
Chapter – 7 (Equilibrium)

Exercise Questions:

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

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

Answer:

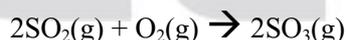
- On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are distributed over a large space.
- On increasing the volume of container, the rates of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decreases on increasing the volume, therefore, the rate of condensation will decrease initially.
- Finally, equilibrium will be restored when the rates of forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

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



Answer:

As per the question,



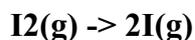
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$= \frac{(1.9)^2 M^2}{(0.6)^2 (0.82) M^3}$$

$$= 12.229 M^{-1} (\text{approx.})$$

Hence, K_c for the equilibrium is $12.229 / M$.

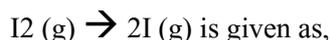
Question :3 At a certain temperature and total pressure of 10^5 PA , iodine vapour contains 40% by volume of I atoms



Calculate K_p for the equilibrium.

Answer:

K_p value at equilibrium for reaction,



Given, 40% volume is occupied by I atoms.

\therefore 60 % volume is occupied by I_2 .

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

$$\text{Partial pressure of } \text{I}_2 = (60/100) \times 10^5 = 60 \text{ kPa}$$

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

Substituting in equation for K_p ,

$$K_p = 2.67 \times 10^4 \text{ KPa}$$

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

- I. $2\text{NOCl}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$
- II. $2\text{Cu}(\text{NO}_3)_2(\text{s}) \rightarrow 2\text{CuO}(\text{s}) + 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- III. $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$
- IV. $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$
- V. $\text{I}_2(\text{s}) + 5\text{F}_2 \rightarrow 2\text{IF}_5$

Answer:

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

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

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

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

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

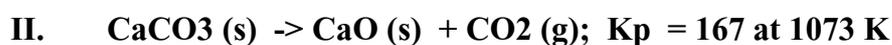
$$\text{iv.) } K_c = \frac{[\text{Fe}(\text{OH})_3(\text{s})]}{[\text{Fe}^{3+}(\text{aq})][\text{OH}^-(\text{aq})]^3}$$

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

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

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

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



Answer:



we know,

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

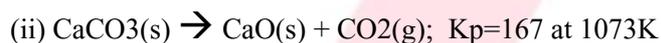
$$\Delta n_g = n_p - n_r$$

$$= (2 + 1) - (2) = 1$$

$$\text{Now, } 1.8 \times 10^{-2} = K_c(RT)^1$$

$$K_c = 1.8 \times 10^{-2} / (0.0821 \times 500)$$

$$K_c = 4.38 \times 10^{-4}$$



$$\Delta n_g = n_p - n_r$$

$$= 1 - 0 = 1$$

$$\text{Now, } K_p = K_c(RT)^1$$

$$167 = K_c (0.0821 \times 1073)$$

$$K_c = 167 / 0.0821 \times 1073$$

$$K_c = 1.89$$

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



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

Answer:

$$\text{For the reverse reaction, } K_c = 1 / K_c$$

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

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

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

Answer:

This is because the molar concentration of a pure solid liquid is independent of the amount present.

Mole concentration = Number of moles / Volume

= Mass / molecular mass / Volume

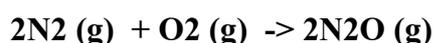
= Mass / volume x Molecular mass

= Density / Molecular mass

Though the density of the solid and pure liquid is fixed and molar is also fixed.

: Molar concentration are constant.

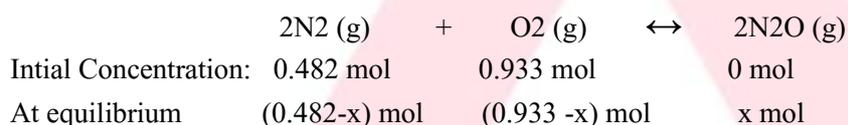
Question :8 Reaction between N₂ and O₂ takes place as follows :



If a mixture of 0.482 mol N₂ and 0.933 mol O₂ is placed in a 10 L reaction vessel and allowed to form N₂O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

Answer:

Let the concentration of N₂O at equilibrium be x. The given reaction is



Therefore, at equilibrium, in the 10 L vessel:

$$\text{N}_2 = 0.482 - x / 10$$

$$\text{O}_2 = 0.933 - x / 10$$

$$\text{N}_2\text{O} = x / 10$$

The value of equilibrium constant i.e. $K_c = 2.0 \times 10^{-37}$ is very small. Therefore, the amount of N₂ and O₂ reacted is also very small. Thus, x can be neglected from the expressions of molar concentrations of N₂ and O₂.

Then,

$$\text{N}_2 = 0.482/10 = 0.0482 \text{ molL}^{-1} \text{ and } \text{O}_2 = 0.933/10 = 0.0933 \text{ molL}^{-1}$$

Now,

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

$$2.0 \times 10^{-37} = 0.01x^2 / (0.482 / 10)^2 \times (0.933 / 10)$$

$$2.0 \times 10^{-37} = 0.01x^2 / 2.1676 \times 10^{-4}$$

$$x^2 = 43.352 \times 10^{-40}$$

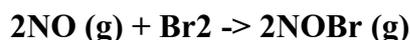
$$\text{or } x = 6.6 \times 10^{-20}$$

$$[\text{N}_2\text{O}] = x / 10$$

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

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

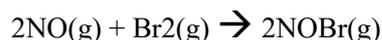
Question :9 Nitric oxide reacts with Br₂ and gives nitrosyl bromide as per reaction given below:



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

Answer:

The given equation is:



$$\text{At } t = 0 \quad 0.087 \quad 0.0437 \quad 0$$

$$\text{At eq} \quad (0.087 - 2x) \quad (0.0437 - x) \quad 2x$$

Given, moles of NOBr at equilibrium = 0.518

$$\text{e.g., } 2x = 0.0518$$

$$x = 0.0259$$

$$\text{Moles of NO at equilibrium} = 0.087 - 2x$$

$$= 0.087 - 2 \times 0.0259$$

$$= 0.087 - 0.0518$$

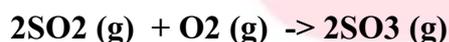
$$= 0.0352 \text{ mol}$$

$$\text{Moles of Br}_2 \text{ at equilibrium} = 0.0437 - x$$

$$= 0.0437 - 0.0259$$

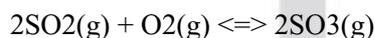
$$= 0.0178 \text{ mol}$$

Question :10 At 450K $K_p = 2.0 \times 10^{10} / \text{bar}$ for the given reaction at equilibrium



What is K_c at this temperature?

Answer:



For the given reaction:

$$\Delta_n = 2 - 3 = -1$$

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

$$R = 0.0831 \text{ bar L bar / K/ mol}$$

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

We know,

$$K_p = K_c (RT)^{\Delta_n}$$

$$K_c = K_p / (RT)^{-1} \text{ [because , } \Delta_n = -1 \text{]}$$

$$= K_p (RT)$$

$$= 2 \times 10^{10} \times 0.0831 \times 450$$

$$= 7.479 \times 10^{11} \text{ L/mol}$$

Question :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?



Answer:

The initial concentration of HI is 0.2 atm. At equilibrium, it has a partial pressure of 0.04 atm.

