 bar		0	0
At equilibrium	4.0-p	4.0-p		p	p

It is given that $K_p = 10.1$

Now

$$\frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} = 10.1$$

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

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

$$p = 12.712 - 3.178p$$

$$4.178p = 12.712$$

$$p = 3.04$$

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

Q. 32. Predict which of the following reaction will have the 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) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g)$ $K_c = 1.8$



ANSWER:-

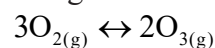
Following conclusions can be drawn from the values of K_c .

- (a) Since the value of K_c is very small, this means that the molar concentration of the products is very small as compared to that of the reactants.
- (b) Since the value of K_c is quite large, this means that the molar concentration of the products is very large as compared to that of the reactants
- (c) Since the value of K_c is 1.8, this means that both the products and reactants have appreciable concentration.

Q. 33. The value of K_c for the reaction $3\text{O}_2(\text{g}) \leftrightarrow 2\text{O}_3(\text{g})$ 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 ?

ANSWER:-

The given reaction is:



$$\text{Then } K_c = \frac{[\text{O}_{3(\text{g})}]^2}{[\text{O}_{2(\text{g})}]^3}$$

It is given that $K_c = 2.0 \times 10^{-50}$ and $[\text{O}_{2(\text{g})}] = 1.6 \times 10^{-2}$

Then, we have,

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

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

$$\Rightarrow [\text{O}_{3(\text{g})}]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow [\text{O}_{3(\text{g})}] = 2.86 \times 10^{-28} \text{ M}$$

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

Q. 34. The reaction, $\text{O}(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ is at equilibrium at 1300 K in a 1 L 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 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

ANSWER:-

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]^3}$$

$$3.90 = \frac{[\text{CH}_4] \times 0.02}{(0.30)(0.10)^3}$$



$$[\text{CH}_4] = \frac{3.90 \times 0.30 \times (0.10)^3}{0.02} = 5.85 \times 10^{-2} \text{ M}$$

Thus, the concentration of methane in the mixture is $5.85 \times 10^{-2} \text{ M}$.

- Q. 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-}

ANSWER:-

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_4^- (base)
F^-	HF (acid)
OH^-	H_2O (acid)/ O^{2-} (base)
CO_3^{2-}	HCO_3^- (acid)
S^{2-}	HS^- (acid)

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

ANSWER:-

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

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

ANSWER:-

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are F^- , HSO_4^- and CO_3^{2-} respectively.

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

ANSWER:-

Brønsted base	Conjugate acid
NH_2^-	NH_3
NH_3	NH_4^+
HCOO^-	HCOOH



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

ANSWER:-

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^-

Q. 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 .

ANSWER:-

- (a) OH^- ion can donate an electron pair. Hence, it acts as Lewis base.
 (b) F^- ion can donate an electron pair. Hence, it acts as Lewis base.
 (c) H^+ ion can accept an electron pair. Hence, it acts as Lewis acid.
 (d) BCl_3 ion can accept an electron pair. Hence, it acts as Lewis acid.

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

ANSWER:-

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

\therefore pH value of soft drink

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

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

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

$$= -\log 3.8 + 3$$

$$= -0.58 + 3$$

$$= 2.42$$



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

ANSWER:-

$$\text{pH} = 3.76$$

it is known that

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

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

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

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

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

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

ANSWER:-

$$k_b = \frac{k_w}{k_a}$$

For F^- and HF:

$$K_b = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

For HCOO^- and HCOOH:

$$K_b = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

For CN^- and HCN:

$$K_b = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

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

ANSWER:-

Ionization of phenol:

	$\text{C}_6\text{H}_5\text{OH}$	+	$+\text{H}_2\text{O}$	\leftrightarrow	$\text{C}_6\text{H}_5\text{O}^- + \text{H}_3\text{O}^+$	+	$+\text{H}_3\text{O}^+$
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, will be very small. Thus we can ignore in the denominator

