

# 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,

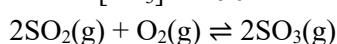
Rate of evaporation = Rate of condensation

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?

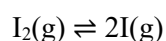


2. The equilibrium constant ( $K_c$ ) for the give reaction is:

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

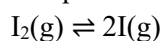
Hence,  $K$  for the equilibrium is  $12.239 M^{-1}$ .

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



Calculate  $K_p$  for the equilibrium.

3.  $K_p$  value at equilibrium for reaction,



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<sub>2</sub>.

Let V be total volume, then volume occupied by I and I<sub>2</sub> are 0.4V and 0.6V respectively.

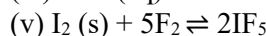
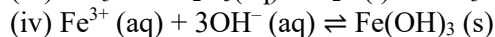
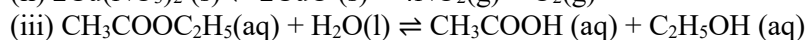
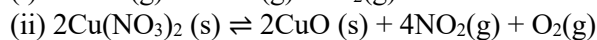
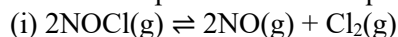
Partial pressure of I<sub>2</sub> = (60/100) × 10<sup>5</sup> = 60 kPa

Partial pressure of I = (40/100) × 10<sup>5</sup> = 40 kPa

Substituting in equation for K<sub>p</sub>,

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

4. Write the expression for the equilibrium constant, K<sub>c</sub> for each of the following reactions:



4. (i)  $K_c = \frac{[\text{NO(g)}]^2 [\text{Cl}_2\text{(g)}]}{[\text{NOCl(g)}]^2}$

(ii)  $K_c = \frac{[\text{CuO(s)}]^2 [\text{NO}_2\text{(g)}]^4 [\text{O}_2\text{(g)}]}{[\text{Cu(NO}_3)_2\text{(s)}]}$

$= [\text{NO}_2\text{(g)}]^4 [\text{O}_2\text{(g)}]$

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

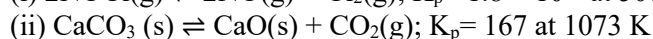
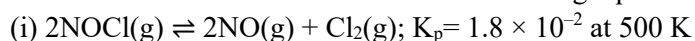
(iv)  $K_c = \frac{[\text{Fe(OH)}_3\text{(s)}]}{[\text{Fe}^{3+}\text{(aq)}][\text{OH}^-\text{(aq)}]^3}$

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

(v)  $K_c = \frac{[\text{IF}_5]^2}{[\text{I}_2\text{(s)}][\text{F}_2]^5}$

$= \frac{[\text{IF}_5]^2}{[\text{F}_2]^5}$

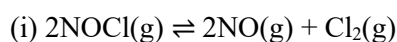
5. Find out the value of K<sub>c</sub> for each of the following equilibria from the value of K<sub>p</sub>:



5. We know that,

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

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



Number of gaseous species on product side is 3 (2 NO and 1 Cl<sub>2</sub>) and on reactant side is 2 (2 NOCl)

$$\text{Thus, } \Delta n = 3 - 2 = 1$$

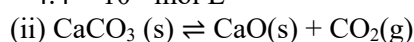
$$T = 500 \text{ K}$$

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

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

$$\begin{aligned} \therefore K_c &= \frac{K_p}{[RT]^{\Delta n}} \\ &= \frac{(1.8 \times 10^{-2}) \text{ atm}}{(0.0821 \text{ L atm K}^{-1} \times 500 \text{ K})^1} \end{aligned}$$

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



Number of gaseous species on product side is 1 (1 CO<sub>2</sub>) and on reactant side is 0.

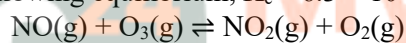
$$\text{Thus, } \Delta n = 1 - 0 = 1$$

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

$$K_p = 167 \text{ atm}$$

$$\begin{aligned} K_c &= \frac{K_p}{[RT]^1} \\ &= \frac{167 \text{ atm}}{0.0821 \text{ L atm K}^{-1} \times 1073 \text{ K}} \\ &= 1.9 \text{ mol L}^{-1} \end{aligned}$$

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  $K_c$  for the reverse reaction?

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

$$\begin{aligned} \text{Then, } K_c \text{ for the reverse reaction will be, } K'_c &= \frac{1}{K_c} \\ &= \frac{1}{6.3 \times 10^{14}} \\ &= 1.59 \times 10^{-15} \end{aligned}$$

7. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?
7. Concentration of solid or pure liquid,

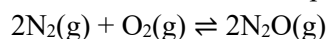
$$\begin{aligned} [\text{substance}] &= \frac{\text{number of mole of substance}}{\text{volume}} \\ &= \frac{\text{amount of substance}}{\text{Molar mass} \times \text{Volume}} \\ &= \frac{\text{Density}}{\text{Molar mass}} \end{aligned}$$

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).

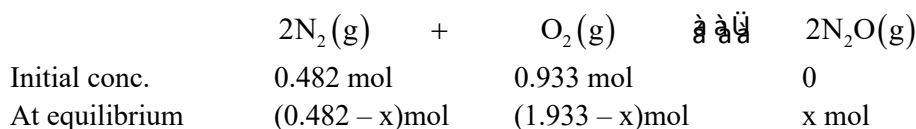
8. Reaction between  $N_2$  and  $O_2$  takes place as follows:



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



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,

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

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

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

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

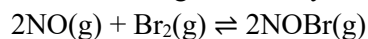
$$\Rightarrow x^2 = 43.35 \times 10^{-40}$$

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

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

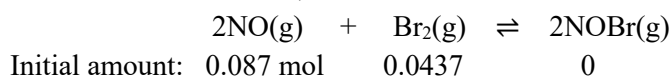
$$= 6.6 \times 10^{-21}$$

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

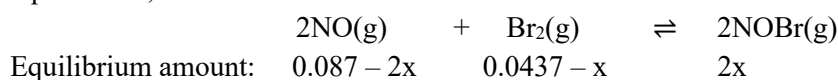


When 0.087 mol of  $NO$  and 0.0437 mol of  $Br_2$  are mixed in a closed container at constant temperature, 0.0518 mol of  $NOBr$  is obtained at equilibrium. Calculate equilibrium amount of  $NO$  and  $Br_2$ .

9. The chemical reaction is,



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



Given, equilibrium concentration of NOBr is 0.0518,

i.e.,  $2x = 0.0518$

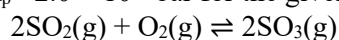
$$x = 0.0259$$

Thus,

$$\begin{aligned}\text{Amount of NO at equilibrium} &= 0.087 - 2 \times 0.0259 \\ &= 0.0352 \text{ mole}\end{aligned}$$

$$\begin{aligned}\text{Amount of Br}_2 \text{ at equilibrium} &= 0.0437 - 0.0259 \\ &= 0.0178 \text{ mole}\end{aligned}$$

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



What is  $K_c$  at this temperature?

10. For the given reaction,

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

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

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

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

We know that,

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

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

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

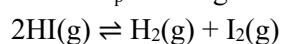
$$= (2.0 \times 10^{10} \text{ bar}^{-1}) (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K})$$

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

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

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

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?



11. Partial pressure of HI = 0.04 atm

sum of partial pressures = total pressure, thus,

$$P(\text{H}_2) + P(\text{I}_2) = P - P(\text{HI})$$

where,

P is total pressure = 0.2 atm

$P(\text{H}_2)$  is Partial pressure of  $\text{H}_2 = x$

$P(\text{I}_2)$  is Partial pressure of  $\text{I}_2 = x$

$P(\text{HI})$  is Partial pressure of HI = 0.04 atm

$$\therefore x + x = 0.2 - 0.04$$

$$= 0.16$$

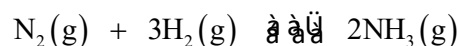
$$\text{i.e., } x = 0.08 \text{ atm}$$

$$K_p = \frac{[p(\text{H}_2) \times p(\text{I}_2)]}{[p(\text{HI})]^2}$$

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

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

12. 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.

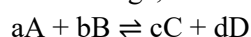
Again,  $Q_c > K_c$ . Hence, the reaction will proceed in the reverse direction.

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,



Equilibrium constant  $K_c$  for the reaction,

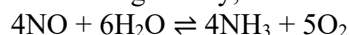
$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

In question, expression for equilibrium constant is given as,

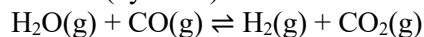
$$K_c = \frac{[NH_3]^4 \times [O_2]^5}{[NO]^4 \times [H_2O]^6}$$

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

The reaction here is given by,

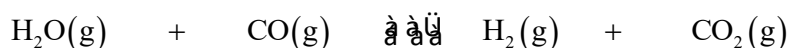


14. One mole of  $H_2O$  and one mole of  $CO$  are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with  $CO$  according to the equation,



Calculate the equilibrium constant for the reaction.