Therefore, a decrease in the presence of HI is $0.2 - 0.04 = 0.16$. The given reaction is:

| | | | |
|----------------|-----------------------------|--------------------------|------------------------|
| | $2\text{HI(g)} \rightarrow$ | $\text{H}_2\text{(g)} +$ | $\text{I}_2\text{(g)}$ |
| Initial conc. | 0.2 atm | 0 | 0 |
| At equilibrium | 0.4 atm | $0.16 / 2$ | $0.16 / 2$ |
| | | 0.08 atm | 0.08 atm |

Therefore,

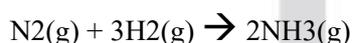
$$\begin{aligned} K_p &= p_{\text{H}_2} \times p_{\text{I}_2} / p_{\text{HI}}^2 \\ &= 0.08 \times 0.08 / (0.04)^2 \\ &= 0.0064 / 0.0016 \\ &= 4.0 \end{aligned}$$

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

Question :12 A mixture of 1.57 Mol of N_2 , 1.92 mol of H_2 and 8.13 Molly of NH_3 is introduced into a 20L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $\text{N}_2 \text{(g)} + 3\text{H}_2 \text{(g)} \rightarrow 2 \text{NH}_3 \text{(g)}$ is 1.7×10^2 . Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Answer:

The given reaction is:



The given concentration of various species is

$$[\text{N}_2] = 1.57 / 20 \text{ mol / L}$$

$$[\text{H}_2] = 1.92 / 20 \text{ mol / L}$$

$$[\text{NH}_3] = 8.31 / 20 \text{ mol / L}$$

Now, reaction quotient Q_c is:

$$\begin{aligned} Q &= [\text{NH}_3]^2 / [\text{N}_2][\text{H}_2]^3 \\ &= (8.13 / 20)^2 / (1.57 / 20)(1.92 / 20)^3 \\ &= 2.4 \times 10^3 \end{aligned}$$

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.

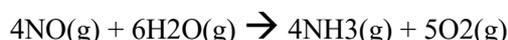
Question :13 The equilibrium constant expression for a gas reaction is,

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

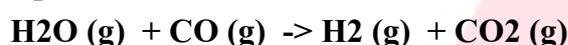
Write the balanced chemical equation corresponding to this expression.

Answer:

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



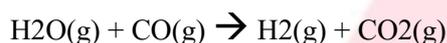
Question :14 One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water reacts with CO according to the equation,



Calculate the equilibrium constant for the reaction.

Answer:

The given reaction is :



| Compound | H_2O | CO | H_2 | CO_2 |
|-------------------|----------------------|-------------|--------------|---------------|
| Initial Conc. | 0.1 M | 0.1 M | 0 | 0 |
| Equilibrium Conc. | 0.06 M | 0.06 M | 0.04 M | 0.04 M |

Therefore, the equilibrium constant for the reaction,

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

$$= \frac{(0.4 \times 0.4)}{(0.6 \times 0.6)}$$

$$= 0.444$$

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



Is 54.8. If 0.5 mol / L 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?

Answer:



when reaction will be reverse



A/C to question,

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

$$\text{Let at equilibrium conc. of } [\text{H}_2] = [\text{I}_2] = x \text{ mol/L}$$

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

$$1/54.8 = x \cdot x / (0.5)^2$$

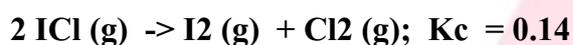
$$1/54.8 = x^2 / (0.5)^2$$

$$x^2 = 0.25/54.8 = 0.00456$$

$$x = 0.0675 \text{ M}$$

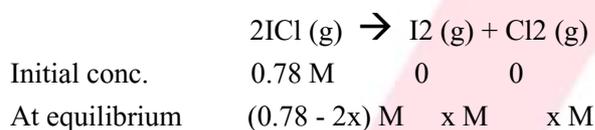
$$[\text{H}_2] = [\text{I}_2] = 0.0675 \text{ M}$$

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



Answer:

The given reaction is:



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

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

$$x^2 / (0.78 - 2x)^2 = 0.14$$

$$x / 0.78 - 2x = 0.374$$

$$x = 0.292 - 0.748x$$

$$1.748x = 0.292$$

$$x = 0.167$$

Hence, at equilibrium,

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

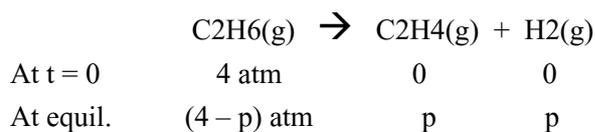
$$[\text{HI}] = (0.78 - 2 \times 0.167) \text{ M}$$

$$= 0.446 \text{ M.}$$

Question :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?



Answer:



We know,

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

$$K_p = P \cdot P / (4 - P)$$

$$0.04 = P^2 / (4 - P)$$

$$1/25 = P^2 / (4 - P)$$

$$4 - P = 25P^2$$

$$25P^2 + P - 4 = 0$$

$$P = \{-1 \pm \sqrt{(1 + 400)}\} / 50$$

$$P = \{-0.02 \pm 0.4\}$$

$$P = 0.38$$

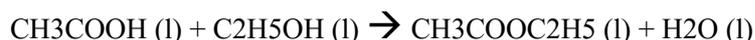
Hence, pressure of $C_2H_6 = 4 - p = 4 - 0.38 = 3.62 \text{ atm}$

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



- I. Write the concentration ratio Q_c , for 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?**

Answer:



$$(i) \text{ Reaction quotient } (Q_c) = [CH_3COOC_2H_5][H_2O] / [C_2H_5OH][CH_3COOH]$$

Here, H_2O is not excess that's why its concentration isn't constant.

(ii)



$$\text{At } t = 0 \quad \quad \quad 1 \text{ mol} \quad \quad \quad 0.180 \text{ mol} \quad \quad \quad 0 \quad \quad \quad 0$$

$$\text{At equil.} \quad \quad \quad (1 - x) \text{ mol} \quad \quad \quad (0.180 - x) \text{ mol} \quad \quad \quad x \quad \quad \quad x$$

Given,

$$[CH_3COOC_2H_5] \text{ at equilibrium} = 0.171 \text{ mol} = x$$

$$\text{So, } x = 0.171 \text{ mol}$$

$$\text{Hence, } [CH_3COOH] = 1 - x = 1 - 0.171 = 0.829$$

$$[C_2H_5OH] = 0.180 - x = 0.180 - 0.171 = 0.009$$

$$[CH_3COOC_2H_5] = [H_2O] = x = 0.171$$

$$\text{Now, } K_c = [CH_3COOC_2H_5][H_2O] / [CH_3COOH][C_2H_5OH]$$

$$= 0.171 \times 0.171 / 0.829 \times 0.009$$

$$= 3.919 \approx 3.92$$

Hence, $K_c = 3.92$

(iii) Similarly,

At time t ,

$$[\text{CH}_3\text{COOH}] = 1 - x = 0.5 - 0.214 = 0.286 \text{ mol}$$

$$[\text{C}_2\text{H}_5\text{OH}] = 0.5 - x = 0.5 - 0.214 = 0.286 \text{ mol}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = x = 0.214 \text{ mol}$$

$$[\text{H}_2\text{O}] = x = 0.214 \text{ mol}$$

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

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

$$= 0.2037 \approx 0.204$$

Here, $Q_c \neq K_c$ hence, equilibrium has not been reached.

Question :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 $0.5 \times 10^{-1} \text{ mol/L}$. If value of K_c is 8.3×10^{-3} , what are the concentrations of PCl_3 and Cl_2 at equilibrium?



Answer:



$$\text{At equil.} \quad 0.05 \quad \quad x \quad \quad x$$

Given,

$$[\text{PCl}_5] \text{ at equilibrium} = 0.05 \text{ M}$$

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

But we know,

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

$$8.3 \times 10^{-3} = \frac{x \cdot x}{0.05}$$

$$8.3 \times 10^{-3} \times 0.05 = x^2$$

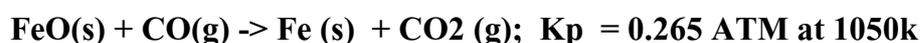
$$x^2 = 0.415 \times 10^{-3} = 4.15 \times 10^{-4}$$

Now, take square root both sides,

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

$$\text{Hence, } [\text{PCl}_3] = [\text{Cl}_2] = 2.04 \times 10^{-2} \text{ M}$$

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



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



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

Answer:

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



Initial Conc. 3.3×10^{-3} 0 0

At equilibrium $3.3 \times 10^{-3} - 2x$ x x

Now, we can write,

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

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

$$x / (3.3 \times 10^{-3} - 2x) = 5.66$$

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

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

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

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

Therefore, at equilibrium,

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

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

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

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

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



Calculate K_c for this reaction at the above temperature.