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

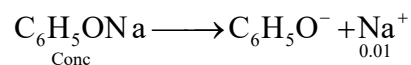
$$= \sqrt{5 \times 10^{-12}}$$

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

$$\text{Since } [H_3O^+] = [C_6H_5O^-]$$

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

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



Also

	C_6H_5ONa	H_2O	\leftrightarrow	$C_6H_5O^-$	H_3O^+
Conc.	$0.05 - 0.05\alpha$			0.05α	0.05α

$$[C_6H_5OH] = 0.05 - 0.05\alpha; 0.05 \text{ M}$$

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

$$[H_3O^+] = 0.05\alpha$$

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

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

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

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

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

ANSWER:-

- (i) To calculate the concentration of HS^- ion
Case I (in the absence of HCl):



	H ₂ S		H ⁺	+	HS ⁻
C _i	0.1		0		0
C _f	0.1-x		x		x

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

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

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

Taking 0.1-xM;0.1M we have $(9.1 \times 10^{-8})(0.1) = x^2$

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

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

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

Case II (in the presence of HCl)

In the presence of 0.1M Of HCl, let [HS⁻] be yM

Then	H ₂ S	↔	H ⁺	+	+HS ⁻
C _i	0.1		0		0
C _f	0.1 - y		y		y

Also HCl↔	H ⁺	Cl ⁻
	0.1	0.1

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

$$K_{a_1} = \frac{[y](0.1+y)}{0.1-y}$$

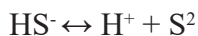
$$9.1 \times 10^{-8} = \frac{y \times 0.1}{0.1} (\because 0.1-y; 0.1M) \text{ (and } 0.1+y; 0.1M)$$

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

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

(ii) To calculate the concentration of [S²⁻]

Case I (in the absence of 0.1 MHCl):



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

Let [S²⁻] be X



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

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

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

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

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

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

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

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

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

ANSWER:-

The dissociation equilibrium is $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$.

The equilibrium concentrations of CH_3COOH , CH_3COO^- and H^+ are $c(1-\alpha)$, $c\alpha$ and $c\alpha$ respectively.

The equilibrium constant expression is $K_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$.

$$K_c = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.74 \times 10^{-5}}{0.05}} = 1.865 \times 10^{-2}$$

$$[\text{CH}_3\text{CO}^-] = [\text{H}^+] = c\alpha = 0.05 \times 1.865 \times 10^{-2} = 9.33 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(9.33 \times 10^{-4}) = 3.03$$

The concentration of acetate ion and its pH are 9.33×10^{-4} and 3.03 respectively.

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

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

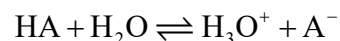
$$[\text{H}^+] = \text{antilog}(-4.15) = 7.08 \times 10^{-5}$$

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



ANSWER:-

The concentration of undissociated acid is $0.01 - 0.000071 = 0.009929\text{M}$.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{0.009929} = 5.05 \times 10^{-7}$$

$$\text{p}K_a = -\log K_a = -\log 5.05 \times 10^{-7} \approx 6.3$$

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

- (a) 0.003 M HCl (b) 0.005 M NaOH
(c) 0.002 M HBr (d) 0.002 M KOH

ANSWER:-

(a) 0.003 M HCl

$$[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.003\text{M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(3.0 \times 10^{-3}) = 2.523$$

(b) 0.005 M NaOH

$$[\text{OH}^-] = [\text{NaOH}] = 0.005\text{M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.005} = 2 \times 10^{-12}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2 \times 10^{-12}) = 11.699$$

(c) 0.002 M HBr

$$[\text{H}^+] = [\text{HBr}] = 0.002$$

$$\text{pH} = -\log[\text{H}^+] = -\log 0.002 = 2.699$$

(d) 0.002 M KOH

$$[\text{OH}^-] = [\text{KOH}] = 0.002\text{M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.002} = 5 \times 10^{-12}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(5 \times 10^{-12}) = 11.301$$

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

- (a) 2 g of TIOH dissolved in water to give 2 litre of solution.
(b) 0.3 g of $\text{Ca}(\text{OH})_2$ 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) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.



