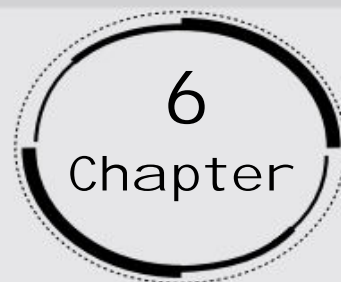


Equilibrium



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

(a). What is the initial effect of the change on vapour pressure?

Ans: The vapour pressure would first fall if the container's volume was rapidly increased. This is due to the fact that the amount of vapour remains constant while the volume increases rapidly. As a result, the same amount of vapour is spread over a wider surface area.

(b). How do rates of evaporation and condensation change initially?

Ans: The rate of evaporation is also constant because the temperature is constant. The density of the vapour phase reduces as the container volume increases. As a result, the rate of vapour particle collisions drops as well. As a result, the rate of condensation initially slows.

(c). What happens when equilibrium is restored finally and what will be the final vapour pressure?

Ans: The rate of evaporation equals the rate of condensation when equilibrium is eventually restored. Only the volume changes in this situation, but the temperature remains fixed. Temperature, not volume, determines vapour pressure. As a result, the final vapour pressure will be the same as the system's initial vapour pressure.

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

Ans: The equilibrium constant for the given reaction will be:

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

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

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

Therefore, the equilibrium constant for the given reaction is 12.239M^{-1} .

- 3. At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of iodine atoms. $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$. Calculate K_p for the equilibrium.**

Ans: Partial pressure for atoms:

$$p_1 = \frac{40}{100} \times p_{\text{total}}$$

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

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

Partial pressure for I_2 molecules:

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

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

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

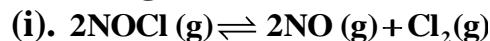
Now for, the given reaction:

$$K_p = \frac{(p\text{I})^2}{p_{\text{I}_2}}$$

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

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

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



Ans: The expression for the equilibrium constant is:

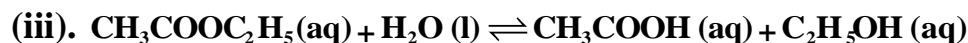
$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$$



Ans: The expression is:

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

$$K_c = [\text{NO}_2]^4 [\text{O}_2]$$



Ans: The expression will be:

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

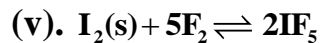
$$K_c = \frac{[\text{CH}_3\text{COOH}] [\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5]}$$



Ans: The expression will be:

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

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

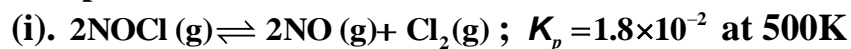


Ans: The expression will be:

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

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

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



Ans: The relationship between K_p and K_c is given as:

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

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

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

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

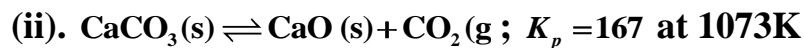
$$K_p = 1.8 \times 10^{-2}$$

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

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

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

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



Ans: Here,

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

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

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

$$K_p = 167$$

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

$$167 = K_c (0.0831 \times 1073)^1$$

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

$$K_c = 1.87 \text{ (Approximately)}$$

- 6. For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000K**
 $\text{NO (g)} + \text{O}_3\text{(g)} \rightleftharpoons \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$ **Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction?**

Ans: According to the question:

The K_c for the forward reaction is 6.3×10^{14}

Then, K_c for the reverse reaction will be:

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

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

$$K'_c = 1.59 \times 10^{-15}$$

The equilibrium constant for the reverse reaction will be: 1.59×10^{-15} .

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

Ans: For a pure substance which is both a solid and a liquid:

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

$$[\text{Pure substance}] = \frac{\text{Mass / Molecular weight}}{\text{Volume}}$$

$$[\text{Pure substance}] = \frac{\text{Mass}}{\text{Volume} \times \text{Molecular mass}}$$

$$[\text{Pure substance}] = \frac{\text{Density}}{\text{Molecular mass}}$$

The molecular mass and density of a pure substance (at a given temperature) are now always fixed and accounted for in the equilibrium constant. As a result, the equilibrium constant statement does not include the values of pure substances.

**8. Reaction between nitrogen and oxygen takes place as follows:
 $2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{N}_2\text{O}(\text{g})$ If a mixture of 0.482 mol of N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.**

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

The initial concentration of N_2 is 0.482mol.

The initial concentration of O_2 is 0.933mol.

At equilibrium the concentration of N_2 is (0.482-x)mol, the concentration of O_2 is (0.933-x)mol and the concentration of N_2O is x mol.

The reaction occurs in a 10L reaction vessel:

$$[\text{N}_2] = \frac{0.482 - x}{10}, [\text{O}_2] = \frac{0.933 - x/2}{10}, [\text{N}_2\text{O}] = \frac{x}{10}$$

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

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

Now, according to the equation:

$$K_c = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

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

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

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

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

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

$$[N_2O] = 6.6 \times 10^{-21}$$

9. Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below: $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$ When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2 .

Ans: The given reaction is:



Now, 2 mol of NOBr are formed from 2 mol of NO . Therefore, 0.0518 mol of NOBr are formed from 0.0518 mol of NO . Again, 2 mol of NOBr are formed from 1 mol of Br .

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

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

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

Therefore, the amount of NO present at equilibrium is:

$$[\text{NO}] = 0.087 - 0.0518 = 0.0352\text{mol}$$

And, the amount of Br present at equilibrium is:

$$[\text{Br}_2] = 0.0437 - 0.0259 = 0.0178\text{mol}$$

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

Ans: For the given reaction:

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

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

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

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

We know that,

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

$$2.0 \times 10^{10} = K_c(0.0831 \times 450)^{-1}$$

$$K_c = \frac{2.0 \times 10^{10}}{(0.0831 \times 450)}$$

$$K_c = 74.79 \times 10^{14} \text{Lmol}$$

11. A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium? $2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$

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

At equilibrium the pressure of HI is 0.04 atm, the pressure for $\text{H}_2 = \frac{0.16}{2} = 0.08\text{atm}$ and the pressure for $\text{O}_2 = \frac{0.16}{2} = 0.08\text{atm}$.