14. The given reaction is:



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

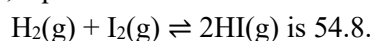
Therefore, the equilibrium constant for the reaction,

$$K_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]}$$

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

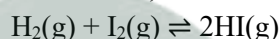
$$= 0.444 \text{ (approximately)}$$

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



If 0.5 mol L<sup>-1</sup> of HI(g) is present at equilibrium at 700 K, what are the concentration of H<sub>2</sub>(g) and I<sub>2</sub>(g) assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

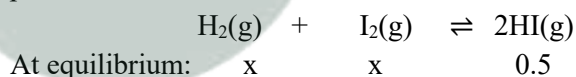
15. For the reaction,



Equilibrium constant is given to be 54.8.

$$\text{i.e., } K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Let x be equilibrium concentration of H<sub>2</sub> at equilibrium. Then equilibrium concentration of I<sub>2</sub> will also be x. Since, initially there was only HI present, equal amount of H<sub>2</sub> and I<sub>2</sub> will be produced.



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

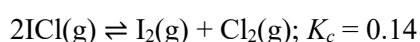
$$= \frac{(0.5)^2}{x^2} = 54.8$$

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

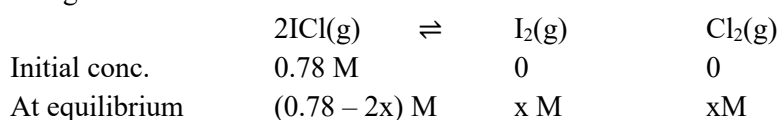
$$= 0.0675$$

Therefore, concentration of H<sub>2</sub> and I<sub>2</sub> is 0.0675 mol L<sup>-1</sup>.

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



16. The given reaction is:



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

$$[H_2] = [I_2] = 0.167 \text{ M}$$

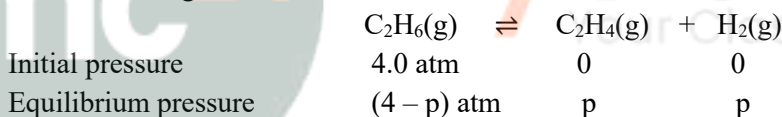
$$[HI] = (0.78 - 2 \times 0.167) \text{ M} \\ = 0.446 \text{ M}$$

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?



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

Therefore, the given reaction is:



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,

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

Where  $p_{C_2H_4}$  = partial pressure of  $C_2H_4$  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

$$0.04 = \frac{p \times p}{(4 - p)}$$

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

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

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

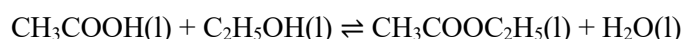
$$p = \frac{-0.04 \pm 0.08}{2}$$

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

$$p = 0.38$$

Therefore, at equilibrium,  $[C_2H_6] = 4 - p = 4 - 0.38 = 3.62 \text{ atm}$ .

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



(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)

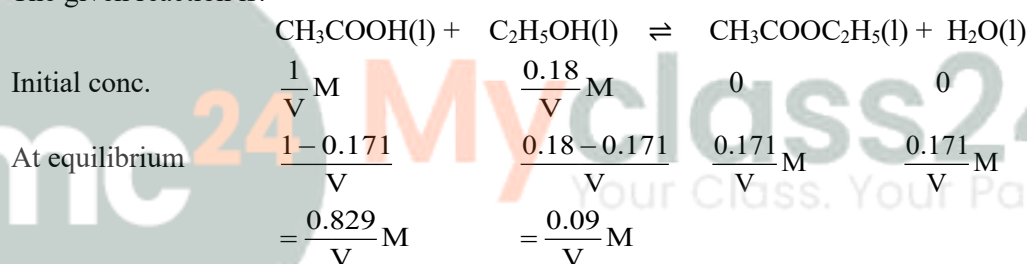
(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(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:



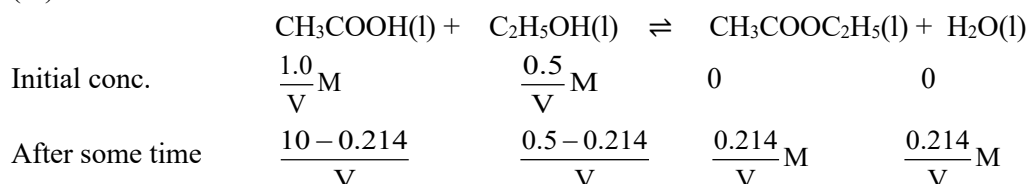
Therefore, equilibrium constant for the given reaction is:

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

$$= \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.09}{V}} = 3.919$$

= 3.92 (approximately)

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



Therefore, the reaction quotient is,

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

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

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

$$= 0.2037$$

$$= 0204 \text{ (approximately)}$$

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

19. A sample of pure  $\text{PCl}_5$  was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of  $\text{PCl}_5$  was found to be  $0.5 \times 10^{-1} \text{ mol L}^{-1}$ . If value of  $K_c$  is  $8.3 \times 10^{-3}$ , what are the concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium?



19. For the given reaction, let's assume that the initial molar concentration of  $\text{PCl}_5$  is  $x \text{ mol/L}$ . The given reaction is:



Initial concentration

$$x \qquad 0 \qquad 0$$

Equilibrium concentration

$$0.05 \qquad (x - 0.05) \qquad (x - 0.05)$$

Moles of  $\text{PCl}_5$  decomposed during the reaction = Moles of  $\text{PCl}_3$  formed = Moles of  $\text{Cl}_2$  formed =

$$(x - 0.05) \text{ mol/L.}$$

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,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

Where,  $[\text{PCl}_3]$  = concentration of  $\text{PCl}_3$  in mol/L at equilibrium

$[\text{Cl}_2]$  = concentration of  $\text{Cl}_2$  in mol/L at equilibrium

$[\text{PCl}_5]$  = concentration of  $\text{PCl}_5$  in mol/L at equilibrium

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

$$(x - 0.05)^2 = 0.000415$$

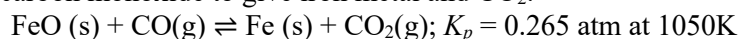
$$(x - 0.05) = 0.0203$$

$$x = 0.07 \text{ mol/L}$$

$$\text{Therefore, } [\text{PCl}_3] = (x - 0.05) = 0.07 - 0.05 = 0.02 \text{ mol/L}$$

$$[\text{Cl}_2] = (x - 0.05) = 0.07 - 0.05 = 0.02 \text{ mol/L.}$$

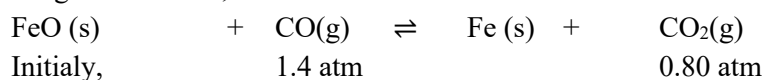
20. One of the reaction that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and  $\text{CO}_2$ .



What are the equilibrium partial pressures of  $\text{CO}$  and  $\text{CO}_2$  at 1050 K if the initial partial pressures are:

$$p_{\text{CO}} = 1.4 \text{ atm and } p_{\text{CO}_2} = 0.80 \text{ atm?}$$

20. For the given reaction,



$$Q_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}}$$

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

$$= 0.571$$

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<sub>2</sub> will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO<sub>2</sub> be p. Then, we can write,

$$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}}$$

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

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

$$\Rightarrow 1.265p = 0.429$$

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

Therefore, equilibrium partial of CO<sub>2</sub>,  $p_{\text{CO}_2} = 0.80 - 0.339 = 0.461 \text{ atm}$ .

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

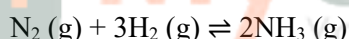
**21.** Equilibrium constant,  $K_c$  for the reaction



At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L<sup>-1</sup> N<sub>2</sub>, 2.0 mol L<sup>-1</sup> H<sub>2</sub> and 0.5 mol L<sup>-1</sup> NH<sub>3</sub>. Is the reaction at equilibrium?

If not in which direction does the reaction tend to proceed to reach equilibrium?