ANSWER:-

- (a) For 2 g of TIOH dissolved in water to give 221 mL of solution:

$$[\text{TIOH}] = [\text{OH}^-] = \frac{2 \times 1}{2 \times 221} = \frac{1}{221} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log \frac{1}{221} = 2.35$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.35 = 11.65$$

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

$$[\text{OH}^-] = 2[\text{Ca}(\text{OH})_2] \left[0.3 \times \frac{1000}{500} = 1.2 \text{ M} \right]$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log 1.2 = 1.79$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.79 = 12.21$$

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

$$[\text{OH}^-] = [\text{NaOH}] = 0.3 \times \frac{1000}{200} = 1.5 \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log 1.5 = 1.43$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.43 = 12.57$$

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

The molarity of HCl solution after dilution is $\frac{13.6 \times 1}{1000} = 0.0136 \text{ M}$

It is equal to hydrogen ion concentration.

$$\text{pH} = -\log[\text{H}^+] = -\log 0.0136 = 1.87$$

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

ANSWER:-

Degree of ionization, $\alpha = 0.132$

Concentration, $c = 0.1 \text{ M}$

Thus, the concentration of $\text{H}_3\text{O}^+ = c \cdot \alpha$

$$= 0.1 \times 0.132$$

$$= 0.0132$$

$$\text{pH} = -\log[\text{H}^+] = -\log 0.0132 = 1.88$$

The acid dissociation constant is $K_a = \frac{c\alpha^2}{1-\alpha} = \frac{0.1 \times (0.132)^2}{1-0.132} = 2.01 \times 10^{-3}$

$$\text{p}K_a = -\log K_a = -\log(2.01 \times 10^{-3}) \approx 2.7$$

Therefore, $\text{pH} = 1.88$

$$\text{p}K_a = 2.7$$



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

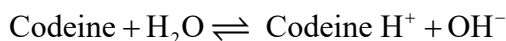
ANSWER:-

Given,

$$c = 0.005 \quad \text{pH} = 9.95$$

$$\text{pOH} = 14 - 9.95 = 4.05$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.05} = 8.913 \times 10^{-5}$$



The ionization constant,

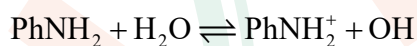
$$K_b = \frac{[\text{Codeine}^+][\text{OH}^-]}{[\text{codeine}]} = \frac{(8.913 \times 10^{-5}) \times (8.913 \times 10^{-5})}{5 \times 10^{-3}} = 1.588 \times 10^{-6}$$

$$\text{pK}_b = -\log(1.588 \times 10^{-6}) = 5.8$$

Q. 52. What is the pH of 0.001M aniline solution? The ionization constant of aniline can be taken from Table 6.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

ANSWER:-

Let c M be the initial concentration of $[C_6H_5NH_3^+]$ and x be the degree of ionization.



$$K_b = \frac{[\text{PhNH}_3^+][\text{OH}^-]}{[\text{PhNH}_2]} = \frac{(cx)(cx)}{c(1-x)} = \frac{cx^2}{1-x}$$

But x is very small. Hence, $1 - x \approx 1$.

$$\text{Hence, } K_b = cx^2.$$

$$\text{The degree of ionization of aniline, } x = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{4.3 \times 10^{-10}}{0.001}} = 6.56 \times 10^{-4}$$

$$[\text{OH}^-] = cx = 0.001 \times 6.56 \times 10^{-4} = 6.56 \times 10^{-7}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{6.56 \times 10^{-7}} = 1.52 \times 10^{-8}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 1.52 \times 10^{-8} = 7.818$$

$$K_a \text{ conjugate base of aniline} = \frac{K_w}{K_b} = \frac{10^{-14}}{4.3 \times 10^{-10}} = 2.32 \times 10^{-5}$$



Q. 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 ?

ANSWER:-

$$c = 0.05\text{M} \quad \text{pK}_a = 4.74$$

$$\text{pK}_a = -\log (\text{K}_a)$$

$$= -(4.74)$$

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

$$\text{K}_a = c\alpha^2 \Rightarrow \alpha = \sqrt{\frac{\text{K}_a}{c}}$$

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

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

Case I: When 0.01 M HCl is taken.

