Chapter: Equilibrium

Exercise

Question 7.1: A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

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

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

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

Answer:

(a) The vapour pressure would first fall if the container's volume was rapidly increased. This is since 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) 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) 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.

Question 7.2: What is Kc for the following equilibrium when the equilibrium concentration of each substance is: $[SO2] = 0.60\ M$, $[O_2] = 0.82\ M$ and $[SO_3] = 1.90\ M$ **?**

$$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$$

Answer:

For the given reaction, the equilibrium constant (K_C) is:

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

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

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

As a result, the equilibrium K is $12.239M^{-1}$

Question 7.3: At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms

$I_2(g) \leftrightarrow 2I(g)$

Calculate K_p for the equilibrium

Answer:

I atoms partial pressure,

$$p_1 = \frac{40}{100} \times p_{total}$$
$$= \frac{40}{100} \times 10^5$$
$$= 4 \times 10^4 Pa$$

I_2 molecule partial pressure,

$$p_{I_2} = \frac{60}{100} \times p_{total}$$
$$= \frac{40}{100} \times 10^5$$
$$= 6 \times 10^4 Pa$$

Now, for the reaction in question,

$$K_p = \frac{(pI)^2}{p_{I_2}}$$
$$= \frac{(4 \times 10^4)^2 Pa^2}{6 \times 10^4 Pa} \times 10^5$$
$$= 2.67 \times 10^4 Pa$$

Question 7.4: Write the expression for the equilibrium constant, (K_C) for each of the following reactions:

(i) $2NOCl(g) \leftrightarrow 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \leftrightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \leftrightarrow CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH(aq) \leftrightarrow Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \leftrightarrow 2IF_5$

Answer:

$$\text{(i) } K_c = \frac{\left[NO_{(g)}\right]^2\left[Cl_{2(g)}\right]}{\left[NOCl_{(g)}\right]^2}$$

(ii)

$$K_c = \frac{\left[CuO_{(s)}\right]^2\left[NO_{(g)}\right]^2\left[O_{2(g)}\right]}{\left[Cu(NO_3)_{2(s)}\right]^2}$$

$$= \left[NO_{(g)}\right]^4\left[O_{2(g)}\right]$$

(iii)

$$K_c = \frac{\left[CH_3COOH_{(aq)}\right]\left[C_2H_5OH_{(aq)}\right]}{\left[CH_3COOC_2H_{5(aq)}\right]\left[H_2O\right]} = \frac{\left[CH_3COOH_{(aq)}\right]\left[C_2H_5OH_{(aq)}\right]}{\left[CH_3COOC_2H_{5(aq)}\right]}$$

(iv)

$$K_c = \frac{\left[Fe(OH)_{3(s)}\right]}{\left[Fe^{3+}{}_{(aq)}\right]\left[OH^-{}_{(aq)}\right]}$$

$$\frac{1}{\left[Fe^{3+}{}_{(aq)}\right]\left[OH^-{}_{(aq)}\right]}$$

(v)

$$K_c = \frac{[IF_5]^2}{\left[I_{2(s)}\right][F_2]^5}$$

$$= \frac{[IF_5]^2}{[F_2]^5}$$

Question 7.5: Find out the value of Kc for each of the following equilibria from the value of K_p :

(i) $2NOCl(g) \leftrightarrow 2NO(g) + Cl_2(g);\ K_p = 1.8\times10^{-2}$ at 500K

(ii) $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g);\ K_p = 167$ at 1073K

Answer:

The following is the relationship between K_p and K_c:

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

(a) Here,

$\Delta n = 3 - 2 = 1$

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

$T = 500\ K$

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

$=4.33\times10^{-4}$ (approximately)

$\Delta n = 2 - 1 = 1$

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

$T = 1073\ K$

$K_p = 167$

Now,

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

$= \ 167 = K_c (0.0831\times1073)^{\Delta n}$

$$K_c = \frac{167}{0.0831\times1073}$$

$= 1.87$

Question 7.6: For the following equilibrium,

$K_C = 6.3\times10^{14}$ at 1000K

$NO(g) + O_3(g) \leftrightarrow NO_2(g) + O_2(g)$

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

Answer:

K_C for the forward reaction is assumed to be 6.3×10^{14}

$$K_C = \frac{1}{K_C}$$

The reversal reaction's K_C will then be, $= \dfrac{1}{6.3\times10^{14}}$

$= \ 1.59\times10^{-15}$

Question 7.7: Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

Answer: For a completely pure substance (both solids and liquids),

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

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

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

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

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.