**21.** The given reaction is:



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.

$$\text{Here, } Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Where, [NH<sub>3</sub>] = concentration of NH<sub>3</sub> in mol/L at a particular instant

[N<sub>2</sub>] = concentration of N<sub>2</sub> in mol/L at a particular instant

[H<sub>2</sub>] = concentration of H<sub>2</sub> in mol/L at a particular instant

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

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:

$2\text{BrCl} (\text{g}) \rightleftharpoons \text{Br}_2 (\text{g}) + \text{Cl}_2 (\text{g})$  for which  $K_c = 32$  at 500 K. If initially pure BrCl is present at a concentration of  $3.3 \times 10^{-3} \text{ mol L}^{-1}$ , what is 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:

	$2\text{BrCl (g)} \rightleftharpoons \text{Br}_2 \text{(g)} + \text{Cl}_2 \text{(g)}$		
Initial conc.	$3.3 \times 10^{-3}$	0	0
At equilibrium	$3.3 \times 10^{-3} - 2x$	x	x

Now, we can write,

$$\frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} = K_c$$

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

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

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

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

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

Therefore, at equilibrium,

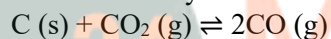
$$[\text{BrCl}] = 3.3 \times 10^{-3} - (2 \times 1.5 \times 10^{-3})$$

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

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

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

23. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO<sub>2</sub> in equilibrium with solid carbon has 90.55% CO by mass



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<sub>2</sub> = (100 - 90.55) = 9.45g

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

$$\text{Number of moles of CO}_2, n_{\text{CO}_2} = \frac{\text{Mass of available CO}_2}{\text{Molar Mass of CO}_2} = \frac{9.45\text{g}}{44\text{g}} = 0.215$$

$$\text{Partial pressure of CO, } p_{\text{CO}} = \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2}} \times p_{\text{total}}$$

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

$$\text{Partial pressure of CO}_2, p_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \times p_{\text{total}}$$

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

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.

$$\text{Therefore, } K_p = \frac{(p_{\text{CO}})^2}{p_{\text{CO}_2}} = \frac{(0.938 \text{ atm})^2}{(0.062 \text{ atm})} = 14.19 \text{ atm}$$

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

Where  $K_c$  = Equilibrium constant

$$K_p = 14.19 \text{ atm}$$

$$R = 0.081 \text{ L atm/K mol}$$

$$T = 1127 \text{ K}$$

$\Delta n_g$  = Sum of stoichiometric coefficients of products – Sum of stoichiometric coefficients of reactants =

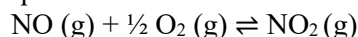
$$2 - 1 = 1.$$

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

24. Calculate

(a)  $\Delta G^\circ$  and

(b) the equilibrium constant for the formation of  $\text{NO}_2$  from  $\text{NO}$  and  $\text{O}_2$  at 298K.



Where:

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

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

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

24. (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,

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

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

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

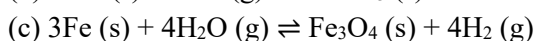
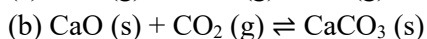
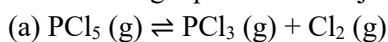
$$= 6.134$$

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

$$= 1.36 \times 10^6$$

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

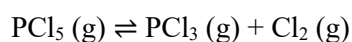
25. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?



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.

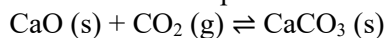
Hence, according to Le Chatelier's principle, if the pressure on the system is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more.

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



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.

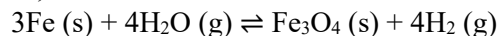
(b) The number of moles of reaction products will decrease. In the given reaction,



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,

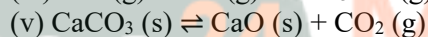
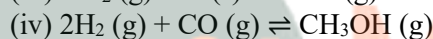
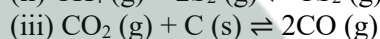
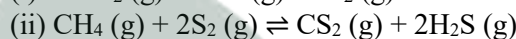
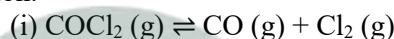


The number of moles of gaseous products equal to gaseous reactants. Thus, the decreasing of pressure does not affect the equilibrium. As a result, the number of moles of reaction products will remain same.

**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.

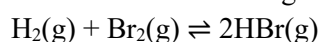


26. The reactions given in (i), (iii), (iv), (v) and (vi) will get affected by increasing the pressure.

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.

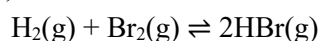
27. The equilibrium constant for the following reaction is  $1.6 \times 10^5$  at 1024 K.



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,



The equilibrium constant ( $K_c$ ) is  $1.6 \times 10^5$

Initial pressure of HBr = 10bar

Temperature = 1024K

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

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

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)

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

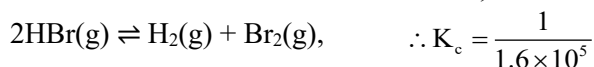
Where  $\Delta n$  = no. of moles of products – no. of moles of reactants

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



Initial 10 bar

At

Equilibrium 10–P P/2 P/2

Using the above formula,

$$K_p = \left( \frac{P_X^x \cdot P_Y^y}{P_A^a \cdot P_B^b} \right)$$

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

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

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

Taking square root of both sides, we get

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

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

$$\Rightarrow 402 P = 20$$

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

$$\Rightarrow P = 4.97 \times 10^{-2} \text{ bar}$$

Hence, at equilibrium

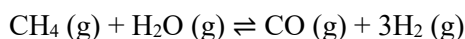
$$P_{\text{H}_2} = P_{\text{Br}_2} = P/2$$

$$\Rightarrow \left( \frac{4.97 \times 10^{-2} \text{ bar}}{2} \right) = 2.48 \times 10^{-2} \text{ bar}$$

$$P_{\text{HBr}} = 10 - P \approx 10 \text{ bar}$$

Thus, the equilibrium pressure of  $\text{H}_2$  and  $\text{Br}_2$  is  $2.48 \times 10^{-2}$  bar and HBr is 10 bar.

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

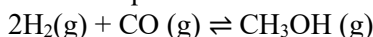


- (a) Write an expression for  $K_p$  for the above reaction.  
(b) How will the values of  $K_p$  and composition of equilibrium mixture be affected by  
(i) increasing the pressure  
(ii) increasing the temperature  
(iii) using a catalyst?
28. (a) For the given reaction,  
(b)

- (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.

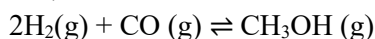
29. Describe the effect of:

- (a) Addition of H<sub>2</sub>
- (b) Addition of CH<sub>3</sub>OH
- (c) Removal of CO
- (d) Removal of CH<sub>3</sub>OH on the equilibrium of the reaction:



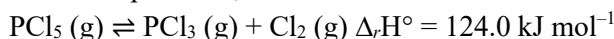
29. According to Le Chatelier's principle, if in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward reaction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse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

For the given reaction,



- (a) If the addition of H<sub>2</sub> 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<sub>3</sub>OH 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<sub>3</sub>OH 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<sub>c</sub> for decomposition of phosphorus pentachloride, PCl<sub>5</sub> is 8.3 × 10<sup>-3</sup>. If decomposition is depicted as,



- (a) Write an expression for K<sub>c</sub> for the reaction.
- (b) What is the value of K<sub>c</sub> for the reverse reaction at the same temperature?
- (c) What would be the effect on K<sub>c</sub> if
  - (i) more PCl<sub>5</sub> is added
  - (ii) pressure is increased?
  - (iii) The temperature is increased?

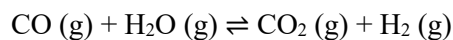
30. (a) 
$$K_c = \frac{[\text{PCl}_3(\text{g})][\text{Cl}_2(\text{g})]}{[\text{PCl}_5(\text{g})]}$$

(b) Value of K<sub>c</sub> for the reverse reaction at the same temperature is:

$$\begin{aligned} K'_c &= \frac{1}{K_c} \\ &= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2 \\ &= 120 - 48 \end{aligned}$$

- (c) (i) K<sub>c</sub> would remain the same because in this case, the temperature remains the same.
- (ii) K<sub>c</sub> is constant at constant temperature. Thus, in the case, K<sub>c</sub> 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<sub>2</sub>. In the second stage, CO formed in the first stage is reacted with more steam in water gas shift reaction,



If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that  $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 4.0$  bar, what will be the partial pressure of H<sub>2</sub> at equilibrium?

$K_p = 10.1$  at 400°C.