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

	CH ₃ COOH	↔	H ⁺	+CH ₃ COO ⁻
Initial conc.	0.05 M		0	0
After dissociation	0.05 - x		0.01 + x	x

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

$$\text{K}_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{\text{CH}_3\text{COOH}}$$

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

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

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

Now

$$\begin{aligned} \alpha &= \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}} \\ &= \frac{1.82 \times 10^{-3} \times 0.05}{0.05} \end{aligned}$$

Case II: When 0.1 M HCl is taken

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

$$[\text{CH}_3\text{COOH}] = 0.05 - X; 0.05 \text{ M}$$



$$[\text{CH}_3\text{COO}^-] = X$$

$$[\text{H}^+] = 0.1 + x; 0.1\text{M}.$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{\text{CH}_3\text{COOH}}$$

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

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

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

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

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

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

Q. 54. The ionization constant of dimethylamine is 5.4×10^{-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?

ANSWER:-

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

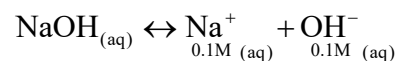
$$C = 0.02\text{M}$$

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

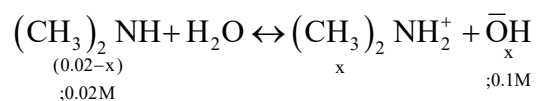
$$= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}}$$

$$= 1 - 0.1643$$

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



And



$$\text{Then } [(\text{CH}_3)_2\text{NH}_2^+] = x$$

$$[\text{OH}^-] = x + 0.1; 0.1$$



$$\Rightarrow K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

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

$$x = 0.0054$$

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

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

(a) Human muscle-fluid, 6.83

(b) Human stomach fluid, 1.2

(c) Human blood, 7.38

(d) Human saliva, 6.4

ANSWER:-

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

$$\text{Hence, } \text{H}^+ = 10^{-\text{pH}}$$

(a) $[\text{H}^+] = 10^{6.83} = 1.48 \times 10^{-7}\text{M}$

(b) $[\text{H}^+] = 10^{1.2} = 6.31 \times 10^{-2}\text{M}$

(c) $[\text{H}^+] = 10^{7.38} = 4.169 \times 10^{-8}\text{M}$

(d) $[\text{H}^+] = 10^{6.4} = 3.981 \times 10^{-7}\text{M}$

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

ANSWER:-

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

$$\text{Hence, } [\text{H}^+] = 10^{-\text{pH}}$$

Milk: $[\text{H}^+] = 10^{-6.8} = 1.58 \times 10^{-7}\text{M}$

Black coffee: $[\text{H}^+] = 10^{(-5.0)} = 1 \times 10^{(-5)}\text{M}$

Tomato juice: $[\text{H}^+] = 10^{(-4.2)} = 6.31 \times 10^{(-5)}\text{M}$

Lemon juice: $[\text{H}^+] = 10^{(-2.2)} = 6.31 \times 10^{(-3)}\text{M}$

Egg white: $[\text{H}^+] = 10^{(-7.8)} = 1.58 \times 10^{(-8)}\text{M}$

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

ANSWER:-

$$[\text{KOH}] = [\text{K}^+] = [\text{OH}^-] = \frac{0.561 \times 1000}{56 \times 200} = 0.050\text{M}$$



$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.05} = 2.0 \times 10^{-13}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2.0 \times 10^{-13}) = 12.699$$

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

ANSWER:-

Solubility of $\text{Sr}(\text{OH})_2 = 19.23 \text{ g/l}$

Then, concentration of $[\text{Sr}^{2+}]$

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

$$= 0.1581\text{M}$$

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

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

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

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

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

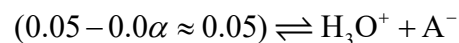
$$\text{pH} = -\log[\text{H}^+] = -\log[3.2 \times 10^{-14}]$$

$$\text{pH} = 13.50$$

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

ANSWER:-

Let the degree of ionization of propanoic acid be α . Then, representing propionic acid as HA, we have:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{\text{HA}}$$

$$= \frac{(0.05\alpha)(0.05\alpha)}{0.05} = 0.05\alpha^2$$

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



$$[H^+] = cx = 0.05 \times 0.0162 = 8.12 \times 10^{-4}$$

$$\text{pH} = \log[H^+] = -\log(8.12 \times 10^{-4}) = 3.09$$

If the solution is 0.01 M in HCl also then,

$$x = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.32 \times 10^{-5}}{0.01}} = 0.00132$$

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

ANSWER:-

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

$$\text{Hence, } H^+ = 10^{-\text{pH}}$$

$$[H^+] = 10^{-2.34} = 4.57 \times 10^{-3} \text{ M} = [CNO^-]$$

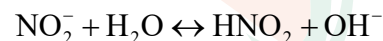
$$K_a = \frac{[H^+][CNO^-]}{[HCNO]} = \frac{(4.57 \times 10^{-3})(4.57 \times 10^{-3})}{0.1} = 2.09 \times 10^{-4}$$

$$\text{“The degree of dissociation} = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{2.09 \times 10^{-4}}{0.1}} = 4.57 \times 10^{-2}$$

- Q. 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.