Therefore, the value of K_p at 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 is 1.7×10^2 . The reaction is: $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Ans: For the given reaction: $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$

The given concentration of various species is

$$[\text{N}_2] = \frac{1.57}{20} \text{molL}^{-1} \quad [\text{H}_2] = \frac{1.92}{20} \text{molL}^{-1}$$

$$[\text{NH}_3] = \frac{8.13}{20} \text{molL}^{-1}$$

Now, reaction quotient Q_c is:

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

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

$$Q_c = 2.4 \times 10^3$$

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

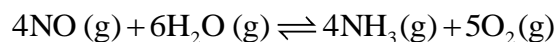
Again, $Q_c > K_c$. Hence, the reaction will proceed in the reverse direction

13. The equilibrium constant expression for a gas reaction is:

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

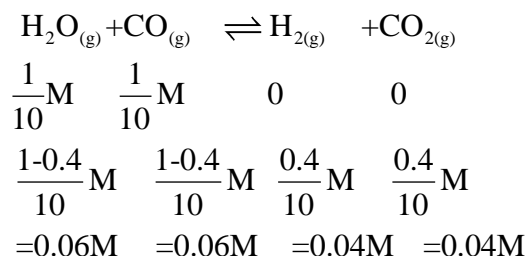
Write the balanced chemical equation corresponding to this expression.

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



14. One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation: $H_2(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ Calculate the equilibrium constant for the reaction.

Ans: The given reaction is:

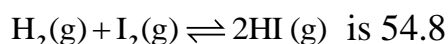


Therefore, the equilibrium constant for the reaction:

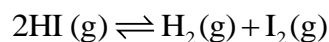
$$\begin{aligned}
 K_c &= \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} \\
 K_c &= \frac{0.04 \times 0.04}{0.06 \times 0.06} \\
 K_c &= 0.444
 \end{aligned}$$

- 15. At 700 K, equilibrium constant for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is 54.8. If 0.5molL^{-1} of $\text{HI}(\text{g})$ 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 $\text{HI}(\text{g})$ and allowed it to reach equilibrium at 700 K?**

Ans: It is given that equilibrium constant K_c for the reaction



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



$$[\text{HI}] = 0.5\text{molL}^{-1} \text{ will be: } \frac{1}{54.8}$$

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

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

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

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

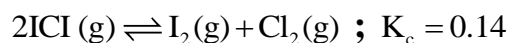
$$\Rightarrow x^2 = \frac{0.25}{54.8}$$

$$\Rightarrow x = 0.06754$$

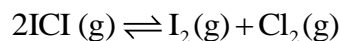
$$x = 0.068 \text{ molL}^{-1} \text{ (approximately)}$$

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

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



Ans: For the given reaction:



The initial concentration of ICl is 0.78M and for I_2 and Cl_2 is zero (0).

At equilibrium, the concentration for ICl is $(0.78 - 2x)\text{M}$ and for I_2 and Cl_2 is $x \text{ M}$.

Now, we can write:

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

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

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

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

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

Therefore, at equilibrium

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

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

$$[\text{HI}] = 0.446\text{M}$$

17. $K_p = 0.04 \text{ atm}$ 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? $\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g})$

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



The initial concentration of C_2H_6 is 4.0 atm and that of C_2H_4 and H_2 is zero (0).

At equilibrium, the concentration of C_2H_6 is $(4.0 - p)$ and that of C_2H_4 and H_2 is p .

Then we can write,

$$\frac{P_{\text{C}_2\text{H}_4} \times P_{\text{H}_2}}{P_{\text{C}_2\text{H}_6}} = K_p$$

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

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

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

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

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

If we take positive value:

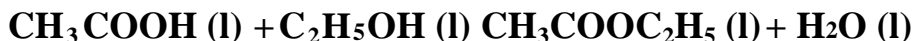
$$p = \frac{0.04}{2}$$

$$p = 0.02$$

So, at equilibrium:

$$[\text{C}_2\text{H}_6] - 4 - p = 4 - 0.02 = 3.98 \text{ atm}$$

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



- (i) Write the concentration ratio (reaction quotient), Q_c , for this reaction (note: water is not in excess and is not a solvent in this reaction)
- (ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- (iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

Ans:

(i) The concentration ratio is $Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$

(ii) The initial concentrations are

$$[\text{CH}_3\text{COOH}] = 1.00$$

$$[\text{C}_2\text{H}_5\text{OH}] = 0.18$$

$$[\text{CH}_3\text{COC}_2\text{H}_4] = 0$$

$$[\text{H}_2\text{O}] = 0$$

The equilibrium concentrations are:

$$[\text{CH}_3\text{COOH}] = \frac{1-0.171}{V} = \frac{0.829}{V}$$

$$[\text{C}_2\text{H}_5\text{OH}] = \frac{0.18-0.171}{V} = \frac{0.009}{V}$$

$$[\text{CH}_3\text{COC}_2\text{H}_4] = \frac{0.171}{V}$$

$$[\text{H}_2\text{O}] = \frac{0.171}{V}$$

The equilibrium constant expression is

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

(iii) The initial concentrations are:

$$[\text{CH}_3\text{COOH}] = 1.00$$

$$[\text{C}_2\text{H}_5\text{OH}] = 0.500$$

$$[\text{CH}_3\text{COC}_2\text{H}_4] = 0$$

$$[\text{H}_2\text{O}] = 0$$

The equilibrium concentrations are:

$$[\text{CH}_3\text{COOH}] = \frac{1-0.214}{V} = \frac{0.786}{V}$$

$$[\text{C}_2\text{H}_5\text{OH}] = \frac{0.500-0.214}{V} = \frac{0.286}{V}$$

$$[\text{CH}_3\text{COC}_2\text{H}_4] = \frac{0.214}{V}$$

$$[\text{H}_2\text{O}] = \frac{0.214}{V}$$

The expression for the reaction quotient is:

$$Q_C = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}} = 0.204$$

As the value of the reaction quotient is not equal to the value of the equilibrium constant, the equilibrium is not yet achieved.