Question 7.8: Reaction between N_2 and O_2 takes place as follows:

$$2N_2(g)+O_2 \leftrightarrow (g)2N_2O(g)$$

Answer: Let x be the equilibrium concentration of N_2O.

The following is the reaction:

	$2N_{2(g)}$	+	$O_{2(g)}$	$\leftrightarrow$	$2N_2O(g)$
Initial conc.	0.482mol		0.933mol		0
Ae equilibrium	(0.482-x)		(1.933-x)		x mol

As a result, in the 10 L vessel at equilibrium:

$$[N_2]=\frac{0.482\text{-x}}{10},\ [O_2]=\frac{0.933\text{-x/2}}{10},[N_2O]=\frac{x}{10}$$

The equilibrium constant, $K_c = 2.0 \times 10^{-37}$, has an extremely tiny value. As a result, the amount of N_2 and O_2 reacted is negligible. As a result, x can be removed from the formulas for N2 and O2 molar concentrations. Then,

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

$$K_c = \frac{\left[N_2O_{(g)}\right]}{\left[N_{2(g)}\right]^2\left[O_{2(g)}\right]}$$

$$= 2.0\times10^{-37} = \frac{\left[\frac{x}{10}\right]^2}{(0.0482)^2(0.933)}$$

$$= x^2 = 43.35\times10^{-40}$$

$$= x = 6.6\times10^{-20}$$

$$\left[N_2O\right] = \frac{x}{10} = \frac{6.6\times10^{-20}}{10}$$

$$= 6.6\times10^{-20}$$

Question 7.9: Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO(g)+Br_2(g) \leftrightarrow 2NOBr(g)$$

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

Answer: The following is the reaction:

$$2NO(g)+Br_2(g) \leftrightarrow 2NOBr(g)$$
$$2\text{mol} \quad 1\text{mol} \quad 2\text{mol}$$

2 mol of $NOBr$ is now produced from 2 mol of NO. As a result, from 0.0518 mol of NO, 0.0518 mol of $NOBr$ is generated.

From 1 mol of Br, 2 mol of $NOBr$ is produced.

As a result, from mol of Br, or 0.0259 mol of NO, 0.0518 mol of $NOBr$ is created.

The starting concentrations of NO and Br are as follows:

$$[NO] = 0.087 \text{ mol } [Br_2] = 0.0437 \text{ mol}$$

As a result, the amount of NO in equilibrium is:

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

And, at equilibrium, the amount of Br present is:

$$[Br_2] = 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

Question 7.10: At 450 K, Kp= 2.0 × 1010/bar **for the given reaction at equilibrium.**

Answer: $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$

What is K_c at this temperature?

Answer: Given,

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

$T = 450\ K$

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

$Kp = 2.0 \times 1010\ bar^{-1}$

As we know that

$$K_p = K_c(RT)\Delta n$$

$$= 2.0\times10^{10}bar^{-1} = K_c(0.083LbarK^{-1}mol^{-1}\times450K)^{-1}$$

$$K_c = \frac{2.0\times10^{10}bar^{-1}}{(0.083LbarK^{-1}mol^{-1}\times450K)^{-1}}$$

$$= \left(2.0\times10^{10}bar^{-1}\right)(0.083LbarK^{-1}mol^{-1}\times450K)$$

$$= 74.79\times10^{10}Lmol^{-1}$$

$$= 7.48\times10^{10}Lmol^{-1}$$

$$= 7.48\times10^{11}\ M^{-1}$$

Question 7.11: 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?**

$$2HI(g) \leftrightarrow H_2(g) + I_2(g)$$

Answer: HI has an initial concentration of 0.2 atm. It has a partial pressure of 0.04 atm at equilibrium. As a result, a drop in HI pressure is $0.2 - 0.04 = 0.16$. The following is the reaction:

	2HI(g)	↔	$H_2(g)$	+	$I_2(g)$
Initial conc.	0.2atm		0		0
At equilibrium	0.04atm		$\frac{0.16}{2}$ = 0.08atm		$\frac{2.15}{2}$ = 0.08atm

Hence,

$$K_p = \frac{p_{H_2} \times p_{I_2}}{p_{HI}^2}$$

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

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

$$= 4.0$$

As a result, the K_p value for the given equilibrium is 4.0.

Question 7.12: A mixture of $1.57\ \text{mol}$ of N_2, $1.92\ \text{mol}$ of H_2 and $8.13\ \text{mol}$ of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) \text{ is } 1.7 \times 10^2$$

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

Answer: Given,

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

The given concentration of various species

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

$$[NH_3] = \frac{8.13}{20}\ \text{mol L}^{-1}$$

Reaction quotient is

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

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

$$= 2.4 \times 10^3$$

The reaction mixture is not in equilibrium because Q_c is less than K_c.

$Q_c > K_c$ is true once more. As a result, the response will go backwards.

Question 7.13: 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.

Answer: The balanced chemical equation for the above expression is written as follows:

$$4NO_{(g)} + 6H_2O \leftrightarrow 4NH_{3(g)} + 5O_{2(g)}$$

Question 7.14: 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,

$$H_2O(g) + CO(g) \leftrightarrow H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction

Answer: In the given reaction

	$H_2O(g)$	+ $CO(g)$	$\leftrightarrow$ $H_2(g)$	+ $CO_2(g)$
Initial conc.	$\frac{1}{10}M$	$\frac{1}{10}M$	0	0
At equilibrium	$\frac{1-0.4}{10}M$	$\frac{1-0.4}{10}M$	$\frac{0.4}{10}M$	$\frac{0.4}{10}M$
	$= 0.06M$	$= 0.06M$	$= 0.04M$	$= 0.04M$

As a result, the reaction's equilibrium constant,

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

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

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

Question 7.15: At 700 K, equilibrium constant for the reaction

$$HI_{2(g)} + I_2 \leftrightarrow 2HI_{(g)}$$

is 54.8. If $0.5\ molL^{-1}$ of $HI_{(g)}$ is present at equilibrium at 700 K, what are the concentration of $H_{2(g)}$ and $I_{2(g)}$ assuming that we initially started with $HI_{(g)}$ and allowed it to reach equilibrium at 700 K?

Answer: The reaction's equilibrium constant, K_c, is known.

$HI_{2(g)} + I_2 \leftrightarrow 2HI_{(g)}$ is 54.8

As a result, when the reaction is in equilibrium, the equilibrium constant for the reaction is

$2HI_{2(g)} \leftrightarrow H_{2(g)} + I_2$

$[HI]0.5\ molL^{-1}$

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

$[H_2]=[I_2]=x\ mol\ L^{-1}$

Therefore, $\frac{[H_2][I_2]}{[HI]^2} = K_c'$

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

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

$= x= 0.068\ molL^{-1}$

At equilibrium,

$[H_2]=[I_2]=0.068\ mol\ L^{-1}$

Question 7.16: What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?

