

CBSE NCERT Solutions for Class 11 Chemistry Chapter 7

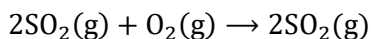
Back of Chapter Questions

1. A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
- What is the initial effect of the change on vapour pressure?
 - How do rates of evaporation and condensation change initially?
 - What happens when equilibrium is restored finally, and what will be the final vapour pressure?

Solution:

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

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



Solution:

Given: $[SO_2] = 0.60M$,

$[O_2] = 0.82M$

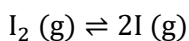
$[SO_3] = 1.90M$

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

$$\begin{aligned}
 K_c &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \\
 &= \frac{(1.90)^2 \text{M}^2}{(0.60)^2(0.821) \text{M}^3} \\
 &= 12.239 \text{M}^{-1}
 \end{aligned}$$

Hence, K for the equilibrium is = 12.239 M⁻¹.

3. At a certain temperature and total pressure of 10⁵Pa, iodine vapour contains 40% by volume of I atoms



Calculate K_p for the equilibrium.

Solution:

Given: total pressure of 10⁵Pa

I atoms = 40% by volume

Partial pressure = mole fraction × total pressure

$$\text{Partial pressure of I atoms } (p_1) = \frac{40}{100} \times p_{\text{total}} \quad (\because \text{volume} \propto \text{mole})$$

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

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

Partial pressure of I₂ molecules,

$$p_{\text{I}_2} = \frac{60}{100} \times p_{\text{total}}$$

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

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

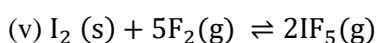
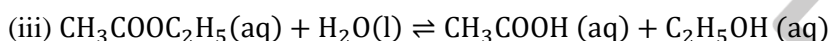
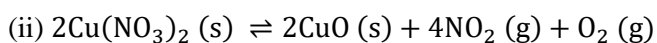
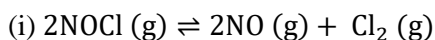
$$\text{Formula : } K_p = \frac{(\text{partial pressure of product})}{(\text{partial pressure of reactant})}$$

$$K_p = \frac{(p_1)^2}{(P_{1_2})}$$

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

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

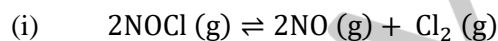
4. Write the expression for the equilibrium constant, K_c for each of the following reactions:



Solution:

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

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

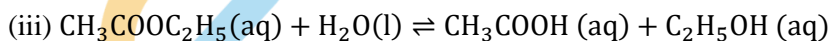


$$K_c = \frac{[\text{NO (g)}]^2 [\text{Cl}_2 \text{(g)}]}{[\text{NOCl (g)}]^2}$$



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

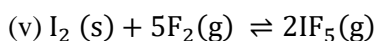
$$= [\text{NO}_2 \text{(g)}]^4 [\text{O}_2 \text{(g)}]$$



$$K_c = \frac{[\text{CH}_3\text{COOH (aq)}]^2 [\text{C}_2\text{H}_5\text{OH (aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_5 \text{(aq)}] [\text{H}_2\text{O(l)}]}$$

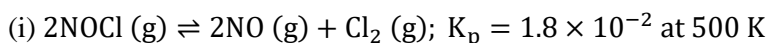


$$K_c = \frac{[\text{Fe(OH)}_3 \text{(s)}]}{[\text{Fe}^{+3} \text{(aq)}] [\text{OH}^- \text{(aq)}]^3} = \frac{1}{[\text{Fe}^{+3} \text{(aq)}] [\text{OH}^- \text{(aq)}]^3}$$



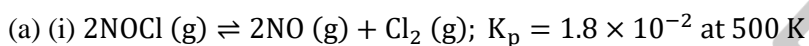
$$K_c = \frac{[\text{IF}_5 \text{(g)}]^2}{[\text{I}_2 \text{(s)}] [\text{F}_2 \text{(g)}]^5} = \frac{[\text{IF}_5 \text{(g)}]^2}{[\text{F}_2 \text{(g)}]^5}$$

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



Solution:

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



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

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

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

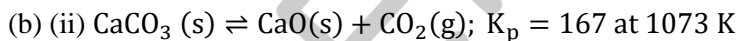
$$K_p = 1.8 \times 10^{-2}$$

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

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

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

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



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

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

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

$$K_p = 167$$

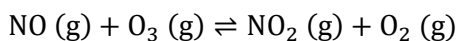
Now, put all values in a formula $K_p = K_c(\text{RT})^{\Delta n}$

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

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

$$= 1.87 \text{ (approximately)}$$

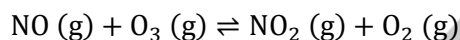
6. For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K



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

Solution:

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



It is given that K_c for the forward reaction is $K_c = \frac{[\text{NO}_2 \text{ (g)}][\text{O}_2 \text{ (g)}]}{[\text{NO (g)}][\text{O}_3 \text{ (g)}]} = 6.3 \times 10^{14}$

Then, K'_c for the reverse reaction = $\frac{[\text{NO (g)}][\text{O}_3 \text{ (g)}]}{[\text{NO}_2 \text{ (g)}][\text{O}_2 \text{ (g)}]}$

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

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

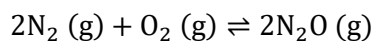
Solution:

For a pure substance (both solids and liquids),

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

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

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



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

Solution:

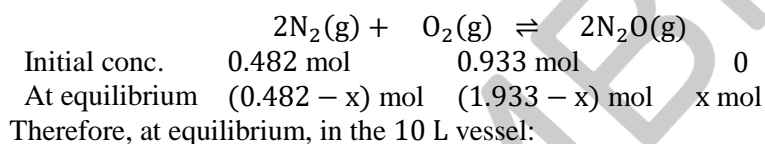
Given: *initial* mol $\text{N}_2 = 0.482$

initial mol $\text{O}_2 =$ and 0.933

the volume of container = 10 L

Let the concentration of N_2O at equilibrium be x .

The given reaction is:



Therefore, at equilibrium, in the 10 L vessel:

$$[\text{N}_2] = \frac{0.482}{10} = 0.0482 \text{ mol L}^{-1} \text{ and } [\text{O}_2] = \frac{0.933}{10} = 0.0933 \text{ mol L}^{-1} \quad [\text{N}_2\text{O}] = \frac{x}{10} \text{ mol L}^{-1}$$

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

$$K_c = \frac{[\text{N}_2\text{O}(\text{g})]^2}{[\text{N}_2(\text{g})]^2[\text{O}_2(\text{g})]}$$

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

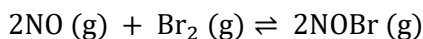
$$\Rightarrow \frac{x^2}{100} = 2.0 \times 10^{-37} \times (0.0482)^2 \times (0.0933)$$

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

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

$$[\text{N}_2\text{O}] = \frac{x}{10} = \frac{6.6 \times 10^{-20}}{10} = 6.6 \times 10^{-21}$$

9. Nitric oxide reacts with Br₂ and gives nitrosyl bromide as per reaction is given below:



When 0.087 mol of NO and 0.0437 mol of Br₂ are mixed in a closed container at a constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br₂.