- 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? $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$**

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



At equilibrium the concentration of PCl_5 is $0.5 \times 10^{-1} \text{ mol L}^{-1}$

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

The expression for equilibrium will be:

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

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

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

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

$$\Rightarrow x = 0.0204$$

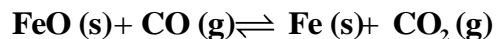
Therefore at equilibrium:

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

- 20. One of the reactions that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2 . $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightleftharpoons \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$; $K_p = 0.0265$ at 1050 K.**

What are the equilibrium partial pressures of CO and CO₂ at 1050 K if the initial partial pressures are: $p_{\text{CO}} = 1.4 \text{ atm}$ and $p_{\text{CO}_2} = 0.80 \text{ atm}$?

Ans: For the given reaction:



The initial concentration of FeO is 1.4 atm and the initial concentration of CO₂ is 0.80 atm.

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

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

$$Q_p = 0.571$$

It is given in the that, $K_p = 0.265$.

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

Therefore, we can say that the pressure of CO will increase while the pressure of CO₂ will decrease. Now, let the increase in pressure of CO be equal to the decrease in pressure of CO₂ be 'p'. Then, we can write:

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

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

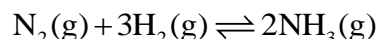
$$0.371 + 0.265p = 0.80 - p$$

$$1.265p = 0.429$$

$$\Rightarrow p = 0.339$$

Therefore, equilibrium partial of CO₂ will be, $p_{\text{CO}_2} = 0.80 - 0.339 = 0.461 \text{ atm}$

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



- 21. Equilibrium constant, K_c for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 500 K is 0.061. 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 $0.5 \text{ mol L}^{-1} \text{ NH}_3$.**

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

Ans: The given reaction is:



At a particular time, the concentration of

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

$$Q_c = \frac{(0.5)^2}{(3.0)(2.0)^3}$$

$$Q_c = 0.0104$$

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?**

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



At equilibrium the concentration of BrCl is $(3.3 \times 10^{-3} - 2x)$

Now, we can write.

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

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

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

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

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

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

Therefore, at equilibrium

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

$$[\text{BrCl}] = 3.3 \times 10^{-3} - 3.0 \times 10^{-3}$$

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

- 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: C (s) + CO₂ (g) ⇌ 2CO (g). Calculate K_c for this reaction at the above temperature.**

Ans: Let, the total mass of the gas mixture = 100 gm

Mass of CO = 90.55 gm

And, mass of CO₂ = (100 – 90.55) = 9.45 gm

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

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

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

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

$$p_{CO} = 0.938 \text{ atm}$$

Partial pressure of CO_2 ,

$$p_{CO_2} = \frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \times p_{\text{total}}$$

$$p_{CO_2} = \frac{0.215}{3.234 + 0.215} \times 1$$

$$p_{CO_2} = 0.062 \text{ atm}$$

Therefore,

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

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

$$K_p = 14.19$$

For the given reaction:

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

We know that,

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

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

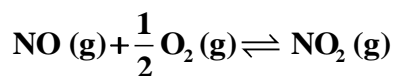
$$K_c = \frac{14.19}{0.082 \times 1127}$$

$$K_c = 0.154$$

24. Calculate:

(a). ΔG° and

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



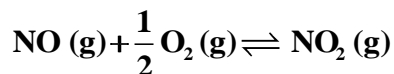
Where:

$$\Delta_f G^\circ (\text{NO}_2) = 52 \text{ kJ/mol}$$

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

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

Ans: For the given reaction:



(a). The ΔG° for the given reaction will be:

$$\Delta G^\circ = \Delta G^\circ (\text{Products}) - \Delta G^\circ (\text{Reactants})$$

$$\Delta G^\circ = 52.0 - [87.0 + 0]$$

$$\Delta G^\circ = -35.0 \text{ kJmol}^{-1}$$

(b). We know that:

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

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

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

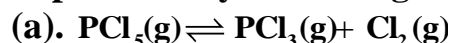
$$\log K_c = 6.134$$

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

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

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

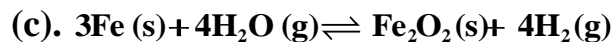


Ans: The amount of moles produced by the reaction will rise. According to Le Chatelier's principle, as pressure is reduced, the equilibrium swings in the direction of a greater number of moles of gas. The number of moles of gaseous products in the reaction is greater than the number of moles of gaseous reactants. As a result,

the reaction will be propelled ahead. As a result, there will be more moles of reaction products.

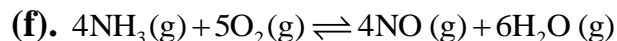
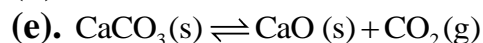
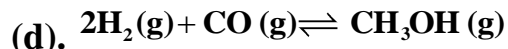
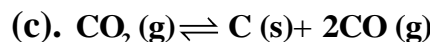
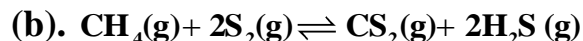
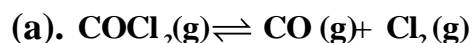


Ans: When the given equation is subjected to a decrease in pressure the number of moles of reaction products will decrease.



Ans: When the given equation is subjected to a decrease in pressure the number of moles of reaction products will remain 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.



Ans: By increasing the pressure, the reactions in (i), (iii), (iv), (v), and (vi) will be changed. Because the number of moles of gaseous reactants is greater than the number of moles of gaseous products, the reaction in (iv) will proceed in the forward direction. Because the number of moles of gaseous reactants is smaller than that of gaseous products, the reactions in (i), (iii), (v), and (vi) will shift backward.

27. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K. $\text{H}_2\text{(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2\text{HBr (g)}$, Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Ans: The K_p for the given reaction is $\text{H}_2\text{(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2\text{HBr (g)}$ 1.6×10^5 .