ANSWER:-

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



$$K_h = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$$

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

$$[\text{NO}_2^-] = 0.04 - x; 0.04$$

$$[\text{HNO}_2] = x$$

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

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

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

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



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

$$[\text{H}_3\text{O}^+] = \frac{10^{-14}}{0.093 \times 10^{-5}} = 10.75 \times 10^{-9} \text{ M}$$

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

$$= 7.96$$

Therefore, degree of hydrolysis

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

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

ANSWER:-

$$\text{pH} = 3.44$$

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

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

$$\text{Then } K_h = \frac{(3.63 \times 10^{-4})^2}{0.02} \quad (\because \text{concentration} = 0.02\text{M})$$

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

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

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

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

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

(i) NaCl

(ii) KBr

(iii) NaCN

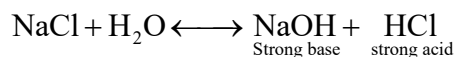
(iv) NH_4NO_3

(v) NaNO_2

(vi) KF

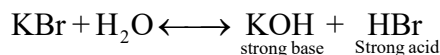
ANSWER:-

(i) NaCl



Therefore, it is a neutral solution.

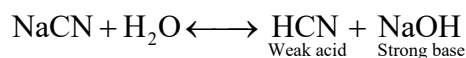
(ii) KBr



Therefore, it is a neutral solution.

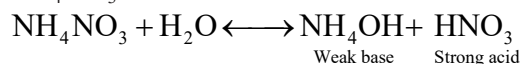


(iii) NaCN



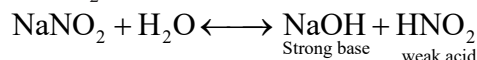
Therefore, it is a basic solution

(iv) NH_4NO_3



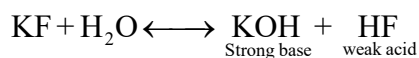
Therefore, it is an acidic solution.

(v) NaNO_2



Therefore, it is a basic solution.

(vi) KF



Therefore, it is a basic solution.

Q. 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?

ANSWER:-

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

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

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

$$= \sqrt{\frac{1.35 \times 10^{-3}}{0.1}}$$

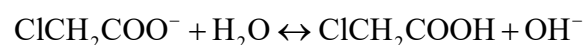
$$\alpha = \sqrt{1.35 \times 10^{-2}}$$

$$= 0.116$$

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

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

$\text{ClCH}_2\text{COONa}$ is the salt of a weak acid i.e., ClCH_2COOH and a strong base i.e., NaOH .



$$K_b = \frac{[\text{ClCH}_2\text{COOH}][\text{OH}^-]}{\text{ClCH}_2\text{COO}^-}$$

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



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

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

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

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

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

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

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

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

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

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

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

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

$$= 7.94$$

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

ANSWER:-

Ionic product,

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

$$\text{Let } [\text{H}^+] = x$$

$$\text{Since } [\text{H}^+] = [\text{OH}^-],$$

$$K_w = x^2.$$

$$\Rightarrow K_w \text{ at } 310\text{K} = 2.7 \times 10^{-14}$$

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

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

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

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

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

$$= 6.78$$

Hence, the pH of neutral water is 6.78.



Q. 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 H₂SO₄ + 10 mL of 0.01M Ca(OH)₂
 (c) 10 mL of 0.1M H₂SO₄ + 10 mL of 0.1M KOH

ANSWER:-

(a) Moles of H₃O⁺ = $\frac{25 \times 0.1}{1000} = 0.0025 \text{ mol}$

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

Thus, excess of OH⁻ = .0015 mol

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

pOH = -log [OH⁻]

= 1.36

pH = 14 - pOH = 14 - 1.368 = 12.635

(b) Moles of H₃O⁺ = $\frac{2 \times 10 \times 0.01}{1000} = 0.0002 \text{ mol}$

Moles of = $\frac{2 \times 10 \times 0.01}{1000} = 0.0002 \text{ mol}$

Since there is neither an excess of H₃O⁺ or OH⁻, the solution is neutral. Hence, pH=7.