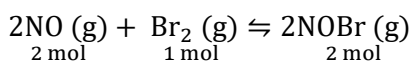
Solution:

Given: initial mol of NO = 0.087

Initial mol of Br₂ = 0.0437

mol of NOBr is obtained at equilibrium = 0.0518

The given reaction is:



According to stoichiometry, 2 mol of NOBr are formed from 2 mol of NO and 1 mole of Br₂ react, 2 mol of NOBr is formed

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

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

$$[\text{NO}] = 0.087 \text{ mol} \quad [\text{Br}_2] = 0.0437 \text{ mol}$$

Therefore, the amount of NO present at equilibrium = 0.087 - 0.0518 = 0.0352 mol

And, the amount of Br₂ present at equilibrium = 0.0437 - 0.0259 = 0.0178 mol

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

$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ What is K_c at this temperature?

Solution:

given :

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

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

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

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

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

Put all values in the above formula

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

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

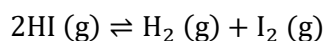
$$= (2.0 \times 10^{10} \text{ bar}^{-1})(0.0831 \text{ L bar K}^{-1}\text{mol}^{-1} \times 450\text{K})$$

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

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

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

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

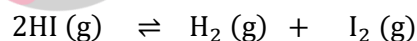


Solution:

Given: pressure = 0.2 atm

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

The initial concentration of HI is 0.2 atm. At equilibrium, it has a partial pressure of 0.04 atm. Therefore, a decrease in the pressure of HI is $0.2 - 0.04 = 0.16$. The given reaction is:



Initial conc.	0.2 atm,	0	0
At equilibrium	0.04atm	0.16	0.16
		$\frac{0.16}{2}$	$\frac{0.16}{2}$
		= 0.08 atm	= 0.08atm

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

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

$$\begin{aligned} &= \frac{0.08 \times 0.08}{(0.04)^2} \\ &= \frac{0.0064}{0.0016} \\ &= 4.0 \end{aligned}$$

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

- 12.** A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2 . Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Solution:

Given: mol of $N_2 = 1.57$

mol of $H_2 = 1.92$

mol of $NH_3 = 8.13$

the volume of vessel = 20 Liter

temperature = 500 K

$K_c = 1.7 \times 10^2$

The given reaction is:



The given concentration of various species is

$$[N_2] = \frac{1.57}{20} \text{ mol L}^{-1} \quad [H_2] = \frac{1.92}{20} \text{ mol L}^{-1} \quad [NH_3] = \frac{8.13}{20} \text{ mol L}^{-1}$$

Now, reaction quotient Q_c is:

$$\begin{aligned} Q_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ &= \frac{\left(\frac{8.13}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3} \\ &= 2.4 \times 10^3 \end{aligned}$$

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,

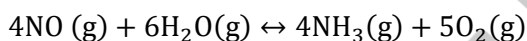
$$K_c = \frac{[\text{NH}_3]^4[\text{O}_2]^5}{[\text{NO}]^4[\text{H}_2\text{O}]^6}$$

Write the balanced chemical equation corresponding to this expression.

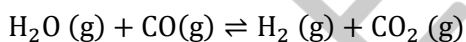
Solution:

$$K_c = \frac{\text{product of the molar concentration of product}}{\text{product of the molar concentration of reactant}}$$

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



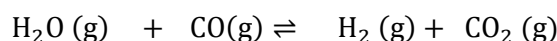
14. One mole of H_2O and one mole of CO is taken in 10 L vessel and heated to 725 K. At equilibrium, 40% of water (by mass) reacts with CO according to the equation,



Calculate the equilibrium constant for the reaction.

Solution:

The given reaction is:

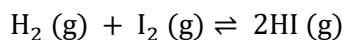


Initial conc	$\frac{1}{10}\text{M}$	$\frac{1}{10}\text{M}$	0	0
At equilibrium	$\frac{1-0.4}{10}\text{M}$	$\frac{1-0.4}{10}\text{M}$	$\frac{0.4}{10}\text{M}$	$\frac{0.4}{10}\text{M}$
	= 0.06 M	= 0.06 M	= 0.04 M	= 0.04 M

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

$$K_c = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} = \frac{[0.04][0.04]}{[0.06][0.06]} = 0.444 \text{ (approximately)}$$

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



is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

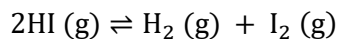
Solution:

Given: equilibrium constant K_c for the reaction $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightleftharpoons 2\text{HI} (\text{g})$ is 54.8.

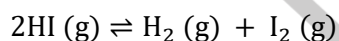
temperature = 700 K

equilibrium constant K_c for the reaction $\frac{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}{[\text{HI}(\text{g})]^2} = 54.8$

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



$$K'_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = \frac{1}{54.8}$$



0.5 x x

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

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

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

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

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

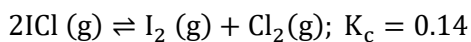
$$\Rightarrow x^2 = \frac{0.25}{54.8}$$

$$\Rightarrow x = 0.06754$$

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

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

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



Solution:

The given reaction is:



Initial conc. 0.78 M 0 0

Conc. at equilibrium (0.78 – 2x)M xM xM

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

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

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

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

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

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

Hence, at equilibrium,

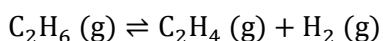
$$[\text{H}_2] = x\text{M} = 0.167\text{M}$$

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

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

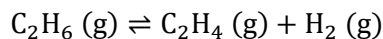
$$= 0.446 \text{ M}$$

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?



Solution:

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



Initial conc.	4.0 atm	0	0
At equilibrium	$4.0 - p$	p	p

Formula : $\frac{p_{\text{C}_2\text{H}_4} \times p_{\text{H}_2}}{p_{\text{C}_2\text{H}_6}} = K_p$

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

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

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

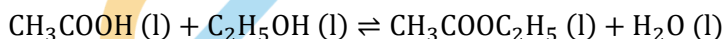
$$\text{Now, } p = \frac{-0.04 \pm \sqrt{(0.04)^2 - 4 \times 1 \times (-0.16)}}{2 \times 1}$$

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

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

$$= 0.38$$

- 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 some time. Has equilibrium been reached?