$2ICl_{(g)} \leftrightarrow I_{2(g)} + Cl_{2(g)};\ K_c = 0.14$

Answer: Given

	$2ICl_{(g)}$	$\leftrightarrow$	$I_{2(g)}$	$Cl_{2(g)}$
Initial conc.	0.78M		0	0
At equilibrium	(0.78-2x)		xM	xM

This can be written as

$\frac{[I_2][Cl_2]}{[ICl]^2} = K_c$

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

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

$= x = 0.292-0.748$

$= 1.748x = 0.292$

$= x = 0.167$

At equilibrium

$$[H_2]=[I_2]=0.167$$
$$[HI]=(0.78\text{-}2\times 0167)M$$
$$0.446M$$

Question 7.17: K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6(g) \leftrightarrow C_2H_4(g)+H_2(g)$$

Answer: Let p denote the pressure exerted at equilibrium by ethene and hydrogen gas (each). Now, based on the reaction,

	$C_2H_6(g)$	$\leftrightarrow$	$C_2H_4(g)$	+	$H_2(g)$
Initial conc.	4.0atm		0		0
At equilibrium	4.0-p		p		p

Which can be written as

$$\frac{p_{C_2H_4}\times p_{H_2}}{p_{C_2H_4}}=K_p$$
$$=\frac{p\times p}{40\text{-}p}=0.04$$
$$=p^2=0.16\text{-}0.04$$
$$=p^2+0.04p\text{-}0.16=0$$
$$p=\frac{-0.04\pm\sqrt{(0.04)^2\text{-}4\times 1\times(-0.16)}}{2\times 1}$$
$$=\frac{-0.04\pm 0.80}{2}$$
$$=\frac{0.76}{2}$$
$$=0.38$$

$$[C_2H_6]\text{-}4\text{-}p=4\text{-}0.38$$
$$=3.62\text{atm}$$

Question 7.18: Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH(l)+C_2H_5OH(l)\leftrightarrow CH_3COOC_2H_5(l)+H_2O$$

(i) Write the concentration ratio (reaction quotient), Qc, 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?

Answer: (i) Reaction Quotient $Q_C = \dfrac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3COOH]\ [C_2H_5OH]}$

(ii) Assume that the reaction mixture's volume is V. Also, we'll assume that water is a solvent and that it's abundant.

The following is the reaction:

$$\begin{array}{lcccc}
 & CH_3COOH_{(l)} + & C_2H_5OH_{(l)} & \leftrightarrow CH_3COOC_2H_{5(l)} & + \quad H_2O \\
\text{Initial conc.} & \dfrac{1}{V}M & \dfrac{0.18}{V}M & 0 & 0 \\
\text{At equilibrium} & \dfrac{1-0.171}{V} & \dfrac{0.18-0.171}{V} & \dfrac{0.171}{V}M & \dfrac{0.171}{V}M \\
 & =\dfrac{0.829}{V}\ M & =\dfrac{0.009}{V}M & &
\end{array}$$

Therefore, equilibrium constant for the given reaction is:

$$Q_C = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3COOH]\ [C_2H_53OH]} = \frac{\dfrac{0.171}{V} \times \dfrac{0.171}{V}}{\dfrac{0.829}{V} \times \dfrac{0.829}{V}}$$

$= 3.919$

$= 3.29\ (\text{approximately})$

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

$$\begin{array}{lcccc}
 & CH_3COOH_{(l)} + & C_2H_5OH_{(l)} & \leftrightarrow CH_3COOC_2H_{5(l)} & + \quad H_2O \\
\text{Initial conc.} & \dfrac{1.0}{V}M & \dfrac{0.5}{V}M & 0 & 0 \\
\text{After some time} & \dfrac{10-0.124}{V} & \dfrac{0.5-0.214}{V} & \dfrac{0.214}{V}M & \dfrac{0.214}{V}M \\
 & =\dfrac{0.786}{V}\ M & =\dfrac{0.286}{V}M & &
\end{array}$$

Therefore, the reaction quotient is,

$$Q_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_3OH]}$$

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

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

$$=0.2037$$

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

Question 7.19: 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 Kc is 8.3 × 10–3, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5(g) \leftrightarrow PCl_3(g)+Cl_2(g)$$

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

	$PCl_5(g)$	$\leftrightarrow$	$PCl_3(g)$	+	$Cl_2(g)$
At equilibrium	$0.5 \times 10–1\text{ mol L}^{-1}$		$x\text{ mol L}^{-1}$		$x\text{ mol L}^{-1}$