Answer:

Let weight of mixture is 100g, then 90.55% CO by mass means 90.55g CO and 9.45g CO₂ present in the mixture.

No of moles of CO = Given weight of CO/molar mass of CO

$$= 90.55/28 = 3.234 \text{ mol [molar mass of CO = 28 g/mol]}$$

No of moles of CO₂ = given weight of CO₂/molar mass of CO₂

$$= 9.45/44 = 0.215 \text{ mol [molar mass of CO}_2 = 44\text{g/mol]}$$

$$\text{Mole fraction of CO (} x_{\text{CO}} \text{)} = n_{\text{CO}} / n_{\text{CO}} + n_{\text{CO}_2}$$

$$= 3.234 / 3.234 + 0.215$$

$$= 0.938$$

$$\text{Mole fraction of CO}_2 = (1 - x_{\text{CO}}) = 1 - 0.938 = 0.062$$

Now, partial pressure of CO = mole fraction of CO \times total pressure

$$= 0.938 \times 1 \text{ atm}$$

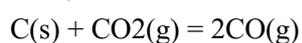
$$= 0.938 \text{ atm}$$

Similarly, partial pressure of CO₂ = mole fraction of CO₂ \times total pressure

$$= 0.062 \times 1 \text{ atm}$$

$$= 0.062 \text{ atm}$$

Now,



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

$$K_p = \frac{(0.938)^2}{(0.062)} = 14.19$$

Δn_g = number of mole of gaseous products - number of mole of gaseous reactants

$$= 2 - 1 = 1$$

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

$$K_c = K_p / RT$$

$$= 14.19 / 0.0821 \times 1127 \quad [T = 1127 \text{ K and } R = 0.0821 \text{ L.atm/K/mol }]$$

$$= 0.15336 \approx 0.153$$

Question :24 Calculate a. And b. The equilibrium constant for the formation of NO₂ from NO and O₂ at 298 K



Where,

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

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

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

Answer:

a.) For the given reaction, we have

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

$$\Delta G^\circ = 52.0 - (87.0 + 0)$$

$$= -35.0 \text{ KJ / mol}$$

b.) We know that,

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

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

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

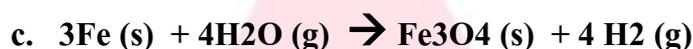
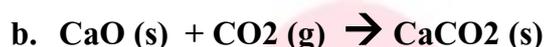
$$= 6.134$$

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

$$= 1.36 \times 10^6$$

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

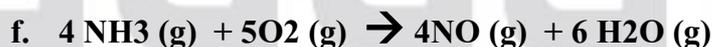
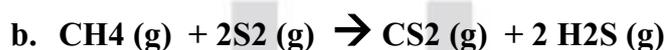
Question :25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?



Answer:

- a.) The 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 remain the same.

Question :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.



Answer:

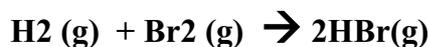
When pressure is increased:

The reaction given in (i), (iii), (iv), (v) and (vi) will get affected.

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

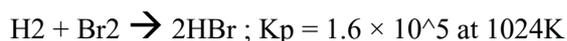
Since the number of moles of gaseous reactants is less than that of gaseous products, the reactions are given in (i), (iii), (v) and (vi) will shift in the backward direction.

Question :27 The equilibrium constant for the following reactions is 1.6×10^5 at 1024K

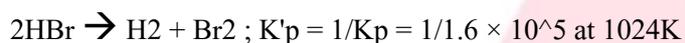


Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Answer:



When reaction will be reverse ,



At initial time , pressure of HBr is 10 bar

Pressure of H₂ and Br₂ are 0 bar .

At equilibrium , pressure of HBr is (10-x) bar

Pressure of H₂ and Br₂ are x/2 bar.

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

$$= \frac{(x/2) \cdot (x/2)}{(10-x)^2}$$

$$1/1.6 \times 10^5 = \frac{x^2}{4(10-x)^2}$$

$$0.625 \times 10^{-5} = \frac{x^2}{4(10-x)^2}$$

Because values of K'p is so small so, (10-x) ≈ 10

$$0.625 \times 10^{-5} = \frac{x^2}{4 \times 100}$$

$$625 \times 4 \times 10^{-5} = x^2$$

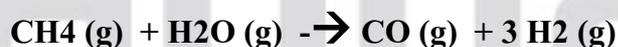
$$x = 0.05$$

$$x/2 = 0.025 = 2.5 \times 10^{-2} \text{ bar}$$

$$\text{Hence, } P(\text{H}_2) = P(\text{Br}_2) = 2.5 \times 10^{-2} \text{ bar}$$

$$\text{So, } P(\text{HBr}) = 10 - x = 10 - 0.05 \approx 10 \text{ bar}$$

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



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

Answer:

- a.) For the given reaction,

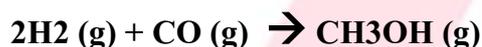
$$K_p = p_{\text{CO}} \times p_{\text{H}_2}^3 / p_{\text{CH}_4} \times p_{\text{H}_2\text{O}}$$

- b.) i.) According to Le Chatelier's principle, the equilibrium will shift in the backward direction.
ii.) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.
iii.) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increase the rate of a reaction. Thus, equilibrium will be attained quickly.

Question :29 Describe the effect of:

- Addition of H₂**
- Addition of CH₃OH**
- Removal of CO**
- Removal of CH₃OH**

On the equilibrium of the reaction :



Answer:

- According to Le Chatelier's principle, on the addition of H₂, the equilibrium of the given reaction will shift in the forward direction.
- On addition of CH₃OH, the equilibrium will shift in the backward direction.
- On removing CO, the equilibrium will shift in the backward direction.
- On removing CH₃OH, the equilibrium will shift in the forward direction.

Question :30 At 473 K, equilibrium constant K_c for decomposition of phosphorous pentachloride, PCI₅ is 8.3 x 10⁻³. If decomposition is depicted as:



- Write an expression for K_c for the reaction**
- What is the value of K_c for the reverse reaction at the same temperature?**
- What would be the effect on K_c if**
 - More PCI₅ is added**
 - Pressure is increased**
 - The temperature is increased**

Answer:

- $K_c = [\text{PCI}_3(\text{g})]\{\text{Cl}_2(\text{g})\} / [\text{PCI}_5(\text{g})]$
- Value of K_c for the reverse reaction at the same temperature is:

$$K'_c = 1 / K_c$$

$$= 1 / 8.3 \times 10^{-3} = 1.2048 \times 10^2$$

$$= 120.48$$

c.) (i) K_c would remain the same because in this case, the temperature remains the same.

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

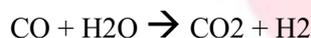
(iii) In an endothermic reaction, the value of K_c increases with an increase in temperature. Since the given reaction is an endothermic reaction, the value of K_c will increase if the temperature is increased.

Question :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 reaction involves the formation of CO and H₂. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction.