Solution:

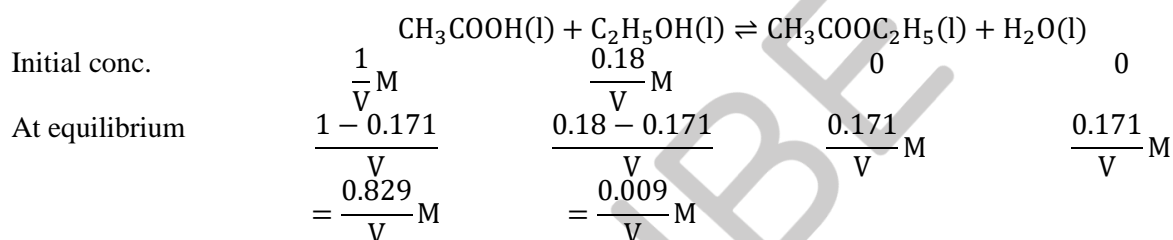
- (i) water is not in excess and is not a solvent in this reaction so all will be considered in the equilibrium expression

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

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

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

The given reaction is:

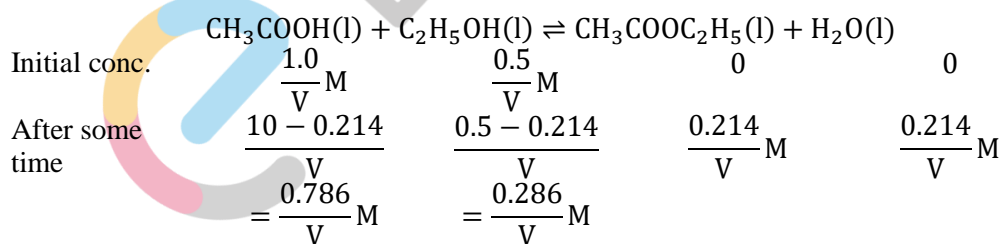


Therefore, the equilibrium constant for the given reaction is:

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.009}{V}} = 3.919 \approx 3.92$$

- (i) (ii) temperature = 293 K,
 Initial mol of acetic acid = 1
initial mol of ethanol = 0.5
 mol of ethyl acetate formed = 0.214

Let the volume of the reaction mixture be V.



Therefore, the reaction quotient is,

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

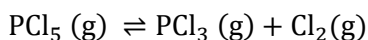
$$= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}}$$

$$= 0.2037$$

$$= 0.204 \text{ (approximately)}$$

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

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



Solution:

Given : temperature = 473

After equilibrium concentration of $\text{PCl}_5 = 0.5 \times 10^{-1} \text{ mol L}^{-1}$

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

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



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

Now we can write the expression for equilibrium as:

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

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

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

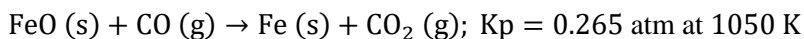
$$\Rightarrow x = 2.04 \times 10^{-2}$$

$$= 0.0204 \approx 0.02$$

Therefore, at equilibrium,

$$[\text{PCl}_3] = [\text{Cl}_2] = x = 0.02 \text{ mol L}^{-1}$$

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



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

Solution:

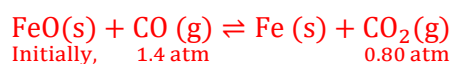
Given: K_p = 0.265 atm

Temperature = 1050K

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

initial partial pressures of CO₂ (P_{CO₂}) = 0.80 atm

For the given reaction,



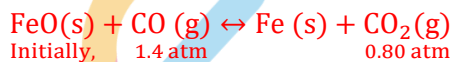
$$\begin{aligned} Q_p &= \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \\ &= \frac{0.80}{1.4} \\ &= 0.571 \end{aligned}$$

It is given that K_p = 0.265.

Since Q_c > K_p, the reaction will proceed in the backward direction.

Therefore, we can say that the pressure of CO will increase while the pressure of CO₂ will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO₂ 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 pressure of CO₂ (P_{CO₂}) = 0.80 – 0.339 = 0.461 atm

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

21. Equilibrium constant, K_c for the reaction



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

Solution:

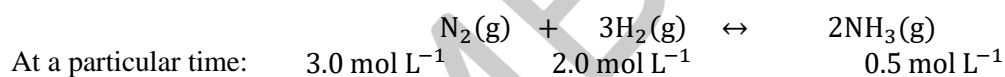
given: *temperature* = 500 K

$$K_c = 0.061$$

composition of $\text{N}_2 = 3.0 \text{ mol L}^{-1}$

composition of $\text{H}_2 = 2.0 \text{ mol L}^{-1}$

composition of $\text{NH}_3 = 0.5 \text{ mol L}^{-1}$.



$$\text{Formula: } Q_c = \frac{[\text{product}]}{[\text{reactant}]} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3}$$

$$= 0.0104$$

It is given that $K_c = 0.061$

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

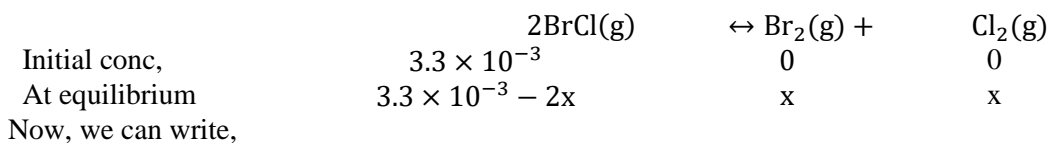
Since $Q_c < K_c$, the reaction will proceed in the forward direction to reach equilibrium.

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

$2\text{BrCl}(\text{g}) \rightleftharpoons \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g})$ 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?

Solution:

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



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

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

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

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

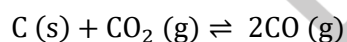
$$\Rightarrow 12.32x = 18.678 \times 10^{-3}$$

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

Therefore, at equilibrium,

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

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



Calculate K_c for this reaction at the above temperature.

Solution:

Given : CO by mass = 90.55%

Temperature = 1127 k

Pressure = 1 atm

We know *molecular weight of CO₂* = 44

molecular weight of CO = 28

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

Mass of CO = 90.55 g

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

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

$$\text{Number of moles of CO}_2 (n_{\text{CO}_2}) = \frac{\text{weight of CO}_2}{\text{molecular weight of CO}_2} = \frac{9.45}{44} = 0.215 \text{ mol}$$

$$\text{The partial pressure of CO } (p_{\text{CO}}) = \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2}} \times p_{\text{total}}$$

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

$$= 0.938 \text{ atm}$$

$$\text{Partial pressure of CO}_2 (p_{\text{CO}_2}) = \frac{\text{mole of CO}_2}{\text{total moles}} \times p_{\text{total}} = \frac{n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \times p_{\text{total}}$$

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

$$= 0.062 \text{ atm}$$

$$\text{Therefore, } K_p = \frac{\text{the partial pressure of the product}}{\text{the partial pressure of reactant}} = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.938)^2}{0.062} = 14.19$$

For the given reaction,

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

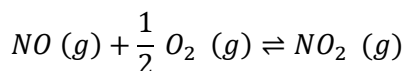
Formula : $K_p = K_c(RT)^{\Delta n}$ put the values in the formula

$$\Rightarrow 14.19 = K_c(0.082 \times 1127)^1$$

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

$$\approx 0.154$$

- 24.** Calculate a) ΔG^\ominus and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K



where

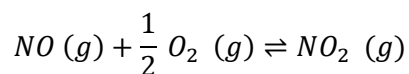
$$\Delta_1 G^\ominus (\text{NO}_2) = 52.0 \text{ kJ/mol}$$