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

$$K'_p = \frac{1}{K_p}$$

$$K'_p = \frac{1}{1.6 \times 10^5}$$

$$K'_p = 6.25 \times 10^{-6}$$

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

So, at equilibrium the concentration of HBr will be $(10 - 2p)$

Now, we can write:

$$\frac{p_{\text{Br}_2} \times p_{\text{H}_2}}{p_{\text{HBr}}^2} = K'_p$$

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

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

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

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

$$(1.005 \times 10^{-3})p = 2.5 \times 10^{-2}$$

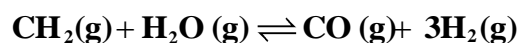
$$p = 2.49 \times 10^{-2} \text{ bar} = 2.5 \times 10^{-2} \text{ bar}$$

Therefore, at equilibrium:

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

$$[\text{HBr}] = 10 - 2 \times (2.49 \times 10^{-2}) = 9.95 \text{ bar}$$

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



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

Ans: For the given equation:

$$K_p = \frac{P_{CO} \times P_{H_2}^3}{P_{CH_4} \times P_{H_2O}}$$

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

(i). Increasing the pressure

Ans: The equilibrium will shift in the backward direction, according to Le Chatelier's principle.

As the reaction shifts in the backward direction as the pressure is increased, the value of K_p decreases.

(ii). Increasing the temperature

Ans: Because the reaction is endothermic, the equilibrium will shift forward, according to Le Chatelier's principle.

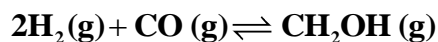
The value of K_p will grow as the temperature rises because the reaction will shift forward.

(iii). Using a catalyst?

Ans: The existence of a catalyst has no effect on the reaction's equilibrium. A catalyst does nothing but speed up a reaction. As a result, equilibrium will be soon achieved.

Because the catalyst only changes the rate of reaction, the value of K_p is unaffected.

29. Describe the effect of the following on the equilibrium of the reaction:



(a). Addition of H_2

Ans: According to Le Chatelier's principle, when H_2 is added to a reaction, the equilibrium shifts in the forward direction.

(b). Addition of CH_3OH

Ans: The equilibrium will shift backwards with the addition of CH_3OH .

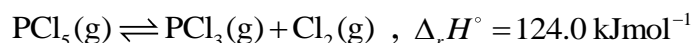
(c). Removal of CO

Ans: When CO is removed from the equation, the equilibrium shifts backward.

(d). Removal of CH_3OH

Ans: When CH_3OH is removed from the equation, the equilibrium shifts forward.

30. At 473 K, equilibrium constant K_p 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.

Ans: The expression for K_c will be:

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

(b). What is the value of K_c for the reverse reaction at the same temperature?

Ans: Value of K_c for the reverse reaction at the same temperature is:

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

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

(c). What would be the effect on K_c if

(i). More PCl_5 is added?

Ans: Because the temperature is constant in this scenario, K_c will remain constant.

(ii). Pressure is increased?

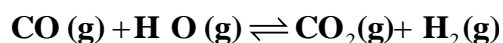
Ans: At constant temperature, K_c remains constant. As a result, K_c would not alter in this scenario.

(iii). The temperature is increased?

Ans: In an endothermic process, the value of K_c rises as the temperature rises. Because the reaction is an endothermic reaction, the value of K_c will rise as the temperature rises.

31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2 . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ If a reaction vessel at $400^\circ C$ is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 10.1$ at $400^\circ C$.

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



At equilibrium the concentration of CO and H_2O will be $(4.0 - p)$.

It is given that, $K_p = 10.1$

Now,

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

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

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

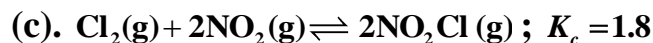
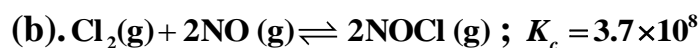
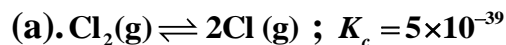
$$\Rightarrow p = 12.712 - 3.178p$$

$$\Rightarrow 4.178p = 12.712$$

$$\Rightarrow p = 3.04$$

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

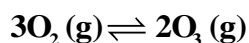
32. Predict which of the following reaction will have appreciable concentration of reactants and products:



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

33. The value of K_c for the reaction $3O_2(g) \rightleftharpoons 2O_3(g)$ 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 ?

Ans: The given reaction is:



$$K_c = \frac{[O_{3(g)}]^2}{[O_{2(g)}]^3}$$

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

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

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

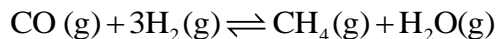
$$\Rightarrow [O_{3(g)}]^2 = 8.192 \times 10^{-50}$$

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

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

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

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



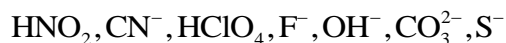
At equilibrium, the concentration of CO is 0.3 M , H_2 is 0.1 M and H_2O is 0.02 M

Therefore,

$$\begin{aligned} \frac{[\text{CH}_{4(g)}][\text{H}_2\text{O}_{(g)}]}{[\text{CO}_{(g)}][\text{H}_{2(g)}]^3} &= K_c \\ \Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} &= 3.90 \\ \Rightarrow x &= \frac{3.90 \times 0.3 \times (0.1)^3}{0.02} \\ &= \frac{0.00117}{0.02} \\ &= 0.0585M \\ &= 5.85 \times 10^{-2}M \end{aligned}$$

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

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



Ans: A conjugate acid-base pair varies from one other by only one proton. In the table below, the conjugate acid-base for each species is listed.

Species	Conjugate acid-base
HNO_2	NO_3^- (base)
CN^-	HCN (acid)
HClO_4	ClO_4^- (base)
F^-	HF (acid)
OH^-	H_2O (acid) / O^{2-} (base)
CO_3^{2-}	HCO_3^- (acid)
S^-	HS^- (acid)

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

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

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

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

Bronsted Acid	Conjugate Base
HF	F^-
H_2SO_4	HSO_4^-
HCO_3^-	CO_3^{2-}

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

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

Bronsted Base	Conjugate Acid
NH_2^-	NH_3
NH_3	NH_4^+
HCOO^-	HCOOH

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

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

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

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

(a). OH^-

Ans: OH^- is a Lewis base since it can donate its lone pair of electrons

(b). F^-

Ans: F^- is a Lewis base since it can donate a pair of electrons.

(c). H^+

Ans: H^+ is a Lewis acid since it can accept a pair of electrons.

(d). BCl_3

Ans: ~~BCl₃~~ Lewis acid since it can accept a pair of electrons.