If a reaction vessel at 400 degree C is charged with an equivalent mixture of CO and steam such that $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 4.0$ bar, what will be the partial pressure of H₂ at equilibrium? $K_p = 10.1$ at 400degree C

Answer:



At $t = 0$, pressure of CO = 4 bar

Pressure of H₂O = 4 bar

At eqlib., pressure of CO = (4 - x)

Pressure of H₂O = (4 - x) bar

Pressure of CO₂ = x bar

Pressure of H₂ = x bar

Now, equilibrium constant (K_c) = $[\text{CO}_2][\text{H}_2]/[\text{CO}][\text{H}_2\text{O}]$

$$K_p = x^2/(4 - x)^2$$

$$10.1 = x^2/(4 - x)^2$$

$$\sqrt{10.1} = x/(4 - x)$$

$$3.17(4 - x) = x$$

$$12.68 - 3.17x = x$$

$$12.68 = 4.17x$$

$$x = 12.68/4.17 = 3.04 \text{ bar}$$

Hence, pressure of H₂ = x bar = 3.04 bar

Question :32 Predict which of the following reactions will have appreciable concentration of reactants and products :

- $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g}) \quad K_c = 5 \times 10^{-39}$
- $\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{NOCl}(\text{g}) \quad K_c = 3.7 \times 10^8$
- $\text{Cl}_2(\text{g}) + 2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}_2\text{Cl}(\text{g}) \quad K_c = 1.8$

Answer:

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

Question :33 The value of K_c for the reaction $3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g})$ is 2.0×10^{-50} at 250 degree C. If the equilibrium concentration of O_2 in air at 25 degree C is 1.6×10^{-2} ,what is the concentration of O_3 ?

Answer:

The given reaction is:



$$\text{Then, } K_c = \frac{[\text{O}_3(\text{g})]^2}{[\text{O}_2(\text{g})]^3}$$

$$\text{It is given that } K_c = 2.0 \times 10^{-50} \text{ and } \text{O}_2(\text{g}) = 1.6 \times 10^{-2}$$

Then we have,

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

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

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

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

$$\text{Hence, the concentration of } \text{O}_2(\text{g}) = 2.86 \times 10^{-28} \text{ M}$$

Question :34 The reaction, $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$

Is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H₂ and 0.02 mol of H₂O and an unknown amount of CH₄ in the flask. Determine the concentration of CH₄ in the mixture. The equilibrium constant K_c for the reaction at given temperature is 3.90.

Answer:

Let the concentration of methane at equilibrium be x.



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

It is given that $K_c = 3.90$.

Therefore,

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

$$[x] [0.02] / (0.3) (0.1)^3 = 3.90$$

$$x = (3.90) (0.3) (0.1)^3 / [0.02]$$

$$x = 0.00117 / 0.02$$

$$= 0.0585 \text{ M}$$

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

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

Question :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-} , S^{2-}

Answer:

A conjugate acid – base pair is a pair that has difference of only one proton.

The conjugate acid – base pair of the following are as follows:

HNO_2 – NO_2^- (Base)

CN^- - HCN (Acid)

HClO_4 – ClO_4^- (Base)

F^- - HF (Acid)

OH^- - H_2O (Acid) O^{2-} (Base)

CO_3^{2-} - HCO_3^- (Acid)

S^{2-} - HS^- (Acid)

Question :36 Which of the following are Lewis acids? H_2O , BF_3 , H^+ , NH_4^+

Answer:

Lewis acids are the acids which can accept a pair of electrons.

H_2O – Lewis base

BF_3 – Lewis acid

H^+ - Lewis acid

NH_4^+ - Lewis acid.

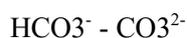
Question :37 What will be the conjugate base of the Bronsted acids: HF , H_2SO_4 , HCO_3^- -?

Answer:

The following shows the conjugate bases for the Bronsted acids:

HF – F^-

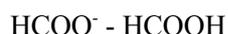
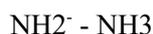
H_2SO_4 – HSO_4^-



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

Answer:

The following shows the conjugate acids for the Bronsted base:



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

Answer:

The conjugate acids and conjugate bases for the given species are listed in the table below:

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

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

- OH^-
- F^-
- H^+
- BCl_3

Answer:

- a.) OH^-

It is Lewis base as it has a tendency to lose a pair of electrons.

- b.) F^-

It is a Lewis base as it has a tendency to lose its lone pair of electrons.

- c.) H^+

It is a Lewis acid as it has a tendency to accept a pair of electrons.

- d.) BCl_3

It is a Lewis acid as it has tendency to accept a pair of electrons.

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

Answer:

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] \\ &= -\log(3.8 \times 10^{-3}) \\ &= -\log 3.8 - \log(10^{-3}) \\ &= -\log 3.8 + 3 \\ &= -0.5798 + 3 \\ &= 2.423 \end{aligned}$$

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

Answer:

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] \\ \log [\text{H}^+] &= -\text{pH} \\ [\text{H}^+] &= \text{antilog}(-\text{pH}) \\ &= \text{Antilog}(-3.76) \\ &= 0.000178 \\ &= 1.78 \times 10^{-4} \\ &: 1.78 \times 10^{-4} \text{ is the concentration of white vinegar sample.} \end{aligned}$$

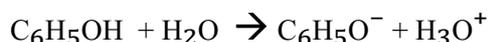
Question :43 The ionization constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4} , 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

Answer:

$$\begin{aligned} \text{For } \text{F}^-, \text{K}_b &= \text{K}_w / \text{K}_a \\ &= 10^{-14} / (6.8 \times 10^{-4}) \\ &= 1.47 \times 10^{-11} \\ \text{For } \text{HCOO}^-, \text{K}_b & \\ &= 10^{-14} / 1.8 \times 10^{-4} \\ &= 5.6 \times 10^{-11} \\ \text{For } \text{CN}^-, & \\ \text{K}_b &= 10^{-14} / (4.8 \times 10^{-9}) \\ &= 2.08 \times 10^{-6} \end{aligned}$$

Question :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 0.05 M in sodium phenolate?

Answer:



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

According to rule of ostwald law,

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

Where, C is the concentration of phenol solution

e.g., C = 0.01 M

$$\text{Now, } [\text{C}_6\text{H}_5\text{O}^-] = [\text{H}_3\text{O}^+] = \sqrt{\{10^{-10} \times 0.05\}} = 2.24 \times 10^{-6} \text{ M}$$

Now, when mixture contains 0.05M phenol and 0.01M phenolate ion then,

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

$$10^{-10} = 0.01\text{M} \times [\text{H}_3\text{O}^+] / 0.05\text{M}$$

$$[\text{H}_3\text{O}^+] = 0.05 \times 10^{-10} / 0.01 = 5 \times 10^{-10} \text{ M}$$

Now, we know, $[\text{H}_3\text{O}^+] = C\alpha$

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

$$\alpha = 5 \times 10^{-10} / 0.05 = 10^{-8}$$

Hence, degree of ionization = 10^{-8}

Question :45 The first ionization constant of H₂S 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 solution is 0.1 M in HCl also? If the second dissociation constant of H₂S is 1.2×10^{-13} , calculate the concentration of S²⁻ under both conditions.

Answer:

(i) To calculate the concentration of HS⁻ ion:

Case I (in the absence of HCl):

Let the concentration of HS⁻ be x M.



$$\text{Ci} \quad 0.1 \quad 0 \quad 0$$

$$\text{Cf} \quad 0.1-x \quad x \quad x$$

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

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

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

Taking 0.1 - x M ; 0.1M, we have

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

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

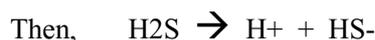
$$x = \sqrt{9.1 \times 10^{-9}}$$

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

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

Case II (in the presence of HCl):

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



$$0.1 \quad 0.1$$

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

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

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

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

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

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

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



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

Let S^{2-} be X .

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

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

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

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

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

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

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

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

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

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

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

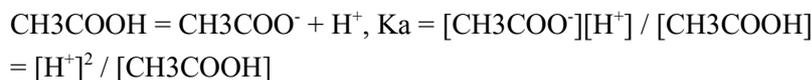
$$X' = \frac{1.092 \times 10^{-20}}{0.1}$$

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

$$K_{a1} = 1.74 \times 10^{-5}$$

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

Answer:



$$[\text{H}^+] = \sqrt{K_a[\text{CH}_3\text{COOH}]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4}\text{M}$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 9.33 \times 10^{-4}\text{M}$$

$$\text{pH} = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$$

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

Answer:



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

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

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

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

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}} = 5.0 \times 10^{-7}$$

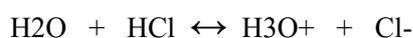
$$\text{p}K_a = -\log K_a = -\log(5.0 \times 10^{-7}) = 7 - 0.699 = 6.301$$

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

- 0.003 M HCl
- 0.005M NaOH
- 0.002 M HBr
- 0.002 M KOH

Answer:

(i) 0.003M HCl:



Since HCl is completely ionized,

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

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

Now

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.003)$$

$$= 2.52$$

Hence, the pH of the solution is 2.52.