Value of equilibrium constant = $K_c=8.3\times10^{-3}$

We can now write the equilibrium expression as:

$$\frac{[PCl_2][Cl_2]}{[PCl_5]}=K_C$$

$$\frac{x\times x}{0.5\times10^{-1}}=8.3\times10^{-3}$$

$$x^2=4.15\times10^{-4}$$

$$x=2.04\times10^{-2}$$

$$=0.0204$$

$$=0.02\text{ (approximately)}$$

$$[PCl_3]=[Cl_2]=0.02molL^{-1}.$$

Question 7.20: 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

$$FeO(s) + CO(g) \leftrightarrow Fe(s) + CO_2(g);\ Kp= 0.265\text{ at }1050\text{ K}.$$

What are the equilibrium partial pressures of CO and $\mathrm{CO_2}$ at 1050 K if the initial partial pressures are: $p_{CO} = 1.4$ atm and $p_{CO_2} = 0.80$ atm?

Answer:

Given

$$\mathrm{FeO_{(g)} + CO_{(g)} \leftrightarrow Fe_{(s)} + CO_{2(g)}}$$

Initialy, 1.4atm 0.080atm

$$Q_p = \frac{p_{co_2}}{p_{co}}$$

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

$$=0.571$$

Since, the reaction will proceed in the backward direction. Therefore, we can say that the pressure of CO will increase while the pressure of $\mathrm{CO_2}$ will decrease. Now, let the increase in pressure of CO = decrease in pressure of $\mathrm{CO_2}$ be p. Then, we can write,

$$K_p = \frac{p_{CO_2}}{p_{Co}}$$

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

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

$$1.265p=0.429$$

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

As a result, partial equilibrium and partial pressure are

$\mathrm{CO_2}, p_{Co_3}$ =0.80-0.339=0.461atm.

CO, p_{Co} =1.4+0.339=1.739atm.

Question 7.21: Equilibrium constant, K_c for the reaction

$\mathrm{N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)}$ **at at 500 K is 0.061.**

At a particular time, the analysis shows that composition of the reaction mixture is $3.0\ \text{mol L}^{-1}$ N2, $2.0\ \text{mol L}^{-1}$ $\mathrm{H_2}$ and $0.5\ \text{mol L}^{-1}$ $\mathrm{NH_3}$**. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?**

Answer:

Given

	$N_{2(8)}$	$3H_{2(8)}$	$\leftrightarrow$	$2NH_{3(3)}$
At a particular time:	$3.0 molL^{-1}$	$2.0 molL^{-1}$		$0.5 molL^{-1}$

As we know that

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

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

$$=0.0104$$

$$K_c = 0.061$$

$Q_c \neq K_c$ There is no equilibrium in the reaction.

$Q_c < K_c$ To reach equilibrium, the reaction will proceed in a forward direction.

Question 7.22: Bromine monochloride, $BrCl$ decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl(g) \leftrightarrow Br_2(g) + Cl_2(g)$$

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

Answer:

Let x be the amount of bromine and chlorine generated when the system is in equilibrium. The following is the reaction:

	$2BrCl_{(g)}$	$\leftrightarrow$	$Br_{2(g)}$	+	$Cl_{2(g)}$
Initial conc.	3.3×10^{-3}		0		0
At equilibrium	$3.3\times10^{-3}-2x$		x		x

We can also write

$$\frac{[Br_2][Cl_2]}{[BrCl]^2}=K_C$$

$$=\frac{x\times x}{\left(3.3\times10^{-3}-2x\right)^2}=32$$

$$=\frac{x}{3.3\times10^{-3}-2x}=5.66$$

$$x=18.678\times10^{-3}-11.32x$$

$$=12.32x=18.678\times10^{-3}$$

$$x=1.5\times10^{-3}$$

$$[BrCl]=3.3\times10^{-3}-\left(2\times1.5\times10^{-3}\right)$$

$$=3.3\times10^{-3}-3.0\times10^{-3}$$

$$=0.3\times10^{-3}$$

$$=3.0\times10^{-4}molL^{-1}$$

Question 7.23: At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass

$$C(s)+CO(g)\leftrightarrow 2CO(g)$$

Calculate K_c for this reaction at the above temperature.