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

Ans: Given,

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

Therefore, the pH value of the soft drink:

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

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

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

$$\text{pH} = -\log 3.8 + 3$$

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

$$\text{pH} = 2.42$$

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

Ans: Given the, $\text{pH} = 3.76$

It is known as:

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

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

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

$$[H^+] = \text{antilog}(-3.76)$$

$$[H^+] = 1.74 \times 10^{-4} \text{ M}$$

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

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

Ans: It is known as:

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

Given, K_a of HF is 6.8×10^{-4}

Hence, K_b of its conjugate base F^- :

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

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

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

Given K_a of HCOOH is 1.8×10^{-4}

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

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

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

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

Given K_a of HCN is 4.8×10^{-9}

Hence, K_b of its conjugate base CN^- :

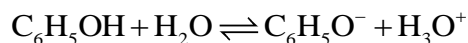
$$K_b = \frac{K_w}{K_a}$$

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

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

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

Ans: According to the reaction of ionization of phenol:



The initial concentration of $\text{C}_6\text{H}_5\text{OH}$ is 0.05 M.

At equilibrium, the concentration of $\text{C}_6\text{H}_5\text{O}^-$ and H_3O^+ will be x , then the concentration of $\text{C}_6\text{H}_5\text{OH}$ will be $(0.05 - x)$.

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

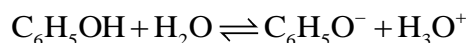
$$K_a = \frac{x \times x}{0.05 - x}$$

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

$$\begin{aligned} \therefore x &= \sqrt{1 \times 10^{-10} \times 0.05} \\ &= \sqrt{5 \times 10^{-12}} \\ &= 2.2 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+] \end{aligned}$$

$$\begin{aligned} \text{Since } [\text{H}_3\text{O}^+] &= [\text{C}_6\text{H}_5\text{O}^-] \\ [\text{C}_6\text{H}_5\text{O}^-] &= 2.2 \times 10^{-6} \text{ M} \end{aligned}$$

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



The concentrations are as follows:

$$[\text{C}_6\text{H}_5\text{OH}] = 0.05 - 0.05\alpha; 0.05 \text{ M}$$

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

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

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

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

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

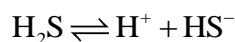
$$\alpha = 1 \times 10^{-8}$$

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

Ans: To calculate the concentration of HS^- ions

Case I (in the absence of HCl):

Let the concentration of HS^- be x M:



The final concentration of H_2S will be $(0.1 - x)$

Then,

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

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

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

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

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

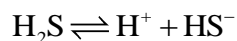
$$x = \sqrt{9.1 \times 10^{-9}}$$

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

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

Case II (in the presence of HCl):

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



The final concentration of H_2S will be $(0.1 - y)$

Now,

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

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

$$9.1 \times 10^{-8} = \frac{y \times 0.1}{0.1}$$

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

The concentration of $[\text{HS}^-] = 9.1 \times 10^{-8}$

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

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

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

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

Also, $[\text{H}^+] = 9.54 \times 10^{-5} \text{ M}$

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

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

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

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

The concentration of S^{2-} be X' M

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

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

Then,

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

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

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

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

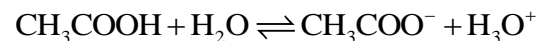
$$X' = \frac{1.092 \times 10^{-20}}{0.1}$$

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

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

- 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 Ans: and its pH.**

Ans: For the reaction:



The final concentration of CH_3COO^- and H_3O^+ is 0.05α . Then the final concentration of CH_3COOH will be $(0.05 - 0.05\alpha)$.

$$\begin{aligned}
 K_a &= \frac{(.05\alpha)(.05\alpha)}{(.05 - 0.05\alpha)} \\
 &= \frac{(.05\alpha)(0.05\alpha)}{.05(1 - \alpha)} \\
 &= \frac{.05\alpha^2}{1 - \alpha}
 \end{aligned}$$

$$\begin{aligned}
 1.74 \times 10^{-5} &= \frac{.05\alpha^2}{1 - \alpha} \\
 1.74 \times 10^{-5} - 1.74 \times 10^{-5}\alpha &= 0.05\alpha^2 \\
 0.05\alpha^2 + 1.74 \times 10^{-5}\alpha - 1.74 \times 10^{-5} & \\
 D &= b^2 - 4ac
 \end{aligned}$$

$$\begin{aligned}
 &= (1.74 \times 10^{-5})^2 - 4(.05)(1.74 \times 10^{-5}) \\
 &= 3.02 \times 10^{-25} + .348 \times 10^{-5}
 \end{aligned}$$

$$\begin{aligned}
 \alpha &= \sqrt{\frac{K_a}{c}} \\
 \alpha &= \sqrt{\frac{1.74 \times 10^{-5}}{.05}} \\
 &= \sqrt{\frac{34.8 \times 10^{-5} \times 10}{10}} \\
 &= \sqrt{3.48 \times 10^{-6}}
 \end{aligned}$$

$$\begin{aligned}
 [\text{CH}_3\text{COO}^-] &= 0.05 \times 1.86 \times 10^{-3} \\
 &= \frac{0.93 \times 10^{-3}}{1000} \\
 &= .000093
 \end{aligned}$$

$$\begin{aligned}
 pH &= -\log[H^+] \\
 &= -\log(.093 \times 10^{-2}) \\
 \therefore pH &= 3.03
 \end{aligned}$$

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

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

Ans: Let the organic compound be HA .



Concentration of is 0.01 M and its pH is 4.15.

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

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

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

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

$$[HA] = 0.01$$

Now,

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

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

$$[HA] = 0.01$$

Then,

$$K_a = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{0.01}$$

$$K_a = 5.01 \times 10^{-7}$$

$$pK_a = -\log K_a$$

$$= -\log K_a$$

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

$$pK_a = 6.3001$$

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

(i). 0.003 M HCl



Since HCl is completely ionized.

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

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

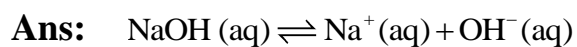
$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.003)$$

$$\text{pH} = 2.52$$

Hence, the pH of the Ans: is 2.52.

(ii). 0.005 M NaOH



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

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

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

$$\text{pOH} = -\log(0.005)$$

$$\text{pOH} = 2.30$$

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

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

$$\text{pH} = 11.70$$

Hence, the pH of the Ans: is 11.70.