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

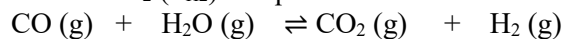
Given: Temperature = 400° C

Partial pressure of CO ( $P_{\text{CO}}$ ) = Partial pressure of H<sub>2</sub>O ( $P_{\text{H}_2\text{O}}$ ) = 4.0 bar

$K_p = 10.1$  bar

$$\text{Formula: } K_p = \left( \frac{P_x^x \cdot P_y^y}{P_A^a \cdot P_B^b} \right)$$

Let the partial pressure of H<sub>2</sub> ( $P_{\text{H}_2}$ ) at equilibrium = P bar



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)

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

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

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

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

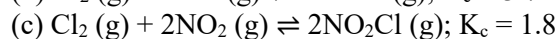
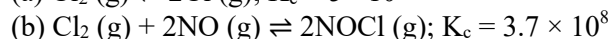
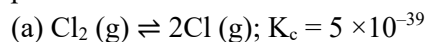
$$\Rightarrow 12.712 - 0.3178P = P$$

$$\Rightarrow 4.178P = 12.712$$

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

Thus, the partial pressure of H<sub>2</sub> ( $P_{\text{H}_2}$ ) at equilibrium = P bar = 3.042 bar.

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



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  $2.0 \times 10^{-50}$  at  $25^\circ\text{C}$ . If the equilibrium concentration of  $O_2$  in the air at  $25^\circ\text{C}$  is  $1.6 \times 10^{-2}$ , 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 =  $2.0 \times 10^{-50}$

Temperature =  $25^\circ\text{C}$

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

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

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

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

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

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

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

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

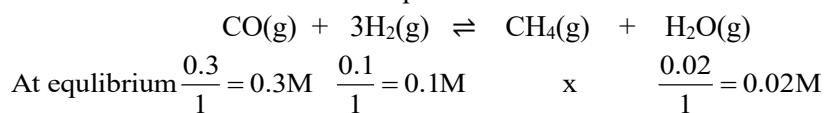
$$\Rightarrow [O_3] = 2.86 \times 10^{-28}\text{ M}$$

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

34. The reaction,  $\text{CO}(g) + 3\text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + \text{H}_2\text{O}(g)$  is at equilibrium at 1300 K in a 1L flask. It also contains 0.30 mol of CO, 0.10 mol of  $\text{H}_2$  and 0.02 mol of  $\text{H}_2\text{O}$  and an unknown amount of  $\text{CH}_4$  in the flask. Determine the concentration of  $\text{CH}_4$  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.



It is given that  $K_c = 3.90$ .

Therefore,

$$\frac{[\text{CH}_4(g)][\text{H}_2\text{O}(g)]}{[\text{CO}(g)][\text{H}_2(g)]} = K_c$$

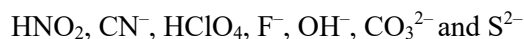
$$\Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} = 3.90$$

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

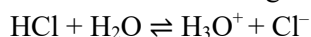
$$\begin{aligned}
 &= \frac{0.00117}{0.02} \\
 &= 0.0585 \text{ M} \\
 &= 5.85 \times 10^{-2} \text{ M}
 \end{aligned}$$

Hence, the concentration of CH<sub>4</sub> at equilibrium is  $5.85 \times 10^{-2}$  M.

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



35. Consider the following acid-base reaction:



HCl is an acid because it donates a proton to water (H<sub>2</sub>O) and H<sub>2</sub>O is a base because it accepts a proton from HCl and hence is a base. Thus, there are two acid-base pairs in the reaction. These are HCl-Cl<sup>-</sup> and H<sub>3</sub>O<sup>+</sup>-H<sub>2</sub>O. These acid-base pairs are called conjugate acid-base pairs.

Species	Conjugate acid-base
HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup> (base)
CN <sup>-</sup>	HCN (acid)
HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup> (base)
F <sup>-</sup>	F (acid)
OH <sup>-</sup>	H <sub>2</sub> O (acid) / O <sup>2-</sup> (base)
CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup> (acid)
S <sup>2-</sup>	HS <sup>-</sup> (acid)

36. Which of the followings are Lewis acids? H<sub>2</sub>O, BF<sub>3</sub>, H<sup>+</sup> and NH<sub>4</sub><sup>+</sup>.
36. Lewis acids are those acids which can accept a pair of electrons. For example, BF<sub>3</sub>, H<sup>+</sup> and NH<sub>4</sub><sup>+</sup> are Lewis acids.

37. What will be the conjugate bases for the Bronsted acids: HF, H<sub>2</sub>SO<sub>4</sub> and HCO<sub>3</sub><sup>-</sup>?

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<sup>+</sup> (loses proton)

Bronsted acids	Loss of proton	Conjugate bases
HF	HF - H <sup>+</sup>	F <sup>-</sup>
H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub> - H <sup>+</sup>	HSO <sub>4</sub> <sup>-</sup>
HCO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup> - H <sup>+</sup>	CO <sub>3</sub> <sup>2-</sup>

38. Write the conjugate acids for the following Bronsted bases: NH<sub>2</sub><sup>-</sup>, NH<sub>3</sub> and HCOO<sup>-</sup>.

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

**Bronsted base**                      **Conjugate acid**



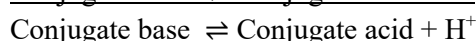
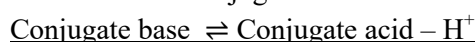
39. The species:  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$  and  $\text{NH}_3$  can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

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.



Species	Conjugate acid (gain of proton)	Conjugate base (lose of proton)
$\text{H}_2\text{O}$	$\text{H}_3\text{O}^+$	$\text{OH}^-$
$\text{HCO}_3^-$	$\text{H}_2\text{CO}_3$	$\text{CO}_3^{2-}$
$\text{HSO}_4^-$	$\text{H}_2\text{SO}_4$	$\text{SO}_4^{2-}$
$\text{NH}_3$	$\text{NH}_4^+$	$\text{NH}_2^-$

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

(a)  $\text{OH}^-$

(b)  $\text{F}^-$

(c)  $\text{H}^+$

(d)  $\text{BCl}_3$

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

(b)  $\text{F}^-$  is a Lewis base since it can donate a pair of electrons.

(c)  $\text{H}^+$  is a Lewis acid since it can accept a pair of electrons.

(d)  $\text{BCl}_3$  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  $3.8 \times 10^{-3}$  M. what is its pH?

41. Given:

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

To calculate of pH, we apply the formula

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

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

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  $\text{H}^+$  ion concentration.

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

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

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

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

$$\Rightarrow \text{pH} = -0.58 + 3$$

$$\Rightarrow \text{pH} = 2.42$$

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 known that,

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

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

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

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

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

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

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

43. Given:

$$\text{The ionization constant of HF} = 6.8 \times 10^{-4}$$

$$\text{The ionization constant of HCOOH} = 1.8 \times 10^{-4}$$

$$\text{The ionization constant of HCN} = 4.8 \times 10^{-9}$$

$$\Rightarrow \text{Conjugate base of HF} = \text{F}^-$$

$$\Rightarrow \text{Conjugate base of HCOOH} = \text{HCOO}^-$$

$$\Rightarrow \text{Conjugate base of HCN} = \text{CN}^-$$

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.,  $\text{F}^-$ ,

Using the formula, we write

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

$$\text{As } K_a \text{ of HF} = 6.8 \times 10^{-4} \text{ (given)}$$

$$K_w = 10^{-14} \text{ (same value for every acid or base)}$$

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

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

To calculate the ionization constant of conjugate base of HCOOH, i.e.,  $\text{HCOO}^-$ ,

Using the formula, we write

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

$$\text{As } K_a \text{ of HCOOH} = 1.8 \times 10^{-4} \text{ (given)}$$

$$K_w = 10^{-14}$$

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

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

To calculate the ionization constant of conjugate base of HCN, i.e.,  $\text{CN}^-$ ,

Using the formula, we write

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

$$\text{As } K_a \text{ of HCN} = 4.8 \times 10^{-9} \text{ (given)}$$

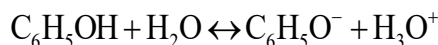
$$K_w = 10^{-14}$$

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

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

44. The ionization constant of phenol is  $1.0 \times 10^{-10}$ . 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:



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,

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

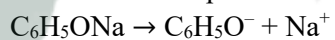
$$= \sqrt{5 \times 10^{-12}}$$

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

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

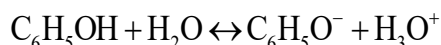
$$[C_6H_5O^-] = 2.2 \times 10^{-6} \text{ M}$$

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



$$\text{Conc.} \quad \quad \quad 0.01$$

Also,



$$\text{Conc. } 0.05 - 0.05\alpha \quad \quad 0.05\alpha \quad 0.05\alpha$$

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

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

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

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

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

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

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

45. Given,  $9.1 \times 10^{-8}$  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  $1.2 \times 10^{-13}$  is the second dissociation constant of  $H_2S$ .