(b) 0.005 M NaOH



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

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

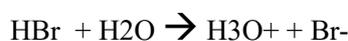
$$\text{pOH} = -\log[\text{OH}^-] = -\log (0.05)$$

$$= 2.30$$

$$\therefore \text{pH} = 14 - 2.30 = 11.70$$

Hence, the pH of the solution is 11.70.

(c) 0.002 M HBr



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

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

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.002)$$

$$= 2.69$$

Hence, the pH of the solution is 2.69.

(d) 0.002 M KOH



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

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

$$\text{Now pOH} = -\log[\text{OH}^-] = -\log (0.002)$$

$$= 2.69$$

$$\therefore \text{pH} = 14 - 2.69 = 11.31$$

Hence, the pH of the solution is 11.31.

Question :49 Calculate the pH of the following solutions :

- 2 g of TIOH dissolved in water to give 2 litre of solution**
- 0.3 g of Ca(OH)₂ dissolved in water to give 500 mL of solution.**
- 0.3 g of NaOH dissolved in water to give 200 mL of solution.**
- 1 mL of 13.6 M of HCl is diluted with water to give 1 litre of solution.**

Answer:

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

$$[\text{TIOH(aq)}] = 2/2 \text{ g/L}$$

$$= 2/2 \times 1/221 \text{ M}$$

$$= 1/221 \text{ M}$$



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

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

$$10^{-14} = [\text{H}^+] [1/221]$$

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

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

$$= 11.65$$

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



$$[\text{Ca(OH)}_2] = 0.3 \times 1000/500 = 0.6 \text{ M}$$

$$[\text{OH}^-(\text{aq})] = 2 \times [\text{Ca(OH)}_2(\text{aq})] = 2 \times 0.6 = 1.2 \text{ M}$$

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

$$= 10^{-14}/1.2 \text{ M}$$

$$= 0.833 \times 10^{-14}$$

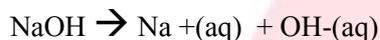
$$\text{pH} = -\log(0.833 \times 10^{-14})$$

$$= -\log(8.33 \times 10^{-13})$$

$$= (-0.902 + 13)$$

$$= 12.098$$

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



$$[\text{NaOH}] = 0.3 \times 1000/200 = 1.5 \text{ M}$$

$$[\text{OH}^-(\text{aq})] = 1.5 \text{ M}$$

$$\text{Then } [\text{H}^+] = 10^{-14} / 1.5$$

$$= 6.66 \times 10^{-13}$$

$$\text{pH} = -\log (6.66 \times 10^{-13})$$

$$= 12.18$$

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

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

$$\text{(Before dilution) (after dilution)}$$

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

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

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

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

$$= (-0.1335 + 2)$$

$$= 1.866 = 1.87$$

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

Answer:

Degree of ionization, $\alpha = 0.132$

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

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

$$= 0.1 \times 0.132$$

$$= 0.0132$$

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

$$= -\log (0.0132)$$

$$= 1.879 : 1.88$$

Now,

$$K_a = C\alpha^2$$

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

$$K_a = 0.0017$$

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

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

Answer:

$$c = 0.005$$

$$\text{pH} = 9.95$$

$$\text{pOH} = 4.05$$

$$\text{pH} = -\log (4.05)$$

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

$$[\text{OH}^-] = 8.91 \times 10^{-5}$$

$$c\alpha = 8.91 \times 10^{-5}$$

$$\alpha = 8.91 \times 10^{-5} / 5 \times 10^{-3} = 1.782 \times 10^{-2}$$

$$\text{Thus, } K_b = c\alpha^2$$

$$= 0.005 \times (1.782)^2 \times 10^{-4}$$

$$= 0.005 \times 3.1755 \times 10^{-4}$$

$$= 0.0158 \times 10^{-4}$$

$$K_b = 1.58 \times 10^{-6}$$

$$\text{p}K_b = -\log K_b$$

$$= -\log (1.58 \times 10^{-6})$$

$$= 5.80$$

Question :52 What is pH of 0.001 M 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.

Answer:

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

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

$$\text{pH} = ?$$

$$\alpha = ?$$

$$K_b = c\alpha^2$$

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

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

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

$$\text{Then (anion)} = c\alpha = 0.001 \times 65.34 \times 10^{-4}$$

$$= 0.65 \times 10^{-5}$$

$$\text{pOH} = -\log (0.65 \times 10^{-5})$$

$$= 6.187$$

$$\text{pH} = 7.813$$

Now

$$K_a \times K_b = K_w$$

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

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

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

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

Question :53 Calculate the degree of ionization of 0.05 M acetic acid if it's pKa value is 4.74 .How is the degree of dissociation affected when it's solution also contains

- a. 0.01 M
- b. 0.1 M of HCl?

Answer:

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

$$\text{pKa} = 4.74$$

$$\text{pKa} = -\log (K_a)$$

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

$$K_a = c \alpha^2$$

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

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

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

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.

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

Answer:

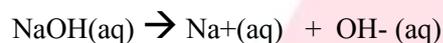
$$K_b = 5.4 \times 10^{-4}$$

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

Then,

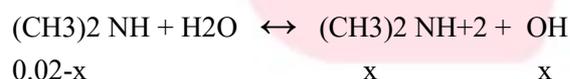
$$\begin{aligned} \alpha &= \sqrt{K_b/c} \\ &= \sqrt{5.4 \times 10^{-4}/0.02} \\ &= 0.1643 \end{aligned}$$

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



$$0.1\text{M} \qquad 0.1\text{M}$$

and



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

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

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

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

$$x = 0.0054$$

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

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

- Human muscle – fluid, 6.83
- Human stomach fluid, 1.2
- Human blood, 7.38
- Human saliva, 6.4.

Answer:

i.) Human saliva, 6.4

$$\text{pH} = 6.4$$

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

ii.) Human stomach fluid, 1.2

$$\text{pH} = 1.2$$

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

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

iii.) Human muscle fluid, 6.83

$$\text{pH} = 6.83$$

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

$$6.4 = 1.48 \times 10^{-7} \text{M}$$

iv.) Human blood, 7.38

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

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

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

Answer:

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

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

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

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

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

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

(ii) pH of black coffee = 5.0

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

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

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

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

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

(iii) pH of tomato juice = 4.2

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

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

(iv) pH of lemon juice = 2.2
Since, $\text{pH} = -\log [\text{H}^+]$
 $2.2 = -\log [\text{H}^+]$
 $\log [\text{H}^+] = -2.2$
 $[\text{H}^+] = \text{antilog}(-2.2)$
 $= 6.31 \times 10^{-3} \text{ M}$

(v) pH of egg white = 7.8
Since, $\text{pH} = -\log [\text{H}^+]$
 $7.8 = -\log [\text{H}^+]$
 $\log [\text{H}^+] = -7.8$
 $[\text{H}^+] = \text{antilog}(-7.8)$
 $= 1.58 \times 10^{-8} \text{ M}$

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

Answer:

$$\begin{aligned}[\text{KOH}(\text{aq})] &= 0.561 / (1/5) \text{ g/L} \\ &= 2.805 \text{ X } (1 / 56.11) \\ &= 0.05 \text{ M}\end{aligned}$$



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

$$[\text{H}^+] = K_w / [\text{OH}^-][\text{H}^+] = 10^{-14} / 0.05$$

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

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

$$\text{pH} = -\log [2 \times 10^{-13}]$$

$$\text{pH} = 12.70$$

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

Answer:

Given, solubility of $\text{Sr}(\text{OH})_2$ is 19.23 g/L

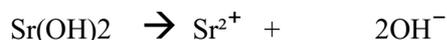
Molecular weight of $\text{Sr}(\text{OH})_2$ is 121.6 g/mol

We know,

Molarity = solubility/molecular weight

$$= 19.23 \text{ g/L}/121.6\text{g/mol}$$

$$= 0.1581 \text{ M}$$



$$0.1581\text{M} \quad 0.1581\text{M} \quad 2 \times 0.1581\text{M} = 0.3162\text{M}$$

$$[\text{Sr}^{2+}] = 0.1581\text{M} \text{ and } [\text{OH}^-] = 0.3162\text{M}$$

We know, ionic product(K_w) = $[\text{H}^+][\text{OH}^-] = 10^{-14}$

$$[\text{H}^+] = 10^{-14} / [\text{OH}^-] = 10^{-14} / 0.3162 = 3.16 \times 10^{-14}$$

Now Arrhenius formula,

$$\text{pH} = -\log[\text{H}^+] = -\log(3.16 \times 10^{-14}) = 14 - 0.4997 = 13.5003$$

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

Answer:



$$\text{At } t = 0 \quad 0.05 \quad 0 \quad 0$$

$$\text{At eqlib. } (0.05 - C\alpha) \quad C\alpha \quad C\alpha$$

We know, from Ostwald's dilution law,

$$K_a = C\alpha^2 \Rightarrow \alpha = \sqrt{\{K_a/C\}}$$

$$= \sqrt{\{1.32 \times 10^{-5}/0.05\}} = 0.016248$$

$$[\text{H}_3\text{O}^+] = C\alpha = 0.05 \times 0.016248 = 8.124 \times 10^{-4} \text{ M}$$

Now use Arrhenius formula for pH

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(8.124 \times 10^{-4}) = 4 - 0.9098 = 3.09$$

Now, when the solution contains 0.01 M HCl

$$K_a = [\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]/[\text{CH}_3\text{CH}_2\text{COOH}]$$

$$1.32 \times 10^{-5} = C\alpha \times 0.01/(0.05 - C\alpha)$$

$$(0.05 - C\alpha) \approx 0.05$$

$$1.32 \times 10^{-5} = C\alpha \times 0.01/0.05$$

$$C\alpha = 5 \times 1.32 \times 10^{-5} = 6.6 \times 10^{-5} \text{ M}$$

$$\text{Hence, degree of ionization } (\alpha) = 6.6 \times 10^{-5}/0.05 = 1.32 \times 10^{-5}$$

Question :60 The pH of 0.1 M solution of cyanide acid (HCNO) is 2.34 . Calculate the ionization constant of the acid and it's degree of ionization in the solution.

Answer:

$$c = 0.1M$$

$$pH = 2.34$$

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

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

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

Also,

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

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

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

$$\alpha = 0.045$$

$$K_a = c \alpha^2$$

$$K_a = 0.1 \times (0.045)^2$$

$$K_a = 0.0002025$$

$$K_a = 2.025 \times 10^{-4}$$

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

Answer:

NaNO₂ is the salt of a strong base (NaOH) and a weak acid (HNO₂).



$$K_h = [HNO_2] [OH^-] / [NO_2^-]$$

$$K_w / k_a = 10^{-14} / 4.5 \times 10^{-4} = 0.22 \times 10^{-10}$$

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

$$[NO_2^-] = 0.04 - x ; 0.04$$

$$[HNO_2] = x$$

$$[OH^-] = x$$

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

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

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

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

$$[H_3O^+] = 10^{-14} / 0.093 \times 10^{-5} = 10.75 \times 10^{-9} M$$

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

$$= 7.96$$

Therefore, degree of hydrolysis

$$= x / 0.04 = (0.093 \times 10^{-5}) / 0.04 = 2.325 \times 10^{-5}$$

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

Answer:

$$\text{pH} = 3.44 \text{ As}$$

We know,

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

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

$$\text{Now, } K_h = 3.63 \times 10^{-4} / 0.02$$

(Given that concentration = 0.02M)

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

As we know that,

$$K_h = K_w / K_a$$

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

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

Question :63 Predict if the solutions of the following salts are neutral, acidic or basic NaCl, KBr, NaCN, NH₄NO₃, NaNO₂, KF.

Answer:

The solution of a salt of strong acid and strong base is neutral while that of weak acid and strong base is basic. and A solution of strong acid and a weak base is acidic.

(i) NaCl

NaCl is formed by HCl { strong acid } and NaOH { strong base } . and we know, A solution of strong acid and strong base is neutral.

Hence, NaCl is neutral.

(ii) KBr is formed by KOH { strong base } and HBr { strong acid } hence, KBr is neutral.

(iii) NaCN is formed by NaOH { strong base } and HCN { weak acid } hence, NaCN is basic.

(iv) NH₄NO₃ is formed by HNO₃ {strong acid } and NH₄OH { weak base } hence , NH₄NO₃ is acidic.

(v)NaNO₂ is formed by NaOH { strong base } and HNO₂ { weak acid comparatively} hence, solution is basic.

(vi) KF is formed by KOH { strong base } and HF { weak acid comparatively }
because Hydrolysis of it
 $F^- + H_2O \rightarrow HF + OH^-$, hence, solution is basic.

Question :64 The ionization constant of chloroacetic acid is 1.35×10^{-3} . What will be the pH of 0.1 M acid and it's 0.1 M sodium salt solution?

Answer:

For finding PH of 0.1 M sodium salt solution use the formula ,

$$PH = -1/2 [\log Kw + \log Ka - \log Kb]$$

Where, Kw is the ionic product

Ka is Ionisation constant of acid

Kb is the Ionisation constant of basic.

Given, Here,

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

$$Ka = 1.35 \times 10^{-3}$$

$$Kb = 0.1$$

$$\text{Now, } PH = -1/2 [\log(10^{-14}) + \log(1.35 \times 10^{-3}) - \log(0.1)]$$

$$= -1/2 [-14 + (-3 + 0.1303) - (-1)]$$

$$= -1/2 [-14 -3 + 0.1303 + 1]$$

$$= -1/2 [-15.8697] = 7.93485 \approx 7.94$$

Hence, PH of 0.1 M acid and sodium salt solution is 7.94

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

Answer:

Ionic product, $Kw = [H^+][OH^-]$

Assuming, $[H^+] = y$

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

$Kw = y^2$, Kw at 310K is

$$2.7 \times 10^{-14}$$

$$: 2.7 \times 10^{-14} = y^2$$

$$Y = 1.64 \times 10^{-7}$$

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

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

$$= -\log[1.64 \times 10^{-7}] = 6.78. \text{ Thus, the pH of neutral water at 310 K temperature is 6.78.}$$

Question :66 Calculate the pH of the resultant mixture :

- 10 mL of 0.2 M Ca(OH)₂ + 25 mL of 0.1 M HCl**
- 10 mL of 0.01 M H₂SO₄ + 10 mL of 0.01 M Ca(OH)₂**
- 10 mL of 0.1 M H₂SO₄ + 10 mL of 0.1 M KOH**

Answer:

(a) Here, for base

$$M_1 = [\text{OH}^-] = 2 \times 0.2 = 0.4 \text{ M}$$

$$V_1 = 10 \text{ ml so, } M_1V_1 = 0.4 \times 10 = 4 \text{ Mml}$$

For acid,

$$M_2 = [\text{H}^+] = 0.1 \text{ M}$$

$$V_2 = 25 \text{ ml so, } M_2V_2 = 0.1 \times 25\text{ml} = 2.5 \text{ Mml}$$

Here, strength of base (M_1V_1) > strength of acid (M_2V_2) so, solution is basic .

$$\text{So, } [\text{OH}^-] = \{M_1V_1 - M_2V_2\}/(V_1 + V_2)$$

$$= (4 - 2.5)/(10 + 25) = 0.043 \text{ M}$$

Now, use Arrhenius formula,

$$\text{POH} = -\log[\text{OH}^-] = -\log(0.043) = 2 - 0.6335 = 1.3665$$

$$\text{So, PH} = 14 - \text{POH} = 14 - 1.3665 = 12.6335$$

Similarly we can solve next all questions

(b) For acid (H₂SO₄),

$$M_1 = [\text{H}^+] = 2 \times 0.01\text{M} = 0.02 \text{ M} , V_1 = 10 \text{ ml}$$

$$\text{So, } M_1V_1 = 0.02 \times 10 = 0.2 \text{ Mml}$$

For base Ca(OH)₂,

$$M_2 = [\text{OH}^-] = 2 \times 0.01 \text{ M} = 0.02\text{M} , V_1 = 10 \text{ ml}$$

$$\text{So, } M_2V_2 = 0.02\text{M} \times 10\text{ml} = 0.2 \text{ Mml}$$

Because strength of H₂SO₄ = strength of base = 0.2 Mml

So, solution is neutral .