(iii). 0.002 M HBr



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

$$\Rightarrow [\text{H}_3\text{O}^+] = 0.002$$

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

$$\text{pH} = -\log(0.002)$$

$$\text{pH} = 2.69$$

Hence, the pH of the Ans:is 2.69.

(iv). 0.002 M KOH

Ans: $\text{KOH (aq)} \rightleftharpoons \text{K}^+ \text{(aq)} + \text{OH}^- \text{(aq)}$

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

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

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

$$\text{pOH} = -\log(0.002)$$

$$\text{pOH} = 2.69$$

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

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

$$\text{pH} = 11.31$$

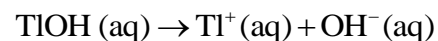
Hence, the pH of the Ans:is 11.31.

49. Calculate the pH of the following solutions:

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

Ans: For 2g of TIOH dissolved in water to give 2 L of solution:

$$\begin{aligned} \left[\text{TIOH}_{(\text{aq})} \right] &= \frac{2}{2} \text{ g / L} \\ &= \frac{2}{2} \times \frac{1}{221} \text{ M} \\ &= \frac{1}{221} \text{ M} \end{aligned}$$



$$\begin{aligned}
 TIOH_{(aq)} &\rightarrow TI_{(aq)}^+ + OH_{(aq)}^- \\
 [OH_{(aq)}^-] &= [TIOH_{(aq)}] = \frac{1}{221} M \\
 K_w &= [H^+][OH^-] \\
 10^{-14} &= [H^+] \left(\frac{1}{221} \right) \\
 221 \times 10^{-14} &= [H^+] \\
 \Rightarrow pH &= -\log[H^+] = -\log(221 \times 10^{-14}) \\
 &= -\log(2.21 \times 10^{-12}) \\
 &= 11.65
 \end{aligned}$$

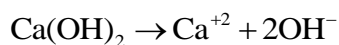
(b). 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

Ans: Molecular weight of $Ca(OH)_2$ is 74g.

$$\text{So, } 0.3 \text{ g } Ca(OH)_2 = \frac{0.3}{74} \text{ mole}$$

$$\text{Molar Concentration} = \frac{\text{Moles in Solution}}{\text{Volume in Solution}}$$

$$\text{Molar concentration of } Ca(OH)_2 = \frac{\frac{0.3}{74} \text{ mole}}{0.5 \text{ L}} = 8.11 \times 10^{-3} \text{ M}$$



$$[OH^-] = 2[Ca(OH)_2]$$

$$[OH^-] = 2 \times (8.11 \times 10^{-3}) \text{ M}$$

$$[OH^-] = 16.22 \times 10^{-3} \text{ M}$$

$$pOH = -\log(16.22 \times 10^{-3})$$

$$pOH = 3 - 1.2101$$

$$pOH = 1.79$$

$$pH = 14 - 1.79$$

$$pH = 12.21$$

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

Ans: 1 mole of = 40g NaOH

Since, 40 gm of NaOH 1 mole of NaOH

So, 0.3 gm of NaOH $\frac{0.3}{40}$ moles

$$\text{Molar Concentration} = \frac{\text{Moles in Solution}}{\text{Volume in Solution}}$$

$$\text{Molar concentration} = \frac{\frac{0.3}{40} \text{ Moles}}{0.2 \text{ L}} = 3.75 \times 10^{-1} \text{ M}$$

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

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

$$\text{pOH} = 1.43$$

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

$$\text{pH} = 12.57$$

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

Ans: For this question:

$$M_1 V_1 = M_2 V_2$$

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

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

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

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

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

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

$$\text{pH} = 1.87$$

50. The degree of ionization of a 0.1M bromoacetic acid Ans:is 0.132. Calculate the pH of the Ans:and the pK_a of bromoacetic acid.

Ans: Degree of ionization, $\alpha = 0.132$

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

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

$$[H_3O^+] = 0.1 \times 0.132$$

$$[H_3O^+] = 0.0132$$

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

$$pH = -\log(0.0132)$$

$$pH = 1.88$$

Now,

$$K_a = C\alpha^2$$

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

$$K_a = 0.0017$$

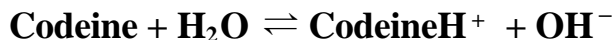
$$pK_a = 2.75$$

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

Ans: $pH = 9.95$,

$$pOH = 14 - pH = 14 - 9.95 = 4.05$$

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



$$\text{The ionization constant, } K_b = \frac{[\text{CodeineH}^+][OH^-]}{[\text{codeine}]} =$$

$$\frac{(8.913 \times 10^{-5}) \times (8.913 \times 10^{-5})}{5 \times 10^{-3}} = 1.588 \times 10^{-6}.$$

$$pK_b = -\log(1.588 \times 10^{-6}) = 5.8$$

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

Ans:

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

$$c = 0.001M$$

$$pH = ?$$

$$\alpha = ?$$

$$K_a = C\alpha^2$$

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

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

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

$$\begin{aligned} \text{Then,} \quad [\text{anion}] &= c\alpha = 0.01 \times 6.53 \times 10^{-5} \\ &= 0.65 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} pOH &= -\log(0.65 \times 10^{-5}) \\ &= 6.187 \end{aligned}$$

$$pH = 7.813$$

Now,

$$K_a \times K_b = K_w$$

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

$$\begin{aligned} K_a &= \frac{10^{-14}}{4.27 \times 10^{-10}} \\ &= 2.34 \times 10^{-5} \end{aligned}$$

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

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

(a) 0.01M

(b) 0.1M in HCl ?

Ans:

$$c = 0.05M$$

$$pK_a = 4.74$$

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

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

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

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

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 0.01M HCl is taken.

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

	CH_3COOH	$H^+ +$	CH_3COO^-
Initial conc.	0.05M	0	0
After dissociation	$0.05 - x$	$0.01 + x$	x

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

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

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

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

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

Now,

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

Case II: When 0.1M HCl is taken.