45. Given:

First ionization constant of  $\text{H}_2\text{S} = 9.1 \times 10^{-8}$

Second dissociation constant of  $\text{H}_2\text{S} = 1.2 \times 10^{-13}$

$[\text{H}_2\text{S}] = 0.1\text{M}$

$[\text{HCl}] = 0.1\text{M}$

To calculate the  $[\text{HS}^-]$

In the absence of  $0.1\text{M HCl}$

Let the concentration of  $\text{HS}^-$  ion be  $x\text{M}$



Then, Using the formula:

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

$$K_{a1} = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]}$$

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  $0.1 - x \approx 0.1$

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

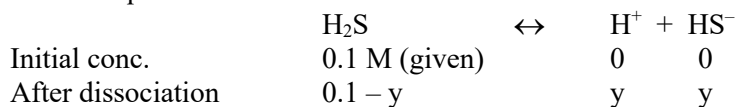
$$\Rightarrow x = \sqrt{9.1 \times 10^{-8}}$$

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

Thus, in the absence of  $\text{HCl}$ , the concentration of  $\text{HS}^-$  ion is  $9.54 \times 10^{-5}\text{M}$ .

In the presence of  $0.1\text{M HCl}$ , let the concentration of  $\text{HS}^-$  ion be  $y\text{M}$ .

Then at equilibrium



Then, using the formula:

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

$$K_{a1} = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]}$$

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  $0.1 - y \approx 0.1$

$$0.1 + y \approx 0.1$$

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

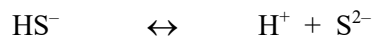
$$\Rightarrow y = 9.1 \times 10^{-8} \text{ M}$$

Thus, in the presence of 0.1M HCl, the concentration of  $\text{HS}^-$  ion is  $9.1 \times 10^{-8} \text{ M}$ .

To calculate  $[\text{S}^{2-}]$

In the absence of HCl

Let the concentration of  $\text{S}^{2-}$  ion be x M



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

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

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

By applying the formula:

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

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

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

$$\therefore 1.2 \times 10^{-13} = \frac{(9.54 \times 10^{-5} \text{ M})(x \text{ M})}{9.54 \times 10^{-5} \text{ M}}$$

$$\Rightarrow x = 1.2 \times 10^{-13} \text{ M}$$

Thus, in the absence of HCl, the concentration of  $\text{S}^{2-}$  ion is  $1.2 \times 10^{-13} \text{ M}$ .

**Case 2:** In the presence of 0.1 M HCl.

Let the concentration of  $\text{S}^{2-}$  ion be x M



$$[\text{HS}^-] = 9.1 \times 10^{-8} \text{ (from first ionization, Case 2)}$$

$$[\text{H}^+] = 0.1 \text{ M (from HCl, Case 2)}$$

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

By applying the formula:

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

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

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

$$\therefore 1.2 \times 10^{-13} = \frac{(0.1 \text{ M})(y \text{ M})}{9.1 \times 10^{-8} \text{ M}}$$

$$\Rightarrow 10.92 \times 10^{-21} = 0.1 y$$

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

Thus, in the presence of 0.1 M HCl, the concentration of  $\text{S}^{2-}$  ion is  $1.092 \times 10^{-19} \text{ M}$ .

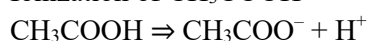
46. The ionization constant of acetic acid is  $1.74 \times 10^{-5}$ . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

46. Given:

$$\text{Ionization constant of acetic acid} = 1.74 \times 10^{-5}$$

0.05 M solution

Ionization of  $\text{CH}_3\text{COOH}$



By applying the formula,

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

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

At equilibrium  $[\text{CH}_3\text{COO}^-] = [\text{H}^+]$

Hence,

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

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

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

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

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

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

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

As,  $[\text{CH}_3\text{COO}^-] = [\text{H}^+]$

Thus, the concentration of acetate ion is  $9.33 \times 10^{-4} \text{ M}$ .

To calculate pH, we apply the formula,

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

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

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

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

$$\Rightarrow \text{pH} = 4 - \log 9.33$$

$$\Rightarrow \text{pH} = 4 - 0.9699$$

$$\Rightarrow \text{pH} = 3.03$$

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  $\text{p}K_a$ .

47. Given:

$$\text{pH of} = 4.15$$

Concentration of HA = 0.01M

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

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

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  $\text{p}K_a$  of an organic acid, we apply the formula:

$$\text{p}K_a = -\log k_a$$

where  $K_a$  is the ionization constant of the acid

Let the HA be the acid

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

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

We can also write,

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

As  $\text{pH} = 4.15$  (given)

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

By taking antilog of both the sides, we get

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

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

Thus, the concentration of anion is  $7.08 \times 10^{-5} \text{ M}$ .

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

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

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

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

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

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

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

$$\text{p}K_a = -\log k_a$$

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

$$\therefore \text{p}K_a = -\log (5.0 \times 10^{-7})$$

$$\Rightarrow \text{p}K_a = -\log 5 - (-7) \log 10$$

$$\Rightarrow \text{p}K_a = 7 - \log 5$$

$$\Rightarrow \text{p}K_a = 7 - 0.699$$

$$\Rightarrow \text{p}K_a = 6.301$$

Thus  $\text{p}k_a$  is 6.301.

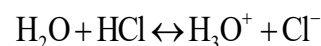
**Note:**  $\text{p}K_a$  is a measure of acid strength. It depends on the identity and chemical properties of the acid.  $\text{pH}$  is a measure of  $[\text{H}^+]$  in a solution. For acids, the smaller the  $\text{p}K_a$ , the more acidic the substance is (the more easily a proton is lost, thus the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

48. Assuming complete dissociation, calculate the  $\text{pH}$  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) 0.003M HCl:



Since HCl is completely ionized,

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

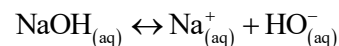
$$\Rightarrow [\text{H}_3\text{O}^+] = 0.003$$

Now,

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] = -\log (.003) \\ &= 2.52\end{aligned}$$

Hence, the pH of the solution is 2.52.

(ii) 0.005MNaOH:



$$[\text{HO}^-] = [\text{NaOH}]$$

$$\Rightarrow [\text{HO}^-] = .005$$

$$\text{pOH} = -\log [\text{HO}^-] = -\log (.005)$$

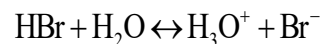
$$\text{pOH} = 2.30$$

$$\therefore \text{pH} = 14 - 2.30$$

$$= 11.70$$

Hence, the pH of the solution is 11.70.

(iii) 0.002 HBr:



$$[\text{H}_3\text{O}^+] = [\text{HBr}]$$

$$\Rightarrow [\text{H}_3\text{O}^+] = .002$$

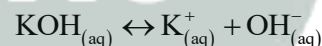
$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log (0.002)$$

$$= 2.69$$

Hence, the pH of the solution is 2.69.

(iv) 0.002 M KOH:



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

$$\Rightarrow [\text{OH}^-] = .002$$

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

$$= 2.69$$

$$\therefore \text{pH} = 14 - 2.69$$

$$= 11.31$$

Hence, the pH of the solution is 11.31.

49. Calculate the pH of the following solutions:

(a) 2 g of TIOH dissolved in water to give 2 litre of solution.