Answer: Total mass of the gaseous mixture be 100 g.

Mass of CO = 90.55 g

And, mass of $CO_2 = \left(100-90.55\right) = 9.45$ g

Number of moles of CO $n_{CO}=\frac{90.55}{28}=3.234mol$

Number of moles of CO_2 $n_{CO_2}=\frac{9.45}{44}=0.215mol$

$$p_{CO}=\frac{n_{CO}}{n_{CO}+n_{CO}}\times p_{teul}$$

$$=\frac{3.234}{3.234+0.215}\times1$$

$$=0.938atm$$

Partial pressure of CO_2

$$p_{Co_2}=\frac{n_{CO_2}}{n_{co}+n_{cO_2}}\times p_{veal}$$

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

$$=0.062\text{atm}$$

$$\text{Therefore, } K_p=\frac{[CO]^2}{[CO_2]}$$

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

$$=14.19$$

In the given reaction we understood that

$$\Delta n=2\text{-}1=1$$

$$K_P=K_C(RT)^{Mn}$$

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

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

$$=0.154(\text{ approximately })$$

Question 7.24: Calculate

a) $\Delta G°$ **and**

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

where,

$\Delta fG°\ (NO_2) = 52.0\ \text{kJ/mol}$

$\Delta fG°\ (NO) = 87.0\ \text{kJ/mol}$

$\Delta fG°\ (O_2) = 0\ \text{kJ/mol}$

Answer:

For the given reaction,

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

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

(b) We know that,

$\Delta G° = RT \log K_c$ $\Delta G° = 2.303\ RT \log K_c$

$$K_c = \frac{-35.0\times10^{-3}}{-2.303\times8.314\times298}$$

$$=6.134$$

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

$$=1.36\times10^{6}$$

Hence, the equilibrium constant for the given reaction K_c is 1.36 × 106

Question 7.25: 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?

(i) $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$

(ii) $CaO(s)+CO_2(g) \leftrightarrow CaCO_3(s)$

(iii) $3Fe(s)+4H_2O(g) \leftrightarrow Fe_2o_3(s)+4H_2(g)$

Answer:

(a) There will be an increase in the number of moles of reaction products. 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.

(b) The quantity of moles produced by the reaction will decrease.

(c) The total number of moles of reaction products does not change.

Question 7.26: 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:

(i) $COCl_2(g) \leftrightarrow CO(g) + Cl_2(g)$

(ii) $CH_4(g) + 2S_2(g) \leftrightarrow CS_2(g) + 2H_2S(g)$

(iii) $CO_2(g) + C(s) \leftrightarrow 2CO(g)$

(iv) $2H_2(g) + CO(g) \leftrightarrow CH_3OH(g)$

(v) $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

(vi) $4NH_3(g) + 5O_2(g) \leftrightarrow 4NO(g) + 6H_2O(g)$

Answer: 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.

Question 7.27: The equilibrium constant for the following reaction is 1.6 ×105 at 1024 K.

$$H_2(g)+Br_2(g)\leftrightarrow 2HBr(g)$$

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

Answer: For the reaction K_p $H_2(g)+Br_2(g)\leftrightarrow 2HBr(g)$ is 1.6×10^5

Hence, the reaction $2HBr(g)\leftrightarrow H_2(g)+Br_2(g)$ the equilibrium constant is

$$K_p^{'}=\frac{1}{K_p}$$

$$=\frac{1}{1.6\times10^5}$$

$$=6.25\times10^{-6}$$

Let p be the equilibrium pressure of both H_2 and Br_2.