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

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

Solution:

For the given reaction,



$$\Delta_f G^\circ(NO_2) = 52.0 \text{ kJ/mol}$$

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

$$\Delta_f G^\circ(O_2) = 0 \text{ kJ/mol}$$

Formula : $\Delta_r G^\circ = \Delta_f G^\circ(\text{products}) - \Delta_f G^\circ(\text{Reactants})$

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

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

(b) formula : $\Delta_r G^\circ = -RT \ln K_c$

$$\Delta_r G^\circ = -2.303 RT \log K_c$$

Put all values in above formula

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

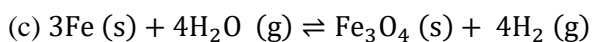
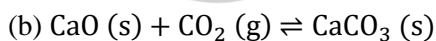
$$\log K_c = 6.134$$

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

$$K_c = 1.36 \times 10^6$$

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

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

**Solution:**

(a) The number of moles of reaction products will increase. According to Le Chatelier's principle, if pressure is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more. In the given reaction, the number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward direction. As a result, the number of moles of reaction products

will increase.

- (b) The number of moles of reaction products will decrease.
 (c) The number of moles of reaction products remains the same.

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

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

Solution:

- (i) $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \quad \Delta n_g = 1$
 (ii) $\text{CH}_4(\text{g}) + 2\text{S}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \quad \Delta n_g = 0$
 (iii) $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g}) \quad \Delta n_g = 1$
 (iv) $2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \quad \Delta n_g = -2$
 (v) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \quad \Delta n_g = 1$
 (vi) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \quad \Delta n_g = 1$

The reaction is given in (ii) $\Delta n_g = 0$ no effect of pressure and no effect on equilibrium because of the number of moles of gaseous reactants is the same that of gaseous products.

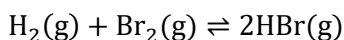
(i), (iii), (iv), (v), and (vi) affected by pressure

The reaction is given in (iv) $\Delta n_g = -2$

will proceed in the forward direction because of the number of moles of gaseous reactants is more than that of gaseous products.

The reactions are given in (i), (iii), (v), and (vi) in all $\Delta n_g = +1$ will shift in the backward direction because the number of moles of gaseous reactants is less than that of gaseous products.

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



Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Solution:

K_p for the reaction $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g}) = 1.6 \times 10^5$.

$$K_p = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]}$$

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

$$K'_p = \frac{[\text{H}_2][\text{Br}_2]}{[\text{HBr}]^2} = \frac{1}{K_p} = \frac{1}{1.6 \times 10^5} = 6.25 \times 10^{-6}$$

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

	$2\text{HBr}(\text{g})$	\leftrightarrow	$\text{H}_2(\text{g})$	$+$	$\text{Br}_2(\text{g})$
Initial conc.	10		0		0
At equilibrium	$10 - 2p$		p		p

Now, we can write,

$$\frac{p_{\text{H}_2} \times p_{\text{Br}_2}}{p_{\text{HBr}}} = K'_p$$

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

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

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

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

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

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

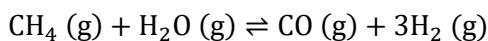
Therefore, at equilibrium,

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

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

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

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



- (a) Write as the expression for K_p for the above reaction.
- (b) How will the values of K_p and composition of equilibrium mixture be affected by
- increasing the pressure.
 - increasing the temperature.
 - using a catalyst?

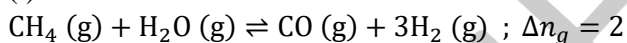
Solution:

(a) For the given reaction,

$$K_p = \frac{P_{\text{CO}} \times [P_{\text{H}_2}]^2}{P_{\text{CH}_4} \times P_{\text{H}_2\text{O}}}$$

(b)

(i)



$$K_p \propto P^2$$

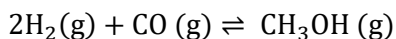
According to Le Chatelier's principle, on increasing pressure, the equilibrium will shift in the backward direction.

(ii) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.

(iii) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increases the rate of a reaction. Thus, equilibrium will be attained quickly.

29. Describe the effect of:

- addition of H_2
- addition of CH_3OH
- removal of CO
- removal of CH_3OH on the equilibrium of the reaction:

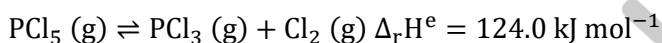
**Solution:**

Given the reaction : $2\text{H}_2(\text{g}) + \text{CO} (\text{g}) \rightleftharpoons \text{CH}_3\text{OH} (\text{g})$ for this reaction $\Delta n_g = -2$

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

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

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



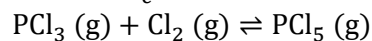
- (a) write an expression for K_c for the reaction.
- (b) what is the value of K_c for the reverse reaction at the same temperature?
- (c) what would be the effect on K_c if
- more PCl_5 is added
 - pressure is increased
 - the temperature is increased?

Solution:

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

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

(a) Value of K_c for the reverse reaction at the same temperature is



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

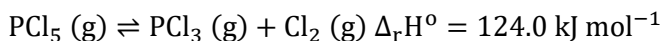
$$K'_c = \frac{1}{K_c} = \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2 = 120.48$$

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

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

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

(iii)

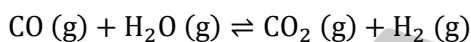


The reaction is endothermic, the value of K_c increases with an increase in temperature. Since the given reaction is an endothermic reaction, the value of K_c will increase if the temperature is increased.

$$\text{Or } \ln \frac{k_2}{k_1} = \Delta H \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

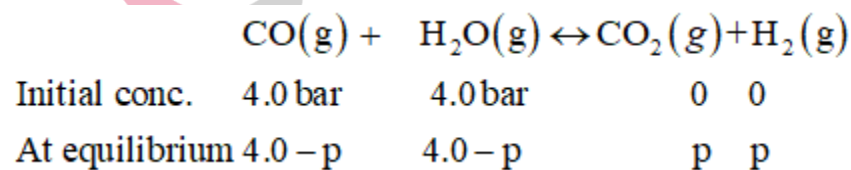
- 31.** Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high-temperature steam. The first stage of two stage reaction involves the formation of CO and H_2 . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,



If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 4.0 \text{ bar}$, what will be the partial pressure of H_2 at equilibrium? $K_p = 10.1$ at 400°C

Solution:

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



It is given that $K_p = 10.1$

Now,

$$\frac{p_{\text{CO}_2} \times p_{\text{H}_2}}{p_{\text{CO}} \times p_{\text{H}_2\text{O}}} = K_p$$

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

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

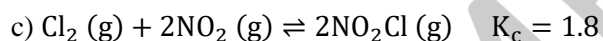
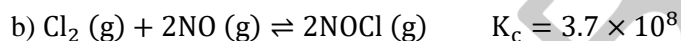
$$\Rightarrow p = 12.712 - 3.178p$$

$$\Rightarrow 4.178p = 12.712$$

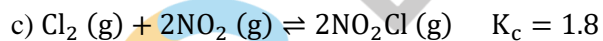
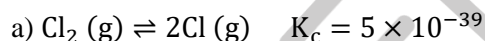
$$\Rightarrow p = 3.04$$