(b) 0.3 g of Ca(OH)<sub>2</sub> 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

$$\text{As we know that } n = \left( \frac{\text{Mass (m)}}{\text{Molar mass (M)}} \right)$$



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

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:

$$\text{Mass of } TiOH(m) = 2g$$

$$\text{Volume}(V) = 2l$$

$$\text{Molar mass of } TiOH(M) = 221 \text{ g/mol}$$

To calculate concentration of  $TiOH$ , we apply the formula,

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

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

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

Now, the ionisation of  $TiOH$



$TiOH$  is completely ionized

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

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

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

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

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

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

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:

$$\text{Mass of } Ca(OH)_2 (m) = 0.3g$$

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

$$\text{Molar mass of } Ca(OH)_2 (M) = 40 \times 2(16 + 1) = 74 \text{ g/mol}$$

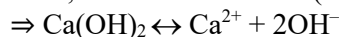
To calculate concentration of  $Ca(OH)_2$ , we apply the formula,

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

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

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

Now, the ionisation of  $\text{Ca}(\text{OH})_2$



$\text{Ca}(\text{OH})_2$  is completely ionized

$$\therefore [\text{Ca}(\text{OH})_2] = 2[\text{OH}^-]$$

$$\Rightarrow 2[\text{OH}^-] = 2 \times 8.1 \times 10^{-3} \text{ M}$$

$$\Rightarrow 16 \times 10^{-3} \text{ M}$$

To calculate pOH, we apply the formula:

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

$$\Rightarrow \text{pOH} = -\log(16 \times 10^{-3})$$

$$\Rightarrow \text{pOH} = -\log 16 - (-3) \log 10$$

$$\Rightarrow \text{pOH} = 3 - 1.201$$

$$\Rightarrow \text{pOH} = 1.79$$

As we know that  $\text{pH} + \text{pOH} = 14$

$$\therefore \text{pH} = 14 - 1.79$$

$$\text{pH} = 12.21$$

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:

$$\text{Mass of NaOH (m)} = 0.3\text{g}$$

$$\text{Volume (V)} = 200 \text{ ml} = \frac{200}{1000} \text{ L} = 0.2\text{L}$$

$$\text{Molar mass of NaOH (M)} = 40 \text{ g/mol}$$

To calculate concentration of NaOH, we apply the formula,

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

$$\Rightarrow [\text{NaOH}] = \left( \frac{0.3\text{g}}{0.2\text{L} \times 40\text{g/mol}} \right)$$

$$\Rightarrow [\text{NaOH}] = 3.75 \times 10^{-2} \text{ M}$$

Now, the ionisation of NaOH



NaOH is completely ionized

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

$$\Rightarrow [\text{OH}^-] = 3.75 \times 10^{-2} \text{ M}$$

To calculate pOH, we apply the formula:

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

$$\Rightarrow \text{pOH} = -\log(3.75 \times 10^{-2}) \text{ M}$$

$$\Rightarrow \text{pOH} = -\log 3.75 - (-2) \log 10$$

$$\Rightarrow \text{pOH} = 2 - \log 3.75$$

$$\Rightarrow \text{pOH} = 1.42$$

As we know that  $\text{pH} + \text{pOH} = 14$

$$\therefore \text{pH} = 14 - 1.42$$

$$\Rightarrow \text{pH} = 12.57$$

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:

$$M_1 = 13.6 \text{ M}$$

$$V_1 = 1 \text{ ml ,}$$

$$V_2 = 1\text{L} = 1000 \text{ ml}$$

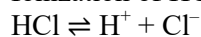
$$\text{As we know that, } M_1 V_1 = M_2 V_2$$

(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



As it is completely ionized

$$\therefore [\text{H}^+] = [\text{HCl}]$$

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

To calculate pH, we apply the formula:

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

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

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

$$\Rightarrow \text{pH} = 2 - \log 1.36$$

$$\Rightarrow \text{pH} = 2 - 0.1335$$

$$\Rightarrow \text{pH} = 1.8665$$

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  $\text{pK}_a$  of bromoacetic acid.

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

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

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

$$= 0.1 \times 0.132$$

$$= 0.0132$$

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

$$= -\log (0.0132)$$

$$= 1.879 : 1.88$$

Now,

$$K_a = C\alpha^2$$

$$= 0.1 \times (0.132)^2$$

$$K_a = .0017$$

$$\text{pK}_a = 2.75$$

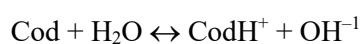
51. The pH of 0.005M codeine ( $\text{C}_{18}\text{H}_{21}\text{NO}_3$ ) solution is 9.95. Calculate its ionization constant and  $\text{pK}_b$ .

51. Given:

pH of Codeine ( $\text{C}_{18}\text{H}_{21}\text{NO}_3$ ) solution = 9.95

$[\text{Cod}] = 0.005 \text{ M}$

Ionisation of Cod:



As we know that  $\text{pH} + \text{pOH} = 14$

$$\therefore 9.95 + \text{pOH} = 14$$

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

$$\Rightarrow \text{pOH} = 4.05$$

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

$$\therefore 4.05 = -\log[\text{OH}^-]$$

By taking antilog of both the sides, we get

$$\text{Antilog } 4.05 = -[\text{OH}^-]$$

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

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,  $\text{Cod} + \text{H}_2\text{O} \leftrightarrow \text{CodH}^+ + \text{OH}^-$

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

As the reaction is completely ionized,

$$\therefore [\text{CodH}^+] = [\text{OH}^-]$$

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

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

$$[\text{Cod}] = 0.005\text{M}$$

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

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

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

To calculate  $\text{P}k_b$  we apply the formula:

$$\text{P}k_a = -\log K_b$$

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

$$\therefore \text{p}k_b = -\log (1.588 \times 10^{-6})$$

$$\Rightarrow \text{P}k_b = -\log 1.588 - (-6) \log 10$$

$$\Rightarrow \text{P}k_b = 5.80$$

Thus, the  $\text{P}k_b$  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.  $K_b = 4.27 \times 10^{-10}$

$$c = 0.001\text{M}$$

$$\text{pH} = ?$$

$$a = ?$$

$$k_b = c\alpha^2$$

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

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

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

$$\begin{aligned} \text{Then, } [\text{anion}] = c\alpha &= .001 \times 65.34 \times 10^{-5} \\ &= .065 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} \text{pOH} &= -\log (.065 \times 10^{-5}) \\ &= 6.187 \end{aligned}$$

$$\text{pH} = 7.813$$

Now,

$$K_a \times K_b = K_w$$

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

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

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

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

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

$$\text{Antilog } -4.74 = K_a$$

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

By applying the formula,  $k_a = c\alpha^2$

Where  $c$  is the concentration and  $\alpha$  is the degree of ionization

We can also write,

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

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

$$C = 0.05M \text{ (given)}$$

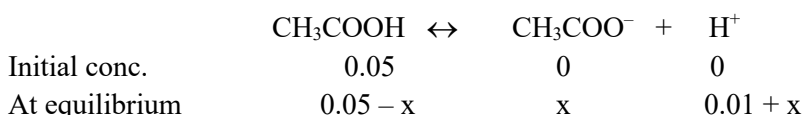
$$\therefore \alpha = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}}$$

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

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



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

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

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

$K_a$  is the ionization constant

$c$  is the concentration

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

$$C = 0.01M \text{ (given)}$$

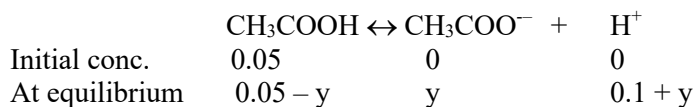
$$\therefore \alpha = \sqrt{\left( \frac{1.82 \times 10^{-5}}{0.01M} \right)}$$

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

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

(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



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

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

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

$K_a$  is the ionization constant

$c$  is the concentration

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

$$C = 0.1\text{M (given)}$$

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

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

Thus, the degree of ionization in the presence of 0.1M HCl is  $1.82 \times 10^{-4}$ .

54. The ionization constant of dimethylamine is  $5.4 \times 10^{-4}$ . 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.  $K_b = 5.4 \times 10^{-4}$

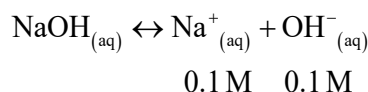
$$c = 0.02 \text{ M}$$

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

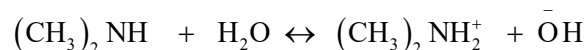
$$= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}}$$

$$= 0.1643$$

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



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 0.1 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:

$$\Rightarrow \text{pH} = 6.83$$

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

$$\Rightarrow 6.83 = -\log [\text{H}^+]$$

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

(b) Human stomach fluid, 1.2:

$$\Rightarrow \text{pH} = 1.2$$

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

$$\Rightarrow [\text{H}^+] = 0.063$$

(c) Human blood, 7.38:

$$\Rightarrow \text{pH} = 7.38$$

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

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

(d) Human saliva, 6.4:

$$\Rightarrow \text{pH} = 6.4$$

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

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

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

**56.** The hydrogen ion concentration in the given substances can be calculated by using the given reaction:  $\text{pH} = -\log[\text{H}^+]$

(i) pH of milk = 6.8

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

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

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

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

$$= 1.5 \times 10^{-7} \text{ M}$$

(ii) pH of black coffee = 5.0

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

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

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

$$[\text{H}^+] = \text{antilog} (-5.0)$$

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

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(iii) pH of tomato juice = 4.2

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

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

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

$$[\text{H}^+] = \text{antilog} (-4.2)$$

$$= 6.31 \times 10^{-5} \text{ M}$$

(iv) pH of lemon juice = 2.2

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

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

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

$$[\text{H}^+] = \text{antilog} (-2.2)$$

$$= 6.31 \times 10^{-3} \text{ M}$$

(v) pH of egg white = 7.8

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

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

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

$$[\text{H}^+] = \text{antilog} (-7.8)$$

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

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) = 0.561 g

Volume (V) = 200 ml =  $\frac{200}{1000}$  L = 0.2L

Molar mass of KOH (M) = 56 g/mol

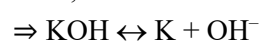
To calculate concentration of KOH, we apply the formula,

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

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

$$\Rightarrow [\text{KOH}] = 0.05 \text{ M}$$

Now, the ionisation of KOH



At equilibrium

$$\therefore [\text{K}] = [\text{OH}^-] = 0.05 \text{ M}$$

To calculate  $[\text{H}^+]$ , we apply the formula:

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

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

Using the formula, we write

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

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

$$[\text{OH}^-] = 0.05 \text{ M (calculated)}$$

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

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

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

To calculate pH, we apply the formula:

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

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

$$\Rightarrow \text{pH} = 13 - \log 2$$

$$\Rightarrow \text{pH} = 12.69$$

Thus, the pH is 12.69.