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

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

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

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

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

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

$$x = \frac{1.82 \times 10^{-5} \times 0.05}{0.1} \quad x = 1.82 \times 10^{-4} \times 0.05\text{M} \quad \text{Now,}$$

$$\begin{aligned} \alpha &= \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}} \\ &= \frac{1.82 \times 10^{-4} \times 0.05}{0.05} \\ &= 1.82 \times 10^{-4} \end{aligned}$$

- 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 Ans: is also 0.1M in NaOH?**

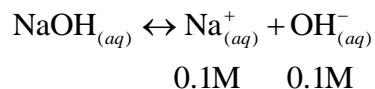
Ans:

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

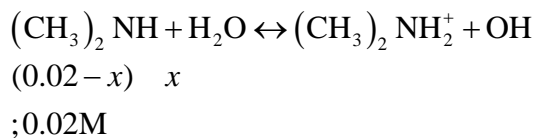
$$c = 0.02\text{M}$$

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

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



And,



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

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

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

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

$$x = 0.0054$$

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

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

Ans:

(a) Human muscle fluid 6.83

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

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

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

(b) Human stomach fluid, 1.2:

$$\text{pH} = 1.2 \quad \times$$

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

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

(c) Human blood, 7.38:

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

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

(d) Human saliva, 6.4:

$$\text{pH} = 6.4$$

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

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

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.

Ans:

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

(i) pH of milk = 6.8

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

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

$$[\text{H}^+] = 10^{-6.8}$$

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

$$= 1.58 \times 10^{-7} \text{ M}$$

(ii) pH of black coffee = 5.0

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

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

$$[\text{H}^+] = 10^{-5.0}$$

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

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

(iii) pH of tomato juice = 4.2

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

$$4.2 = -\log[H^+]$$

$$[H^+] = 10^{-4.2}$$

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

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

(iv) pH of lemon juice = 2.2

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

$$2.2 = -\log[H^+]$$

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

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

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

(v) pH of egg white = 7.8

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

$$7.8 = -\log[H^+]$$

$$[H^+] = 10^{-7.8}$$

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

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

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

Ans:

$$\begin{aligned}
 [KOH_{aq}] &= \frac{0.561}{\frac{1}{5}} \text{ g/L} \\
 &= 2.805 \text{ g/L} \\
 &= 2.805 \times \frac{1}{56.11} M \\
 &= .05 M \\
 KOH_{aq} &\rightarrow K^+_{(aq)} + OH^-_{(aq)} \\
 [OH^-] &= .05 M = [K^+] \\
 [H^+][H^-] &= K_w \\
 [H^+] &= \frac{K_w}{[OH^-]} \\
 &= \frac{10^{-14}}{0.05} \\
 &= 2 \times 10^{-11} M \\
 \therefore pH &= 12.70
 \end{aligned}$$

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

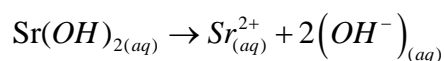
Ans:

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

Then, concentration of $Sr(OH)_2$

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

$$= 0.1581 M$$



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

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

Now,

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

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

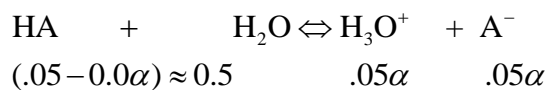
$$\Rightarrow [\text{H}^+] = 3.2 \times 10^{-14}$$

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

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

Ans:

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



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

$$= \frac{(.05\alpha)(.05\alpha)}{0.05}$$

$$= .05\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{.05}}$$

$$= 1.63 \times 10^{-2}$$

$$\text{Then, } [H_3O^+] = .05\alpha = .05 \times 1.63 \times 10^{-2} = K_b .15 \times 10^{-4} M$$

$$\therefore \text{pH} = 3.09$$

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

$$\text{Then, } [H_3O^+] = 0.01$$

$$[A^-] = 0.05\alpha'$$

$$[HA] = .05$$

$$K_a = \frac{0.01 \times 0.05\alpha'}{.05}$$

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

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

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

Ans:

$$c = 0.1M$$

$$\text{pH} = 2.34$$

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

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

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

Also,

$$[H^+] = c\alpha \quad 4.5 \times 10^{-3} = 0.1 \times \alpha \quad \frac{4.5 \times 10^{-3}}{0.1} = \alpha \quad \alpha = 4.5 \times 10^{-3} = .045 \quad \text{Then,}$$

$$K_a = c\alpha^2$$

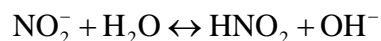
$$= 0.1 \times (4.5 \times 10^{-3})^2$$

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

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

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

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



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

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5 \times 10^{-4}} = .22 \times 10^{-10}$$

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

$$[\text{NO}_2^-] = .04 - x; 0.04$$

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

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

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

$$x^2 = .0088 \times 10^{-10}$$

$$x = .093 \times 10^{-5}$$

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

$$[\text{H}_3\text{O}^+] = \frac{10^{-14}}{.093 \times 10^{-5}} = 10.75 \times 10^{-9} M$$

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

$$= 7.96$$

Therefore, degree of hydrolysis

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

$$= 2.325 \times 10^{-5}$$

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

Ans:

$$\text{pH} = 3.44$$

We know that,

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

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

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

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

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

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

NaCl, KBr, NaCN, NH_4NO_3 , NaNO_2 and KF

Ans:

(i) NaCl :



Strong base Strong base

Therefore, it is a neutral solution.

(ii) KBr:



Strong base Strong base

Therefore, it is a neutral solution.

iii) NaCN:



Weak acid Strong base

Therefore, it is a basic solution.

(iv) NH_4NO_3



Weak acid Strong base

Therefore, it is an acidic solution.

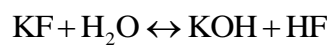
(v) NaNO_2



Strong base Weak acid

Therefore, it is a basic solution.

(vi) KF



Strong base Weak acid

Therefore, it is a basic solution.

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

Ans:

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

$$\Rightarrow K_b = c\alpha^2 \therefore \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.35 \times 10^{-3}}{0.1}} \quad (\because \text{concentration of acid} = 0.1\text{M})$$

$$\alpha = \sqrt{1.35 \times 10^{-3}} = 0.116$$

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

$$= 0.1 \times 0.116$$

$$= 0.0116$$

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

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



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

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

$$K_b = \frac{10^{-14}}{1.35 \times 10^{-3}} \\ = 0.740 \times 10^{-11}$$

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

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

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

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

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

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

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

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

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

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

$$= 7.94$$

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

Ans:

Ionic product,

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

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

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

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

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

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

Hence, the pH of neutral water is 6.78.