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

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



Solution:



for (a) the values of $K_c = 5 \times 10^{-39}$ is very less, i.e. reactant is very more

b) $Cl_2 (g) + 2NO (g) \rightleftharpoons 2NOCl (g)$ $K_c = 3.7 \times 10^8$ is very high i.e. product is very more



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

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

Solution:

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

$$[\text{O}_2(\text{g})] = 1.6 \times 10^{-2}$$

The given reaction $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$

$$K_c = \frac{\text{product of the molar concentration of product}}{\text{product of the molar concentration of reactant}} = \frac{[\text{O}_3(\text{g})]^2}{[\text{O}_2(\text{g})]^3}$$

Put all the given values in the expression of K_c

$$2.0 \times 10^{-50} = \frac{[\text{O}_3(\text{g})]^2}{[1.6 \times 10^{-2}]^3}$$

$$\Rightarrow [\text{O}_3(\text{g})]^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3$$

$$\Rightarrow [\text{O}_3(\text{g})]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow [\text{O}_3(\text{g})]^2 = 2.86 \times 10^{-28}\text{M}$$

Hence, the concentration of $\text{O}_3 = 2.86 \times 10^{-28}\text{M}$

- 34.** The reaction, $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ is at equilibrium at 1300 K in a 1L flask. It also contains 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Solution:

Given : Temperature = 1300 K

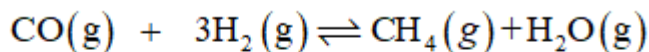
mol of CO = 0.30

mol of H_2 = 0.10

mol of H_2O = 0.02

amount of CH_4 = unknown

Let the concentration of methane at equilibrium be x.



$$\text{At equilibrium } \frac{0.3}{1} = 0.3\text{M} \quad \frac{0.1}{1} = 0.1\text{M} \quad x \quad \frac{0.02}{1} = 0.02\text{M}$$

It is given that $K_c = 3.90$.

Therefore,

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

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

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

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

$$= 0.0585 \text{ M}$$

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

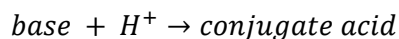
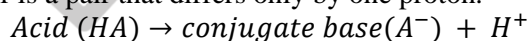
Hence, the concentration of CH_4 at equilibrium is $5.85 \times 10^{-2} \text{ M}$.

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

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

Solution:

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



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

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

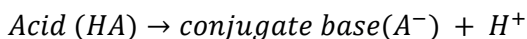
36. Which of the followings are Lewis acids? H_2O , BF_3 , H^+ , and NH_4^+

Solution:

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

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

Solution:



Proton (H^+) donors are acid

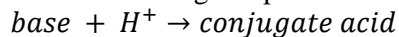
The table below lists the conjugate bases for the given Brønsted acids.

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

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

Solution:

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



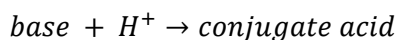
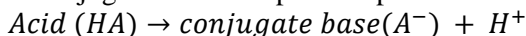
The table below lists the conjugate acids for the given Brønsted bases.

Species	Conjugate acid for base
NH_2^-	NH_3
NH_3	NH_4^+
HCOO^-	HCOOH

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

Solution:

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



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

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

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

- (a) OH^-
- (b) F^-
- (c) H^+
- (d) BCl_3

Solution:

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

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

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

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

Solution:

Given,

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

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

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

$$(\because \log M \times N = \log M + \log N)$$

$$= -\log(3.8 - \log 10^3)$$

$$(\because \log M^N = N \log M)$$

$$= -\log(3.8 + 3)$$

$$= -0.58 + 3$$

$$= 2.42$$

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

Solution:

Given, pH = 3.76

It is known that,

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

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

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

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

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

Hence, the concentration of hydrogen ion $[\text{H}^+]$ 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 6.8×10^{-4} , 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

Solution:

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

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

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

Formula : $K_b K_a = K_w$

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

K_a of HF = 6.8×10^{-4}

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

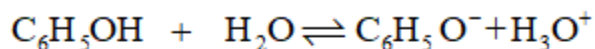
K_a of HCOOH = 1.8×10^{-4} Hence, K_b of its conjugate base $HCOO^- = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$

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

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

Solution:

Given : Ionization of phenol = 1.0×10^{-10}



Initial conc. 0.05 0 0

At equilibrium $0.05 - x$ x x

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

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

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

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

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

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

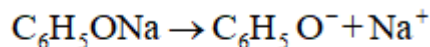
$$= \sqrt{5 \times 10^{-12}}$$

$$= 2.2 \times 10^{-6} \text{M} = [\text{H}_3\text{O}^+]$$

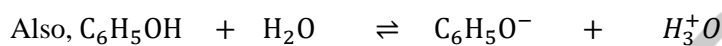
$$\text{Since } [\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{O}^-]$$

$$[\text{C}_6\text{H}_5\text{O}^-] = 2.2 \times 10^{-6} \text{M}$$

Now, let α be the degree of ionization of phenol in the presence of 0.01 M $\text{C}_6\text{H}_5\text{ONa}$.



Conc.	0.01
--------------	-------------



Conc. 0.05 – 0.05 α	0.01 + 0.05 α	0.05 α
----------------------------	----------------------	---------------

$$[\text{C}_6\text{H}_5\text{OH}] = 0.05 - 0.05\alpha \approx 0.05 \text{M} (\because \alpha \approx 0)$$

$$[\text{C}_6\text{H}_5\text{O}^-] = 0.01 + 0.05\alpha \approx 0.01 \text{M}$$

$$[\text{H}_3\text{O}^+] = 0.05\alpha$$

$$K_a = \frac{[\text{C}_6\text{H}_5\text{O}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{OH}]}$$

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

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

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

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

Solution:

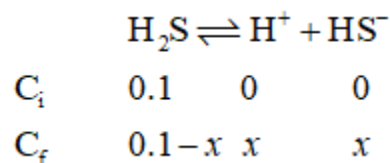
Given: first ionization constant of $\text{H}_2\text{S} = 9.1 \times 10^{-8}$

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

(i) To calculate the concentration of HS^- ion:

Case a: (in the absence of HCl): concentration of H_2S solution = 0.1 M

Let the concentration of $\text{HS}^- = x \text{ M}$.



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

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

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

\therefore first ionization constant of $\text{H}_2\text{S} = 9.1 \times 10^{-8}$ so x can be ignored and $0.1 - x \text{ M} \approx 0.1 \text{ M}$, we have $(9.1 \times 10^{-8})(0.1) = x^2$.