(c) Moles of H₃O⁺ = $\frac{2 \times 10 \times 0.1}{1000} = 0.002 \text{ mol}$

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

Excess of H₃O⁺ = 0.001 mol

Thus $[\text{H}_3\text{O}^+] = \frac{0.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = 0.05$

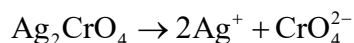
∴ pH = -log (0.05)

= 1.30

Q. 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 6.9. Determine also the molarities of individual ions.

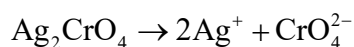
- (1) Silver chromate: (2) Barium chromate: (3) Ferric hydroxide:
 (4) Lead dichloride PbCl₂ ⇌ Pb²⁺ + 2Cl⁻ (5) Mercurous iodide:



ANSWER:-**(1)** Silver chromate:

then

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

Let the solubility of Ag_2CrO_4 be s .

$$[\text{Ag}^+] = 2s \text{ and } [\text{CrO}_4^{2-}] = s$$

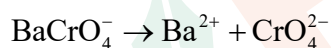
Then

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

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

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

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

(2) Barium chromate:

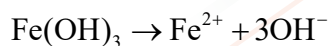
$$\text{Thus } [\text{Ba}^{2+}] = s \text{ and } [\text{CrO}_4^{2-}] = s$$

$$\Rightarrow K_{sp} = s^2$$

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

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

$$\text{Molarity of } \text{Ba}^{2+} = \text{Molarity of } \text{CrO}_4^{2-} = s = 1.09 \times 10^{-5} \text{ M}$$

(3) Ferric hydroxide:

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

Let s be the solubility of $\text{Fe}(\text{OH})_3$

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

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

$$K_{sp} = s(3s)^3 = 27s^4 = 1.0 \times 10^{-38}$$

$$[\text{Fe}^{3+}] = s = 1.38 \times 10^{-10} \text{ M}$$

$$[\text{OH}^-] = 3s = 4.14 \times 10^{-10} \text{ M}$$



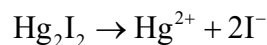


$$[\text{Pb}^{2+}] = s, [\text{Cl}^-] = 2s$$

$$K_{\text{sp}} = s \times (2s)^2 = 4s^3 = 1.6 \times 10^{-5}$$

$$[\text{Pb}^{2+}] = s = 0.0159\text{M}$$

$$[\text{Cl}^-] = 2s = 0.0318\text{M}$$



$$K_{\text{sp}} = [\text{Hg}_2^{2+}]^2 [\text{I}^-]^2$$

Let s be the solubility of Hg_2I_2

$$\Rightarrow [\text{Hg}_2^{2+}] = s \text{ and } [\text{I}^-] = 2s$$

$$\text{Thus } K_{\text{sp}} = s(2s)^2$$

$$\Rightarrow K_{\text{sp}} = 4s^3$$

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

$$1.125 \times 10^{-29} = s^3$$

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

$$\text{Molarity of } \text{Hg}_2^{2+} = s = 2.24 \times 10^{-10}\text{M}$$

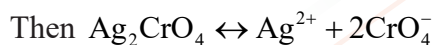
$$\text{Molarity of } \text{I}^- = 2s = 4.48 \times 10^{-10}\text{M}$$

<https://t.me/vedalland12>

Q. 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.

ANSWER:-

Let s be the solubility of Ag_2CrO_4 .

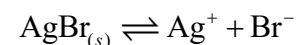


$$K_{\text{sp}} = (2s)^2 s = 4s^3$$

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

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

Let s' be the solubility of AgBr .



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

$$\therefore s' = 7.07 \times 10^{-7}\text{M}$$

Therefore, the ratio of the molarities of their saturated solution is $\frac{s}{s'} = \frac{6.5 \times 10^{-5}\text{M}}{7.07 \times 10^{-7}\text{M}} = 91.9$

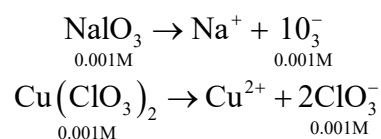


- Q. 69.** Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

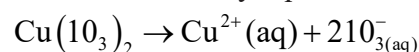
ANSWER:-

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,



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



Ionic product of copper iodate:

$$\begin{aligned} &= [\text{Cu}^{2+}][\text{IO}_3^-]^2 \\ &= (0.001)(0.001)^2 \\ &= 1 \times 10^{-9} \end{aligned}$$

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

- Q. 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?