66. Calculate the pH of the resultant mixtures:

a) 10mL of 0.2M Ca(OH)_2 + 25mL of 0.1MHCl

Ans: Moles of $\text{H}_3\text{O}^+ = \frac{25 \times 0.1}{1000} = .0025 \text{ mol}$

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

Thus, excess of $\text{OH}^- = .0015 \text{ mol}$

b) 10mL of 0.01M H_2SO_4 + 10mL of 0.01M Ca(OH)_2

Ans: Moles of $\text{H}_3\text{O}^+ = \frac{2 \times 10 \times 0.1}{1000} = .0002 \text{ mol}$

Moles of $\text{OH}^- = \frac{2 \times 10 \times 0.1}{1000} = .0002 \text{ mol}$

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

The solution is neutral. Hence, $\text{pH} = 7$.

c) 10mL of 0.1M H_2SO_4 + 10mL of 0.1MKOH

Ans: Moles of $\text{H}_3\text{O}^+ = \frac{2 \times 10 \times 0.1}{1000} = .002 \text{ mol}$

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

Excess of $\text{H}_3\text{O}^+ = .001 \text{ mol}$

Thus, $[H_3O^+] = \frac{.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = .05 \therefore pH = -\log(0.05) = 1.30$

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

Ans:



Then,

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

Let the solubility of Ag_2CrO_4 be s .

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

Then,

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

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

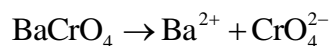
$$.275 \times 10^{-12} = s^3$$

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

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

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

(2) Barium chromate:



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

Let the solubility of BaCrO_4 be s .

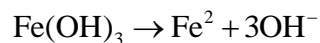
$$\text{So, } [\text{Ba}^{2+}] = s \text{ and } [\text{CrO}_4^{2-}] = s \Rightarrow K_{sp} = s^2$$

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

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

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

(3) Ferric hydroxide:

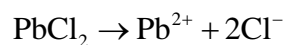


$$K_{sp} = [Fe^{2+}][OH^{-}]^3$$

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

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

(4) Lead chloride:



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

Let K_{sp} be the solubility of $PbCl_2$.

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

$$\begin{aligned} \text{Thus, } K_{sp} &= s.(2s)^2 \\ &= 4s^3 \end{aligned}$$

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

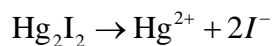
$$\Rightarrow 0.4 \times 10^{-5} = s^3$$

$$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} M = S.1$$

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

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

(5) Mercurous iodide:



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

Let s be the solubility of Hg_2I_2 .

$$\Rightarrow [Hg_2^{2+}] = s \text{ and } [I^{-}] = 2s$$

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

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

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

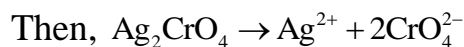
$$\Rightarrow s = 2.24 \times 10^{-10} \text{ M}$$

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

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

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

Ans: Let s be the solubility of Ag_2CrO_4

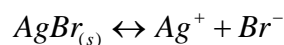


$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

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

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

Let s' be the solubility of AgBr .



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

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

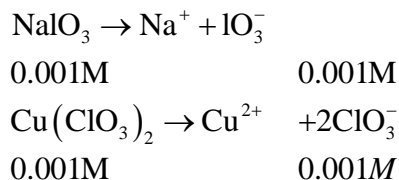
Therefore, the ratio of the molarities of their saturated solution is

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

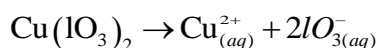
- 69. Equal volumes of 0.002M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate?**

(For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$)

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



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



Ionic product of copper iodate:

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

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

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

Ans:

$$\begin{aligned} &\text{Since pH} = 3.19, \\ &[\text{H}_3\text{O}^+] = 6.46 \times 10^{-4}\text{M} \\ &\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \leftrightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+ \\ &K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} \\ &\frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10 \end{aligned}$$

Let the solubility of C_6H_5COOAg be $x \text{ mol/L}$.

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

Now, let the solubility of C_6H_5COOAg be $x' \text{ mol/L}$.

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?

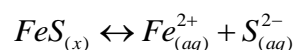
(For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$)

Ans: Let the maximum concentration of each solution be $x \text{ mol/L}$. After mixing, the volume of the concentrations of each solution will be reduced to half i.e., $x/2$.

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

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

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



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

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

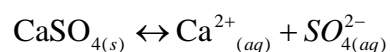
$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

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

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 sulphide.

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

Ans:



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

Let the solubility of $CaSO_4$ be s .

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

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

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

Molecular mass of $CaSO_4 = 136 \text{ g/mol}$

Solubility of $CaSO_4$ in gram/L

$$= 3.02 \times 10^{-3} \times 136$$

$$= 0.41 \text{ g/L}$$

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

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

73. The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is $1.0 \times 10^{-19} \text{ M}$. If 10mL of this is added to 5mL of 0.04M solution of the following:

$\text{FeSO}_4, \text{MnCl}_2, \text{ZnCl}_2$ and CdCl_2 , in which of these solutions precipitation will take place?

Given K_{sp} for $\text{FeS} = 6.3 \times 10^{-18}, \text{MnS} = 2.5 \times 10^{-13}, \text{ZnS} = 1.6 \times 10^{-24}$

$$\text{CdS} = 8.0 \times 10^{-27}$$

Ans: For precipitation to take place, it is required that the calculated ionic product exceeds the K_{sp} value.

Before mixing:

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

$$\text{volume} = 10 \text{ mL} \quad \text{volume} = 5 \text{ mL}$$

After mixing:

$$[S^{2-}] = ? \quad [M^{2+}] = ?$$

$$\text{volume} = (10 + 5) = 15 \text{ mL} \quad \text{volume} = 15 \text{ mL}$$

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

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

$$\begin{aligned} \text{Ionic product} &= [M^{2+}][S^{2-}] \\ &= (1.33 \times 10^{-2})(6.67 \times 10^{-20}) \\ &= 8.87 \times 10^{-22} \end{aligned}$$

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