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

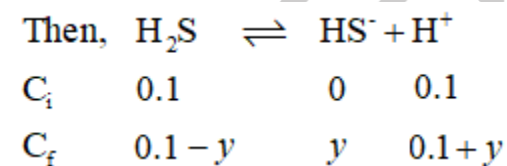
$$x = \sqrt{9.1 \times 10^{-9}}$$

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

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

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

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



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

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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

$$[\text{H}^+] = 0.1 \text{M} \quad \text{(From HCl, case II)}$$

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



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

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

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

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

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

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

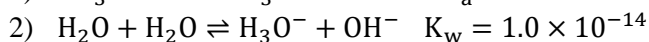
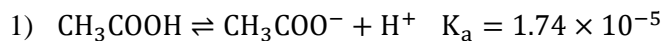
$$\Rightarrow K_{a_1} = 1.74 \times 10^{-5}$$

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

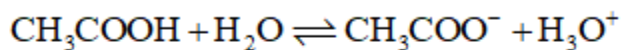
Solution:

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

Concentration of acetic acid solution = 0.05 M solution

Method 1

Since $K_a \gg K_w$:



$$C_i = \begin{array}{ccc} 0.05 & 0 & 0 \\ 0.05 - .05\alpha & 0.05\alpha & 0.05\alpha \end{array}$$

$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.74 \times 10^{-5}}{0.05}} = 0.018$ or 18 % so α can not be neglected so quadratic equation have to solve

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

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

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

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

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

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

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

$$= \frac{-1.74 \times 10^{-5} \pm \sqrt{(1.74 \times 10^{-5})^2 - 4(0.05)(-1.74 \times 10^{-5})}}{2 \times 0.05}$$

$$\alpha = \frac{-1.74 \times 10^{-5} \pm \sqrt{(1.74 \times 10^{-5})^2 + (0.348 \times 10^{-5})}}{2 \times 0.05}$$

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

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

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

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

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

$$= .000093$$

Method 2

Degree of dissociation,

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

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

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

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

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

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

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



Thus, concentration of $\text{CH}_3\text{COO}^- = c \cdot \alpha$

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

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

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

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

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

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

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

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

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

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

Solution:

given: $pH = 4.15$

Let the organic acid be HA (weak acid)

Concentration of HA = 0.01 M

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

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

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

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

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

$$[HA] = 0.01$$

Then,

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

$$pK_a = -\log K_a$$

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

$$pK_a = 6.3001$$

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

(A) 0.003 M HCl

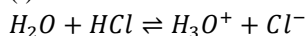
(B) 0.005 M NaOH

(C) 0.002 M HBr

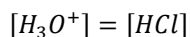
(D) 0.002 M KOH

Solution:

(i) 0.003M HCl:



Since HCl is completely ionized,



$$\Rightarrow [H_3O^+] = 0.003$$

Now,

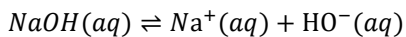
$$pH = -\log[H_3O^+]$$

$$= -\log(0.003) = -\log(3 \times 10^{-3}) = -[\log(3) + \log(10^{-3})] = -[0.477 + 3] =$$

$$= 2.52$$

Hence, the pH of the solution is 2.52.

(ii) 0.005M NaOH



$$[OH^-] = [NaOH] \quad (\because NaOH \text{ is strong base})$$

$$\Rightarrow [OH^-] = 0.005$$

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

$$pOH = 2.30$$

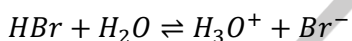
$$\therefore pH + pOH = pK_w ; pH = 14 - pOH$$

$$pH = 14 - 2.30$$

$$= 11.70$$

Hence, the pH of the solution is 11.70.

(iii) 0.002 HBr:



$$[H_3O^+] = [HBr]$$

$$\Rightarrow [H_3O^+] = 0.002$$

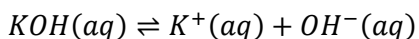
$$\therefore pH = -\log[H_3O^+]$$

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

$$= 2.69$$

Hence, the pH of the solution is 2.69.

(iv) 0.002 M KOH:



$$[OH^-] = [KOH]$$

$$\Rightarrow [OH^-] = 0.002$$

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

$$= 2.69$$

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

$$pH = 14 - 2.69$$

$$= 11.31$$

Hence, the pH of the solution is 11.31.

49. Calculate the pH of the following solutions:

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

(B) 0.3 g of Ca(OH)₂ dissolved in water to give 500 mL of solution.

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

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

Solution:

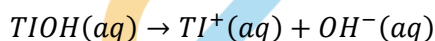
(a) For 2g of TlOH dissolved in water to give 2 L of solution:

$$\text{Moles of TlOH} = \frac{\text{weight}}{\text{molecular weight}} = \frac{2}{221}$$

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

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

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



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

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

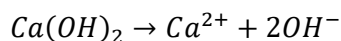
$$10^{-14} = [\text{H}^+] \left(\frac{1}{221} \right)$$

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

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

$$= 11.65$$

(b) For 0.3 g of Ca(OH)₂ dissolved in water to give 500 mL of solution:



$$\text{Molar mass of } Ca(OH)_2 = 40 + 2(17) = 74$$

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

$$[OH^-(aq)] = 2 \times [Ca(OH)_2] = 2 \times 0.0176M \\ = 0.035 M$$

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

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

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

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

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

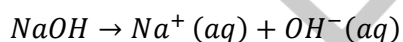
$$= -[\log(0.2833 \times 10^{-12})]$$

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

$$= -(-0.5477 - 12)$$

$$= 12.54$$

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



Molecular weight of NaOH

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

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

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

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

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

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

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

$$\begin{aligned}
 pH &= -[\log(0.2666 \times 10^{-12})] = -[\log(0.2666) \times \log(10^{-12})] = \\
 &= -[\log(0.2666) \times (-12\log(10))] = \\
 &= 12 - \log(0.2666) = 12 + 0.57 = 12.574
 \end{aligned}$$

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

$$13.6 \times 1 \text{ mL} = M_2 \times 1000 \text{ mL}$$

(Before dilution) (After dilution)

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

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

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

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

$$= (-0.1335 + 2)$$

$$= 1.866 \approx 1.87$$

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

Solution:

$$\text{Degree of ionization } (\alpha) = 0.132$$

$$\text{Concentration } (c) = 0.1 \text{ M}$$

$$\text{Thus, the concentration of } H_3O^+ = c \cdot \alpha$$

$$= 0.1 \times 0.132$$

$$= 0.0132$$

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

$$= -\log(0.0132)$$

$$= 1.879 \approx 1.88$$

Now,

$$K_a = C\alpha^2$$

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

$$K_a = 0.00174$$

$$pK_a = 2.75$$

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

Solution:

$$\text{pH of solution} = 9.95$$

$$\text{Concentration (c)} = 0.005 \text{ M}$$

$$\text{Thus, the concentration of } H_3O^+ = c \cdot \alpha$$

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

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

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

$$K_a = C\alpha^2$$

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

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

$$\text{p}K_a = 2.75$$

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

Solution:

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

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

$$\alpha = ?$$

$$k_b = c\alpha^2$$

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

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

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

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

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

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

$$= 6.187$$

$$pH = 7.813$$

the ionization constant of the conjugate acid of aniline

$$K_a \times K_b = K_w$$

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

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

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

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

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

(a) 0.01M in HCl

(b) 0.1M in HCl?