Hence, pH of solution is 7 .

(c) For acid (H₂SO₄),

$$M_1 = [\text{H}^+] = 2 \times 0.1 \text{ M} = 0.2 \text{ M} , V_1 = 10\text{ml}$$

$$M_1V_1 = 0.2 \text{ M} \times 10 \text{ ml} = 2\text{Mml}$$

For base (KOH),

$$M_2 = 0.1\text{M} , V_2 = 10\text{ml}$$

$$\text{So, } M_2V_2 = 0.1\text{M} \times 10 \text{ Mml} = 1 \text{ Mml}$$

Because strength of acid (H₂SO₄) > strength of base (KOH)

So, solution is acidic.

$$\text{Now, } [\text{H}^+] = (M_1V_1 - M_2V_2)/(V_1+V_2)$$

$$= (2 - 1)/(10+10) = 0.05 \text{ M}$$

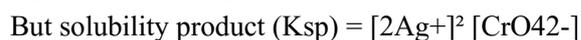
$$\text{pH} = -\log[\text{H}^+] = -\log(5 \times 10^{-2}) = 2 - 0.6990$$

$$= 1.301 \approx 1.3$$

Question :67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and Mercury's iodide at 298 K from their solubility product constant given in table 7.9 . Determine also the molarities of individual ions.

Answer:

(a) Silver chromate



Let solubility of silver chromate is s

$$K_{sp} = [2s]^2 [s] = 4s^3$$

$$s^3 = K_{sp}/4 = 1.1 \times 10^{-12}/4 = 2.75 \times 10^{-13}$$

Take log both sides,

$$3\log s = \log(2.75 \times 10^{-13}) = -12.5607$$

$$s = 6.503 \times 10^{-5} \text{ M } \{ \text{using antilog concept} \}$$

$$\text{So, } [\text{Ag}^+] = 2s = 1.3006 \times 10^{-5} \text{ M}$$

$$[\text{CrO}_4^{2-}] = s = 6.503 \times 10^{-5} \text{ M}$$

(b) $\text{BaCrO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{CrO}_4^{2-}; K_{sp} = 1.2 \times 10^{-10}$

Let solubility of BaCrO_4 is s M

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

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

$$s = \sqrt{K_{sp}} = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} \text{ M}$$

$$\text{So, } [\text{Ba}^{2+}] = [\text{CrO}_4^{2-}] = 1.1 \times 10^{-5} \text{ M}$$

(c) $\text{Fe(OH)}_3 \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-; K_{sp} = 10^{-38}$

Let solubility of Fe(OH)_3 is s M

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

$$K_{sp} = s \cdot 27s^3$$

$$27s^4 = K_{sp}$$

$$s^4 = K_{sp}/27 = 10^{-38}/27 = 0.037 \times 10^{-38}$$

Take log both sides,

$$4\log s = \log(0.037 \times 10^{-38}) = -39.4318$$

$$\log s = -9.8579 = \log(1.421 \times 10^{-10})$$

$$s = 1.387 \times 10^{-10} \{ \text{by using antilog concept} \}$$

$$\text{So, } [\text{Fe}^{3+}] = 1.387 \times 10^{-10} \text{ M}$$

$$[\text{OH}^-] = 3s = 3 \times 1.387 \times 10^{-10} \text{ M}$$

$$= 4.161 \times 10^{-10} \text{ M}$$

(d) $\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-; K_{sp} = 1.6 \times 10^{-5}$

Let solubility of PbCl_2 is s M

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

$$K_{sp} = s.4s^2$$

$$4s^3 = K_{sp}$$

$$s^3 = K_{sp}/4 = 1.6 \times 10^{-5}/4 = 0.4 \times 10^{-5} \text{ M}$$

$$3 \log s = \log(4 \times 10^{-6}) = -6 + 0.6021 = -5.3979$$

$$\log s = -1.7993 = 2(\text{bar}).2007$$

Take antilog both sides,

$$s = 1.585 \times 10^{-2} \text{ M}$$

$$\text{Hence, } [\text{Pb}^{2+}] = 1.585 \times 10^{-2} \text{ M}$$

$$[\text{Cl}^-] = 2s = 2 \times 1.585 \times 10^{-2} \text{ M} = 3.17 \times 10^{-2} \text{ M}$$

$$(e) \text{Hg}_2\text{I}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{I}^- ; K_{sp} = 4.5 \times 10^{-29}$$

Let solubility of Hg_2I_2 is s M

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

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

$$s^3 = K_{sp}/4 = 4.5 \times 10^{-29}/4 = 1.125 \times 10^{-29}$$

$$3 \log s = \log(1.125 \times 10^{-29}) = -29 + 0.0512 = -28.9488$$

$$\log s = -9.6496 = 10(\text{bar}).3504$$

$$s = 2.241 \times 10^{-10} \text{ M} \{\text{by using antilog}\}$$

$$[\text{Hg}_2^{2+}] = s = 2.241 \times 10^{-10} \text{ M}$$

$$[\text{I}^-] = 2s = 2 \times 2.241 \times 10^{-10} = 4.482 \times 10^{-10} \text{ M}$$

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

Answer:

Silver chromate :



$$[\text{Ag}^+] = 2s_1, \text{CrO}_4^{2-} = s_1$$

$$K_{sp} = (2s_1)^2(s_1) = 4s_1^3 = 1.1 \times 10^{-12}$$

$$S_1 = 6.5 \times 10^{-5} \dots(1)$$



$$[\text{Ag}^+] = [\text{Br}^-] = s_2$$

$$K_{sp} = (s_2) \times (s_2) = s_2^2 = 5.0 \times 10^{-13}$$

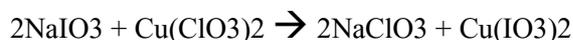
$$S_2 = 7.07 \times 10^{-7} \dots(2)$$

Divide equation (1) by equation (2) to obtain the ratio of the molarities of saturated solutions:

$$S_1 / s_2 = 6.50 \times 10^{-5} / 7.07 \times 10^{-7} = 91.9$$

Question :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?

Answer:



Equal volume of 0.002M solutions of NaIO₃ and Cu(IO₃)₂ are mixed together. So, molar concentration of each species will be halved.

so, conc. Of each = $0.002\text{M}/2 = 0.001\text{ M}$

e.g., $[\text{Cu}^{2+}]_{\text{mix}} = [\text{IO}_3^-]_{\text{mix}} = 0.001\text{ M}$

Now, $\text{Cu}(\text{IO}_3)_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{IO}_3^-$

Solubility product $\{K_{\text{sp}}\} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$

For precipitation, ionic product $> K_{\text{sp}}$

e.g., $[\text{Cu}^{2+}][\text{IO}_3^-]^2 > K_{\text{sp}}$

But here,

$$0.001 \times 0.001 = 10^{-9} < 7.4 \times 10^{-8}$$

It is less than K_{sp} . hence, there won't be precipitation.