	$2HBr_{(g)}$	$\leftrightarrow$	$H_{2(s)}$	$+$	$Br_{2(z)}$
Initial conc.	10		0		0
At equilibrium	$10-2p$		p		p

Which can be written as

$$\frac{p_{HB}\times p_2^{\times}p}{p_{HBr}^2}=K_P^{¢}$$

$$\frac{p\times p}{(10\text{-}2p)^2}=6.25\times10^{-6}$$

$$\frac{p}{10\text{-}2p}=2.5\times10^{-3}$$

$$p=2.5\times10^{-2}\text{-}\left(5.0\times10^{-3}\right)p$$

$$p+\left(5.0\times10^{-3}\right)p=2.5\times10^{-2}$$

$$\left(1005\times10^{-3}\right)p=2.5\times10^{-2}$$

$$p=2.49\times10^{-2}\text{ bar }=2.5\times10^{-2}\text{ bar (approximately)}$$

At equilibrium

$$[H_2]=[Br_2]=2.49\times10^{-2}\ \text{bar}$$

$$[HBr]=10-2\times\left(2.49\times10^{-2}\right)\ \text{bar}$$

$$=9.95\text{bar}=10\text{bar}(\ \text{approximately})$$

Question 7.28: Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$$CH_4(g)+H_2O(g)\leftrightarrow CO(g)+3H_2(g)$$

(a)Write as 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: Given

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

(b)

(i) The equilibrium will change in the backward direction, according to Le Chatelier's principle.

(ii) Because the reaction is endothermic, the equilibrium will shift forward, according to Le Chatelier's principle.

(iii) 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.

Question 7.29: Describe the effect of:

a) Addition of H_2

b) Addition of CH_3OH

c) Removal of CO

d) Removal of CH_3OH **on the equilibrium of the reaction:**

$$2H_2(g)+CO(g)\leftrightarrow CH_3OH(g)$$

Answer:

(a) According to Le Chatelier's principle, when H2 is added to a reaction, the equilibrium shifts in the forward direction.

(b) With the addition of CH_3OH, the equilibrium will shift backward.

(c) When CO is removed from the equation, the equilibrium shifts backward.

(d) When CH_3OH is removed from the equation, the equilibrium shifts forward.

Question 7.30: At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as

$$PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g) \quad \Delta_H{}^{\circ} = 124.0 kJmol^{-1}$$

a) Write an expression for K_c for the reaction.

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

c) What would be the effect on K_c if

(i) more PCl_5 is added

(ii) pressure is increased?

(iii) The temperature is increased?

Answer: (a) $K_e \frac{\left[PCl_{3(k)}\right]\left[Cl_{2(\varepsilon)}\right]}{\left[PCl_{s(z)}\right]}$

(b) At the same temperature, the value of K_c for the reverse reaction is:

$$K_e^{'} = \frac{1}{K_c}$$

$$= \frac{1}{8.3\times10^{-3}} = 1.2048\times10^{2}$$

$$= 120\text{-}48$$

(c) (i) K_c would be constant because the temperature is constant in this situation.

(ii) At constant temperature, K_c is constant. As a result, K_c would not alter in this scenario.

(ii)In an endothermic reaction, the value of K_c rises as the temperature rises. Because the reaction in question is an endothermic reaction, the value of K_c will rise as the temperature rises.

Question 7.31: 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,

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$$

If a reaction vessel at 400°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?

Kp= 10.1 at 400°C

Answer: Assume that both carbon dioxide and hydrogen gas have partial pressures of p. The following is the reaction:

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

In given reaction

$$K_p = 10.1$$

$$\frac{p_{CO_1} \times p_{H_2}}{p_{CO} \times p_2} = K_p$$

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

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

$$p = 12.712 - 3.178p$$

$$4.178p = 12.712$$

$$p = 3.04$$

As a result, the partial pressure of H_2 at equilibrium will be 3.04 bar.