Solution:

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

$$pK_a = 4.74$$

$$pK_a = -\log(K_a)$$

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

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

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

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

Case I: When 0.01 M HCl is taken.

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

	$\text{CH}_3\text{COOH} \leftrightarrow \text{H}^+ + \text{CH}_3\text{COO}^-$
Initial conc.	0.05M 0 0
After dissociation	$0.05 - x$ $0.01 + x$ x

As the dissociation of a very small amount of acetic acid will take place, the values
 $0.05 - x \approx 0.05$

$$0.01 + x \approx 0.01 \text{ taken}$$

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

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

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

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

Now,

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

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

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

Case II: When 0.1 M HCl is taken.

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

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

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

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

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

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

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

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

Now,

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

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

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

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

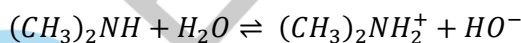
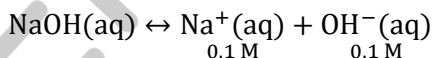
Solution:

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

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

$$\text{Then, } \alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 0.643$$

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



At equi. $(0.02-x) \qquad \qquad \qquad x \qquad \qquad x+0.1$

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

$$(\text{CH}_3)_2\text{NH} = 0.02 - x \approx 0.02$$

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

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

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

$$x = 0.0054$$

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.

Solution:

(a) Human muscle fluid 6.83:

$$\text{pH} = 6.83$$

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

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

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

(b) Human stomach fluid, 1.2:

$$\text{pH} = 1.2$$

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

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

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

(c) Human Blood, 7.38

$$\text{pH} = 7.38$$

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

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

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

(d) Human saliva, 6.4:

$$\text{pH} = 6.4$$

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

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

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

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.

Solution:

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

(i) the pH of milk = 6.8

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

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

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

$$[\text{H}^+] = 1.5 \times 10^{-7} \text{M}$$

(ii) the pH of black coffee = 5.0

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

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

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

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

(iii) the pH of tomato juice = 4.2

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

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

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

(iv) the pH of lemon juice = 2.2

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

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

$$[\text{H}^+] = 10^{-2.2}$$

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

(v) the pH of egg white = 7.8

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

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

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

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

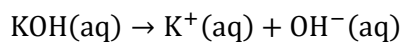
57. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Solution:

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

moles of KOH=0.561/56

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



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

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

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

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

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

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

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

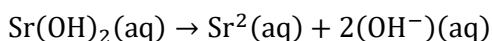
$$= -[\log 2 - 13\log 10] = 12.70$$

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.

Solution:

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

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



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

$$[\text{OH}^-] = 2 \times 0.1581 \text{ M} = 0.3162 \text{ M}$$

Now,

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

$$\frac{10^{-14}}{0.3162} = [\text{H}^+]$$

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

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

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

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

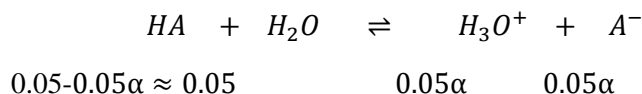
$$\text{pH} = 13.495 \approx 13.50$$

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

Solution:

Let the degree of ionization of propanoic acid be α

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



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.05\alpha)(0.05\alpha)}{0.05} = 0.05\alpha^2$$

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

$$\text{Then, } [\text{H}_3\text{O}^+] = 0.05\alpha = 0.05 \times 1.63 \times 10^{-2} = 8.15 \times 10^{-4}\text{M}$$

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

$$\text{pH} = -[\log 8.15 \times 10^{-4}]$$

$$= -[\log 8.15 + \log 10^{-4}]$$

$$= -[\log 8.15 - 4\log 10]$$

$$= 4 - 0.911 = 3.09$$

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

$$\text{Then, } [\text{H}_3\text{O}^+] = 0.01$$

$$[\text{A}^+] = 0.05\alpha'$$

$$[\text{HA}] = 0.05$$

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

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

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

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

Solution:

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

$$\text{pH} = 2.34$$

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

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

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

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

Also,

$$[H^+] = c\alpha$$

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

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

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

Then,

$$K_a = c\alpha^2$$

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

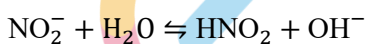
$$= 202.5 \times 10^{-6}$$

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

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

Solution:

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



$$K_h = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{[\text{HNO}_2][\text{OH}^-][H^+]}{[\text{NO}_2^-][H^+]} \quad \therefore k_w = [\text{OH}^-][H^+] = 10^{-14}; K_a = \frac{[\text{NO}_2^-][H^+]}{[\text{HNO}_2]}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

$$= 7.96$$

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

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

Solution:

pyridinium hydrochloride ($\text{C}_5\text{H}_7\text{ClN}^+$) is salt of a weak base ($\text{C}_5\text{H}_5\text{N}$) and strong acid (HCl)

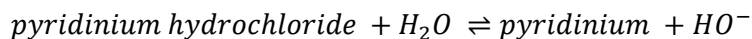
$$\text{pH} = 3.44$$

We know that,

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

$$-3.44 = \log [\text{H}^+]$$

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



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

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

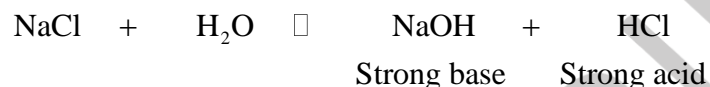
$$\text{Now, } K_h = \frac{K_w}{K_a}$$

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

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

Solution:

(i) NaCl



It is a salt of strong acid and strong base. Therefore it is a neutral solution. And its $\text{pH}=7$

(ii) KBr



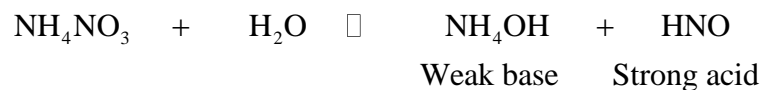
It is a salt of strong acid and strong base. Therefore it is a neutral solution. And its $\text{pH}=7$

(iii) NaCN:



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

(iv) NH_4NO_3



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

(v) NaNO_2



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

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

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

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

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

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

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

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

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

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

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

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

$$= -[\log(1.162 \times 10^{-8})]$$

$$= -[\log 1.162 - (8 \log 10)]$$

$$= \log 1.162 + 8 \log 10$$

$$= 7.94$$

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

Solution:

Ionic product,

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

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

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

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

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

$$\begin{aligned} \Rightarrow x &= 1.64 \times 10^{-7} \\ \Rightarrow [\text{H}^+] &= 1.64 \times 10^{-7} \\ \Rightarrow \text{pH} &= -\log[\text{H}^+] \\ &= -\log[1.64 \times 10^{-7}] \\ &= -[\log 1.64 + \log 10^{-7}] \\ &= -\log 1.64 + 7\log 10 \\ &= 6.78 \end{aligned}$$

Hence, the pH of neutral water is 6.78.