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

Answer:

Given:

The ionization constant of benzoic acid (K_a) is 6.46×10^{-5}

K_{sp} for silver benzoate is 2.5×10^{-13}

pH = 3.19

Ionization of silver benzoate:



Solubility in water: Let solubility in water is $x\text{ mol/l}$ Then

$[\text{C}_6\text{H}_5\text{COO}^-] = [\text{Ag}^+] = x\text{ mol/l}$

As we know that,

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

Where A and B are the ions dissolved

In the above reaction,

$$[\text{A}^+] = \text{C}_6\text{H}_5\text{COO}^-$$

$$[\text{B}^-] = \text{Ag}^+$$

$$: K_{\text{sp}} = [\text{C}_6\text{H}_5\text{COO}^-][\text{Ag}^+]$$

As $K_{\text{sp}} = 2.5 \times 10^{-13}$ (given)

$$2.5 \times 10^{-13} = x^2$$

$$x = 5 \times 10^{-7}$$

Solubility in buffer of pH = 3.19

As we know that,

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

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

By taking antilog of both the sides, we get

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

$$[\text{H}^+] = 6.457 \times 10^{-4} \text{ M}$$

$\text{C}_6\text{H}_5\text{COO}^-$ ions combine with the H^+ ions of benzoic acid but $[\text{H}^+]$ remains almost constant because we have buffer solution. Now,



As we know that,

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

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$= \frac{[\text{C}_6\text{H}_5\text{COOH}]^2}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{[\text{H}^+]}{K_a}$$

$$[\text{H}^+] = 6.457 \times 10^{-4} \text{ M (calculated above)}$$

$$K_a = 6.46 \times 10^{-5} \text{ (given)}$$

$$: \frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{6.457 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

$$[\text{C}_6\text{H}_5\text{COOH}] = 10 [\text{C}_6\text{H}_5\text{COO}^-]$$

Suppose solubility in the buffer solution is y mol/l.

Then as most of the benzoate ion is converted into benzoic acid molecules (which remains almost ionized) we have

$$Y = [\text{Ag}^+] = [\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COOH}]$$

$$\text{As } [\text{C}_6\text{H}_5\text{COOH}] = 10 [\text{C}_6\text{H}_5\text{COO}^-] \text{ (calculated above)}$$

$$: y = [\text{C}_6\text{H}_5\text{COO}^-] + 10 [\text{C}_6\text{H}_5\text{COO}^-]$$

$$y = 11 [\text{C}_6\text{H}_5\text{COO}^-]$$

$$[\text{C}_6\text{H}_5\text{COO}^-] = y / 11$$

As we know that,

$$K_{sp} = [\text{C}_6\text{H}_5\text{COO}^-][\text{Ag}^+]$$

$$\text{As } K_{sp} = 2.5 \times 10^{-13} \text{ (given)}$$

$$[\text{Ag}^+] = y, [\text{C}_6\text{H}_5\text{COO}^-] = y / 11$$

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

$$Y^2 = 2.75 \times 10^{-12}$$

$$Y = \sqrt{2.75 \times 10^{-12}}$$

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

Now,

(Solubility in buffer solution / solubility in pure water)

$$= (y / x) = (1.66 \times 10^{-6} / 5 \times 10^{-7}) = 3.32$$

Thus, the silver benzoate is 3.32 times more soluble in a buffer of pH compared to its solubility in pure water

Question :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?

Answer:



Let F ml of molar solution are mixed so that no precipitation of FeS is noticed. Let molarity of FeSO₄ and Na₂S be α M

Thus,

$$\begin{aligned} [\text{Fe}^{2+}][\text{S}^{2-}] &= K_{\text{SP}} \\ &= 6.3 \times 10^{-18} \\ &= [a \times V / 2V][a \times V / 2V] \\ &= 6.3 \times 10^{-18} \\ a &= 5.02 \times 10^{-9}\text{M} \end{aligned}$$

Question :72 What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K?

Answer:



Let s is the solubility of CaSO₄

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

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

A/C to question,

$$K_{\text{sp}} = 9.1 \times 10^{-6}$$

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

$$s = \sqrt{9.1 \times 10^{-6}} = 3.017 \times 10^{-3} \text{ M}$$

$$\text{So, solubility of CaSO}_4 = 3.017 \times 10^{-3} \text{ M}$$

$$= 3.017 \times 10^{-3} \text{ mol/L}$$

$$= 3.017 \times 10^{-3} \times 136\text{g/L} \text{ [weight = molecule weight } \times \text{ mole . and molar weight = 136g/mol]}$$

$$= 410.3 \times 10^{-3} \text{ g/L}$$

$$= 0.4103 \text{ g/L}$$

It means 0.4103 g CaSO₄ is dissolved in 1 L

Therefore, 1g CaSO₄ is dissolved in 1/0.4103

$$= 2.437 \text{ L}$$

Question :73 The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following : FeSO₄, MnCl₂, ZnCl₂, and CdCl₂, in which of these solutions precipitation will takes place?

Answer:

Here given,

$[S^{2-}]$ (conc. of sulphide ion) = 10^{-19} M

A/C to question,

10mL of sulphide ion is mixed with 5mL of 0.04M solution of different solute so, that final volume of solution is 15mL.

So, $[S^{2-}]_{\text{mix}} = 10 \times 10^{-19}/15 = 6.67 \times 10^{-19}$ M

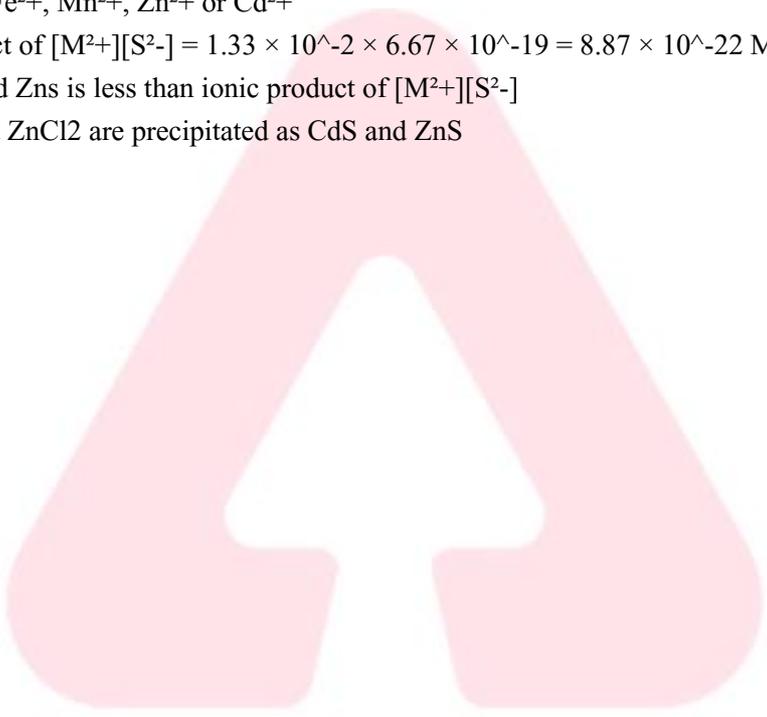
$[M^{2+}] = 5 \times 0.04/15 = 1.33 \times 10^{-2}$ M

Here, M^{2+} shows Fe^{2+} , Mn^{2+} , Zn^{2+} or Cd^{2+}

Now , ionic product of $[M^{2+}][S^{2-}] = 1.33 \times 10^{-2} \times 6.67 \times 10^{-19} = 8.87 \times 10^{-22}$ M

But K_{sp} of Cds and Zns is less than ionic product of $[M^{2+}][S^{2-}]$

Hence , $CdCl_2$ and $ZnCl_2$ are precipitated as CdS and ZnS


adda247