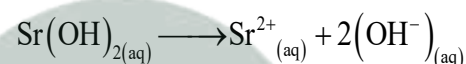
**58.** The solubility of  $\text{Sr}(\text{OH})_2$  at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

**58.** Solubility of  $\text{Sr}(\text{OH})_2 = 19.23$  g/L

Then, concentration of  $\text{Sr}(\text{OH})_2$

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

$$= 0.1581 \text{M}$$



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

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

Now,

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

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

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

$$\therefore \text{pH} = 13.495; 13.50$$

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

**59.** Given:

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

$$C = 0.005 \text{M}$$

Assuming  $\alpha$  to be very small, applying formula directly, we have

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

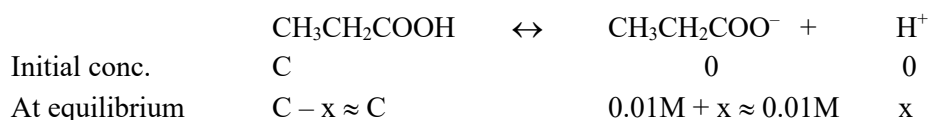
$$\Rightarrow \alpha = \sqrt{\frac{1.32 \times 10^{-5}}{0.005 \text{M}}}$$

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

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

Let the degree of ionization of propanoic acid be x.

Ionization of propanoic acid



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

Hence,

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

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

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.  $c = 0.01 \text{ M}$

$$\text{pH} = 2.34$$

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

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

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

Also,

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

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

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

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

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  $4.5 \times 10^{-4}$ . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

61. Given:

$$K_a \text{ of nitrous acid is } 4.5 \times 10^{-4}$$

$$[\text{NO}_2] = 0.04 \text{ M}$$

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),

$$K_h = K_w / K_a$$

$\text{NaNO}_2$  is the salt of a strong base (NaOH) and a weak acid ( $\text{HNO}_2$ )

Using the formula, we write

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

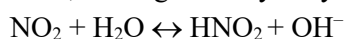
As  $K_w = 10^{-14}$  (same value)

$K_a = 4.5 \times 10^{-4}$  (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  $0.22 \times 10^{-10}$ .



$[\text{NO}_2] = 0.04 \text{ M}$  (given)

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

$$[\text{NO}_2] = 0.04 \text{ M} - x \approx 0.04 \text{ M}$$

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

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

Using the formula,

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

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

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

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

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

Now,

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

Using the formula, we write

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

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

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

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

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

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

$$\text{pH} = -\log (\text{H}^+)$$

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

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

$$\Rightarrow \text{pH} = 7.96$$

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,

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

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

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

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

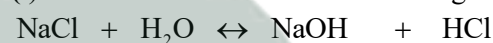
$$\text{Now, } K_h = \frac{K_w}{K_a}$$

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

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

NaCl, KBr, NaCN,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_2$  and KF

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



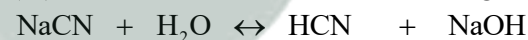
Strong base    Strong acid

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



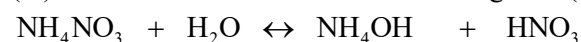
Strong base    Strong acid

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



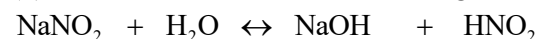
Weak acid    Strong base

(iv)  $\text{NH}_4\text{NO}_3$  is acidic as it is a salt of strong acid ( $\text{HNO}_3$ ) and weak base ( $\text{NH}_4\text{OH}$ ).



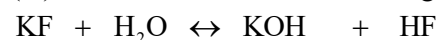
Weak acid    Strong base

(v)  $\text{NaNO}_2$  is basic as it is a salt of strong base (NaOH) and weak acid ( $\text{HNO}_2$ ).



Strong base    Weak acid

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



Strong base    Weak acid

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

64. It is given that  $K_a$  for  $\text{ClCH}_2\text{COOH}$  is  $1.35 \times 10^{-3}$ .

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

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

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

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

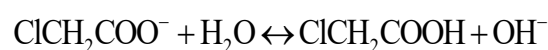
$$= 0.116$$

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

$$= .0116$$

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

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



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

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

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

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

$$\text{Also, } K_b = \frac{x^2}{0.1} \quad (\text{where } x \text{ is the concentration of } \text{OH}^- \text{ and } \text{ClCH}_2\text{COOH})$$

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

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

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

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

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

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

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

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

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

$$= 7.94$$

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

65. Given:

$$\text{Ionic product of water } (K_w) = 2.7 \times 10^{-14}$$

$$\text{As we know that } K_w = [\text{H}^+][\text{OH}^-]$$

$$\text{For neutral water } [\text{H}^+] = [\text{OH}^-]$$

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

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

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

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

$$\begin{aligned} \text{Since, } \text{pH} &= -\log [\text{H}^+] \\ \Rightarrow \text{pH} &= -\log (1.643 \times 10^{-7}) \\ \Rightarrow \text{pH} &= -\log 1.643 + 7 \log 10 \\ \Rightarrow \text{pH} &= 7 - 0.1256 \\ \Rightarrow \text{pH} &= 6.78 \end{aligned}$$

Thus, the pH of the neutral water is 6.78.

66. Calculate the pH of the resultant mixtures:
- 10 mL of 0.2M Ca(OH)<sub>2</sub> + 25 mL of 0.1M HCl
  - 10 mL of 0.01M H<sub>2</sub>SO<sub>4</sub> + 10 mL of 0.01M Ca(OH)<sub>2</sub>
  - 10 mL of 0.1M H<sub>2</sub>SO<sub>4</sub> + 10 mL of 0.1M KOH

66. (a) Moles of H<sub>2</sub>O<sup>+</sup> =  $\frac{25 \times 0.1}{1000} = .0025 \text{ mol}$

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

Thus, excess of OH<sup>-</sup> = .0015 mol

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

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ &= 1.36 \end{aligned}$$

$$\text{pH} = 14 - 1.36$$

$$= 12.63 \quad (\text{not matched})$$

(b) Moles of H<sub>3</sub>O<sup>+</sup> =  $\frac{2 \times 10 \times 0.01}{1000} = .0002 \text{ mol}$

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

Since there is neither an excess of H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup>.

(c) Moles of H<sub>3</sub>O<sup>+</sup> =  $\frac{2 \times 10 \times 0.1}{1000} = .002 \text{ mol}$

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

Excess of H<sub>3</sub>O<sup>+</sup> = .001 mol

$$\text{Thus, } [\text{H}_3\text{O}^+] = \frac{.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = .05$$

$$\begin{aligned} \therefore \text{pH} &= -\log (0.05) \\ &= 1.30 \end{aligned}$$

The solution is neutral. Hence, pH = 7.

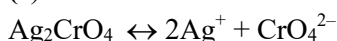
67. Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9. Determine also the molarities of individual ions.

67. To determine the solubility, we apply the formula

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

Where K<sub>sp</sub> is the solubility product which is equal to the product of ionic concentrations in a saturated solution.