ANSWER:-

Let s be the solubility of silver benzoate in water.

$$[\text{Ag}^+] = [\text{PhCOO}^-] = s \text{ M}$$

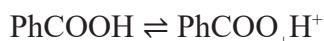
$$K_{sp} = [\text{PhCOO}^-][\text{Ag}^+] = s \times s = s^2 = 2.5 \times 10^{-13}$$

$s = 5.0 \times 10^{-7}$ M. This is solubility of silver benzoate in pure water.

$$\text{pH} = -\log[\text{H}^+] = 3.19$$

$$[\text{H}^+] = 6.456 \times 10^{-4}$$

Benzoate ions combine with protons to form benzoic acid but hydrogen ion concentration is constant due to buffer solution.



$$K_a = \frac{[\text{PhCOO}^-][\text{H}^+]}{[\text{PhCOOH}]}$$

$$\frac{[\text{PhCOOH}]}{[\text{PhCOO}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{6.456 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$



Let y M be the solubility in the buffer solution.

$$y = [\text{Ag}^+] = [\text{PhCOO}^-] + [\text{PhCOOH}] = [\text{PhCOO}^-] + 10[\text{PhCOO}^-] = 11[\text{PhCOO}^-]$$

$$[\text{PhCOO}^-] = \frac{y}{11}$$

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

$$2.5 \times 10^{-13} = \frac{y}{11} \times y$$

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

$$\frac{y}{s} = \frac{1.66 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.32$$

Thus, silver benzoate is 3.32 times more soluble in buffer.

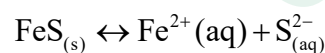
Q. 71. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{\text{sp}} = 6.3 \times 10^{-18}$)

ANSWER:-

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. $\frac{x}{2}$

$$\therefore [\text{FeSO}_4] = [\text{Na}_2\text{S}] = \frac{x}{2} \text{ M}$$

$$\text{Also } [\text{S}^{2-}] = [\text{Na}_2\text{S}] = \frac{x}{2} \text{ M} \quad \text{Then } [\text{Fe}^{2+}] = [\text{FeSO}_4] = \frac{x}{2} \text{ M}$$



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

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

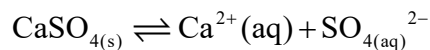
$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

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

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.



- Q. 72.** What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K ? (For calcium sulphate, K_{sp} is 9.1×10^{-6} .)

ANSWER:-

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

Let the solubility of CaSO_4 be .

$$\text{Then } K_{sp} = s^2$$

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

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

Molecular mass of $\text{CaSO}_4 = 136 \text{ g/mol}$

Solubility of CaSO_4 in gram /L = $3.02 \times 10^{-3} \times 136 = 0.41 \text{ g/L}$

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

Therefore, to dissolve 1 g of CaSO_4 we require = $\frac{1}{0.41} \text{ L} = 2.44 \text{ L}$ of water

The minimum volume of water required to dissolve 1 g of calcium sulfate at 298 K is approximately 2.44 litres.

- Q. 73.** The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is $1.0 \times 10^{-19} \text{ M}$. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $\text{FeSO}_4, \text{MnCl}_2, \text{ZnCl}_2$ and CdCl_2 . in which of these solutions precipitation will take place?

ANSWER:-

For precipitation to take place, it is required that the calculated ionic product exceeds

Before mixing:

$$[\text{S}^{2-}] = 1.0 \times 10^{-19} \text{ M}$$

$$\text{Volume} = 10 \text{ ml}$$

After mixing:

$$[\text{S}^{2-}] = ?$$

$$\text{Volume} = 10 \text{ ml} + 5 \text{ ml} = 15 \text{ ml}$$

$$[\text{M}^{2+}] = 0.04 \text{ M}$$

$$\text{Volume} = 5 \text{ ml}$$

$$[\text{M}^{2+}] = ?$$

$$\text{Volume} = 15 \text{ ml}$$

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

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

$$\text{Ionic Product} = [\text{M}^{2+}][\text{S}^{2-}]$$

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

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

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