66. Calculate the pH of the resultant mixtures:

- (a) 10 mL of 0.2M $\text{Ca}(\text{OH})_2$ + 25 mL of 0.1M HCl
 (b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $\text{Ca}(\text{OH})_2$
 (c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

Solution:

$$\text{(a) Moles of } \text{H}_3\text{O}^+ = \text{molarity} \times \text{volume (litre)} = \frac{25 \times 0.1}{1000} = 0.0025 \text{ mol}$$

$$\text{Moles of } \text{OH}^- = \text{molarity} \times \text{volume (litre)} = \frac{10 \times 0.2 \times 2}{1000} = 0.0040 \text{ mol}$$

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

Thus, $[\text{OH}^-] > [\text{H}^+]$

$$[\text{OH}^-] = \frac{\text{Moles of } \text{OH}^- - \text{Moles of } \text{H}_3\text{O}^+}{\text{total volume}} = \frac{0.0040 - 0.0025}{35 \times 10^{-3}}$$

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

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

$$= 1.36$$

$$\text{pH} = \text{pK}_w - \text{pOH} = 14 - 1.36$$

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

$$(b) \text{ Moles of } H_3O^+ = \frac{2 \times 10 \times 0.01}{1000} = 0.0002 \text{ mol}$$

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

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

$$(c) \text{ Moles of } H_3O^+ = \frac{2 \times 10 \times 0.1}{1000} = 0.002 \text{ mol}$$

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

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

$$H_3O^+ > OH^-$$

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

$$\therefore \text{pH} = -\log(0.05)$$

$$= 1.30$$

The solution is acidic.

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

Solution:

(1) Silver chromate:



Then,

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

Let the solubility of Ag_2CrO_4 be s .

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

Then,

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

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

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

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

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

$$\text{Molarity of CrO}_4^{2-} = s = 0.65 \times 10^{-4} \text{M}$$

(2) Barium chromate:



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

Let solubility of BaCrO_4 be s .

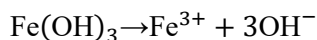
$$\text{So, } [\text{Ba}^{2+}] = s \text{ and } [\text{CrO}_4^{2-}] = s \Rightarrow K_{\text{SP}} = s^2$$

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

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

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

(3) Ferric hydroxide:



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

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

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

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

$$= s \times 27s^3$$

$$K_{\text{SP}} = 27s^4$$

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

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

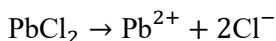
$$0.037 \times 10^{-38} = s^4$$

$$0.00037 \times 10^{-36} = s^4 \Rightarrow 1.39 \times 10^{-10} \text{M} = S$$

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

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

(4) Lead chloride:



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

Let K_{SP} be the solubility of PbCl_2 .

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

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

$$= 4s^3$$

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

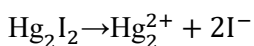
$$\Rightarrow 0.4 \times 10^{-5} = s^3$$

$$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} \text{M} = s$$

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

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

(5) Mercurous iodide:



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

Let s be the solubility of Hg_2I_2 .

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

$$\text{Thus, } \text{Hg}_2\text{I}_2 = s(2s)^2 \Rightarrow K_{\text{xy}} = 4s^3$$

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

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

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

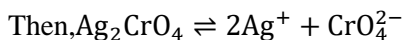
$$\text{Molarity of } \text{Hg}_2^{2+} = s = 2.24 \times 10^{-10} \text{M}$$

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

- 68.** The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Solution:

Let s be the solubility of Ag_2CrO_4 .



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

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

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

Let s' be the solubility of AgBr .



$$s'^2 \quad s'$$

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

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

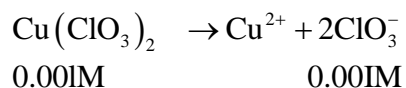
Therefore, the ratio of the molarities of their saturated solution is

$$\frac{s}{s'} = \frac{6.5 \times 10^{-5} \text{ M}}{7.07 \times 10^{-7} \text{ M}} = 91.9$$

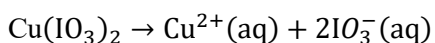
- 69.** Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{\text{sp}} = 7.4 \times 10^{-8}$).

Solution:

When equal volumes of sodium iodate and cupric chlorate solutions are mixed together, then the molar concentrations of both solutions are reduced to half i.e., 0.001 M. Then,



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



Ionic product of copper iodate:

$$= [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

$$= (0.001)(0.001)^2$$

$$= 1 \times 10^{-9}$$

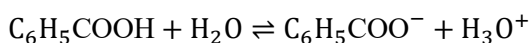
Since the ionic product (1×10^{-9}) $<$ K_{sp} (7.4×10^{-8}), precipitation will not occur.

- 70.** The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13} . How many times is silver benzoate more soluble in a buffer of pH 3.19. Compared to its solubility in pure water?

Solution:

Since pH = 3.19,

$$[H_3O^+] = 6.46 \times 10^{-4} M$$



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

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

Let the solubility of C_6H_5COOAg be x mol/L.

Then,

$$[Ag^+] = x$$

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

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

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

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

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

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

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

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

Then, $[Ag^+] = x' M$ and $[C_6H_5COO^-] = x' M$

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

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

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

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

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

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

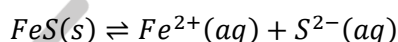
Solution:

Let the maximum concentration of each solution be x mol/L. After mixing, the volume of the concentrations of each solution will be reduced to half i.e., $x/2$.

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

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

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



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

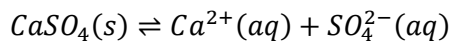
$$6.3 \times 10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right)$$

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

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

If the concentrations of both solutions are equal to or less than $5.02 \times 10^{-9} M$, Then there will be no precipitation of iron sulphate.

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

Solution:

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

Let the solubility of $CaSO_4$ be s .

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

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

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

The molecular mass of $CaSO_4 = 136 \text{ g/mol}$

The solubility of $CaSO_4$ in gram/L

$$= 3.02 \times 10^{-3} \times 136$$

$$= 0.41 \text{ g/L}$$

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

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

- 73.** The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is $1.0 \times 10^{-19} \text{ M}$. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

Solution:

For precipitation to take place, it is required that the calculated ionic product exceeds the K_{sp} value.

Before mixing:

$$[S^{2-}] = 1.0 \times 10^{-19} M ; \text{volume}_1 = 10 \text{ mL}$$

$$[M^{2+}] = 0.04M ; \text{volume}_2 = 5 \text{ mL}$$

After mixing:

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

$$\text{Total Volume} = (10\text{mL} + 5\text{mL}) = 15 \text{ mL}$$

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

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

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

$$\text{Ionic product} = [M^{2+}][S^{2-}] = (1.33 \times 10^{-2})(6.67 \times 10^{-20}) = 8.87 \times 10^{-22}$$

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