- (a) Silver chromate ionization of silver chromate:



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:



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  $BaCrO_4$

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

$$[CrO_4^{2-}] = s$$

$$\therefore 1.2 \times 10^{-10} = (s \times s)$$

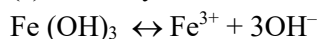
$$\Rightarrow 1.2 \times 10^{-10} = (s)^2$$

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

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

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

(c) Ferric hydroxide ionization of ferric hydroxide



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  $Fe(OH)_3$

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

$$[3\text{OH}^-] = 3s$$

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

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

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

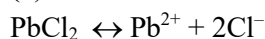
$$\Rightarrow s = \sqrt[4]{0.37 \times 10^{-38}}$$

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

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

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

(d) Lead chloride ionization of lead chloride:



As we know that,

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

Where A and B are the ions dissolved

In the above reaction,

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

$$\Rightarrow [\text{B}^-] = [\text{Cl}^-]$$

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

As  $K_{sp}$  of  $\text{PbCl}_2 = 1.6 \times 10^{-5}$  (given)

Let 's' be the solubility of  $\text{PbCl}_2$

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

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

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

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

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

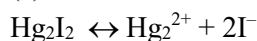
$$\Rightarrow s = \sqrt[3]{0.4 \times 10^{-5}}$$

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

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

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

(e) Mercurous Iodide ionization of mercurous iodide:



As we know that,

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

Where A and B are the ions dissolved

In the above reaction,

$$\Rightarrow [\text{A}^+] = [\text{Hg}_2^{2+}]$$

$$\Rightarrow [\text{B}^-] = [\text{I}^-]^2$$

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

As  $K_{sp}$  of  $\text{Hg}_2\text{I}_2 = 4.5 \times 10^{-29}$

Let 's' be the solubility of  $\text{Hg}_2\text{I}_2$

$$[\text{Hg}_2^{2+}] = s$$

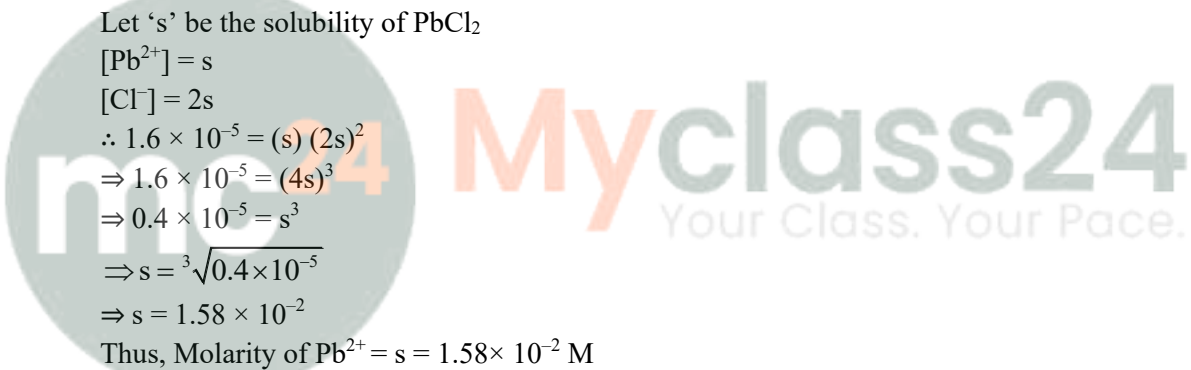
$$[\text{I}^-] = 2s$$

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

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

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

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



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

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

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

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

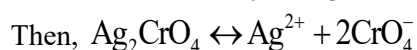
$\Rightarrow$  In a saturated solution,  $K_{sp} = [\text{A}^+][\text{B}^-]$ .

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

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

68. The solubility product constant of  $\text{Ag}_2\text{CrO}_4$  and  $\text{AgBr}$  are  $1.1 \times 10^{-12}$  and  $5.0 \times 10^{-13}$  respectively. Calculate the ratio of the molarities of their saturated solutions.

68. Let  $s$  be the solubility of  $\text{Ag}_2\text{CrO}_4$ .

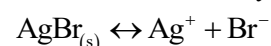


$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

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

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

Let  $s'$  be the solubility of  $\text{AgBr}$ .



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

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

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

$$\frac{s}{s'} = \frac{6.5 \times 10^{-5} \text{ M}}{7.07 \times 10^{-7} \text{ M}} = 91.9$$

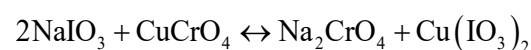
69. Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate  $K_{sp} = 7.4 \times 10^{-8}$ ).

69. Given:

$$K_{sp} \text{ of cupric iodate} = 7.4 \times 10^{-8}$$

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

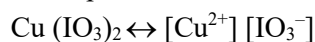
Ionization of sodium iodate:



$$\text{After mixing, } [\text{NaIO}_3] = [\text{IO}_3^-] = \frac{0.002 \text{ M}}{2} = 10^{-3} \text{ M}$$

$$[\text{CuCrO}_4] = [\text{Cu}^{2+}] = \frac{0.002 \text{ M}}{2} = 10^{-3} \text{ M}$$

For cupric iodate, the ionization is:



As we know that,

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

Where A and B are the ions dissolved

In the above reaction,

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

$$\Rightarrow [\text{B}^-] = [\text{IO}_3^-]$$

$$\therefore K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]$$

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

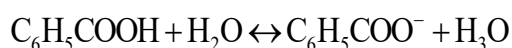
$$\Rightarrow K_{sp} = 10^{-9}$$

As we know that precipitation only occur when  $K_{sp} < [\text{A}^+][\text{B}^-]$ .

70. The ionization constant of benzoic acid is  $6.46 \times 10^{-5}$  and  $K_{sp}$  for silver benzoate are  $2.5 \times 10^{-13}$ . 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,

$$[\text{H}_3\text{O}^+] = 6.45 \times 10^{-4} \text{ M}$$



$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let the solubility of  $\text{C}_6\text{H}_5\text{COOAg}$  be  $x$  mol/L.

Then,

$$[\text{Ag}^+] = x$$

$$[\text{C}_6\text{H}_5\text{COOH}] + [\text{C}_6\text{H}_5\text{COO}^-] = x$$

$$10[\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COO}^-] = x$$

$$[\text{C}_6\text{H}_5\text{COO}^-] = \frac{x}{11}$$

$$K_{sp} [\text{Ag}^+] [\text{C}_6\text{H}_5\text{COO}^-]$$

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

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

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

Now, let the solubility of  $\text{C}_6\text{H}_5\text{COOAg}$  be  $x'$  mol/L.

Then,  $[\text{Ag}^+] = x'$  M and  $[\text{C}_6\text{H}_5\text{COO}^-] = x'$  M.

$$K_{sp} = [\text{Ag}^+] [\text{C}_6\text{H}_5\text{COO}^-]$$

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

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

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

Hence,  $\text{C}_6\text{H}_5\text{COOAg}$  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,  $K_{sp} = 6.3 \times 10^{-18}$ ).

71. Given:

$$K_{sp} \text{ of FeS} = 6.3 \times 10^{-18}$$

Let the concentration of solution of  $\text{FeSO}_4$  and  $\text{Na}_2\text{S}$  is  $x$  mol/L.

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

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

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

Ionization of ferrous sulphide:



As we know that,

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

Where A and B are the ions

In the above reaction,

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

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

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

As  $K_{sp} = 6.3 \times 10^{-18}$  (given)

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

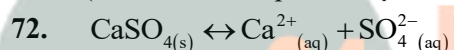
$$\Rightarrow \left(\frac{x^2}{4}\right) = 6.3 \times 10^{-18}$$

$$\text{Thus, } x = 5.02 \times 10^{-9}$$

As we know that precipitation only occur when  $K_{sp} < [\text{A}^+][\text{B}^-]$ .

Thus, if the concentration of ferrous sulphate and sodium sulphide are equal to or less than that of  $5.02 \times 10^{-9}$ , 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  $9.1 \times 10^{-6}$ ).



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

Let the solubility of  $\text{CaSO}_4$  be  $s$ .

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

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

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

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

Solubility of  $\text{CaSO}_4$  in gram/L

$$= 3.02 \times 10^{-3} \times 136$$

$$= 0.41 \text{ g/L}$$

This means that we need 1L of water to dissolve 0.41g of  $\text{CaSO}_4$ .

Therefore, to dissolve 1g of  $\text{CaSO}_4$  we require  $= \frac{1}{0.41} \text{ L} = 2.44 \text{ L}$  of water.

73. The concentration of sulphide ion in 0.1M 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  $\text{CdCl}_2$ . in which of these solutions precipitation will take place?

73. Given:

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

Volume of solution containing  $\text{S}^{2-}$  ion = 10 ml

Volume of metals salt solution added = 5ml

As 10 ml of solution containing  $\text{S}^{2-}$  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:

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

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

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

$$\Rightarrow [Fe^{2+}] = [Mn^{2+}] = [Zn^{2+}] = [Cd^{2+}] = \frac{5}{15} \times 0.04 = 1.33 \times 10^{-2}$$

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<sub>2</sub> and CdCl<sub>2</sub> solutions will be precipitated.



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