Question 7.32: Predict which of the following reaction will have appreciable concentration of reactants and products:

(a) $Cl_2(g) \leftrightarrow 2Cl(g);\ K = 5 \times 10^{-39}$

(b) $Cl_2(g) + 2NO(g) \leftrightarrow 2NOCl(g);\ K_c = 3.7 \times 10^{8}$

(c) $Cl_2(g) + 2NO_2(g) \leftrightarrow 2NO_2Cl(g);\ K_c = 1.8$

Answer: A reaction contains considerable concentration of reactants and products if the value of Kc is between 10^{-3} and 103. As a result, the reaction in (c) will have a significant amount of reactants and products.

Question 7.33: The value of Kc for the reaction $3O_2(g) \leftrightarrow 2O_3(g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} , , what is the concentration of O_3 ?

Answer: Given reaction

$$3O_{2(g)} \leftrightarrow 2O_{3(g)}$$

$$\text{Then, } K_C = \frac{\left[O_{3(z)}\right]^2}{\left[O_{2(z)}\right]^3}$$

It is given that $K_C = 2.0 \times 10^{-50}$ and $\left[O_{2(g)}\right] = 1.6 \times 10^{-2}$

Next,

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

$$= \left[O_{3(B)}\right]^2 = 2.0 \times 10^{-50} \times \left(1.6 \times 10^{-2}\right)^3$$

$$= \left[O_{3(B)}\right]^2 = 8.192 \times 10^{-36}$$

$$= \left[O_{3(B)}\right] = 2.86 \times 10^{-28} M$$

As a result, the concentration of O_3 is $2.86 \times 10^{(-28)} M$

Question 7.34: The reaction, $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$ 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.

Answer: Let x be the equilibrium concentration of methane.

	$CO_{(8)}$	+	$3H_{2(g)}$ $\leftrightarrow$	$CH_{4(8)}$	$+ H_2O_{(g)}$
At equilibrium	$\frac{0.3}{1} = 0.3M$		$\frac{0.1}{1} = 0.IM$	x	$\frac{0.02}{1} = 0.02M$

It is given that $K_c = 3.90$

Hence,

$$\frac{\left[CH_{4(g)}\right]\left[H_2O_{(g)}\right]}{\left[CO_{(g)}\right]\left[H_{2(g)}\right]} = Kc$$

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

$$= x = \frac{3.90 \times 0.3 \times (0.1)3}{0.02} = \frac{0.00117}{0.02} = 0.0585M$$

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

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

Question 7.35: What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

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

Answer: 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 in the chloroplasts of leaves during the day.

Species Conjugate acid-base

HNO_2 NO_2^- (base)

CN^- HCN (acid)

$HClO_4$ ClO_4^- (base)

F - HF (acid)

OH^- H_2O (acid) /O^{2-} (base)

CO_2^- 3 HCO_3^- (acid)

S_2^- HS^- (acid)

Question 7.36: Which of the followings are Lewis acids? H_2O, BF_3, H^+ and NH_4^+**?**

Answer: The Lewis acids are those that can accept two electrons. Lewis acids include, for example, H_2O, BF_3, H^+ and NH_4^+.

Question 7.37: What will be the conjugate bases for the Bronsted acids: HF, H_2SO_4 and HCO_3 **?**

Answer: The conjugate bases for the specified Bronsted acids are listed in the table below.

Bronsted acid	Conjugate base

HF	F-
H_2SO_4	HSO_4^-
HCO_3^-	CO_3^{2-}

Question 7.38: Write the conjugate acids for the following Bronsted bases: NH_2^- , NH_3 and $HCOO^-$ **.**

Answer: The conjugate acids for each Bronsted base are listed in the table below.

Bronsted base	Conjugate acid
NH_2^-	NH_3
NH_3	NH_4^+
$HCOO^-$	HCOOH

Question 7.39: The species: H_2O, HCO_3^-, HSO_4^- and NH_3 **can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.**

Answer:

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

Question 7.40: Classify the following species into Lewi's acids and Lewis bases and show how these acts as Lewis acid/base:

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

Answer: (a) It may give its lone pair of electrons, OH^- is a Lewis base.

(b) It can donate a pair of electrons; F^- is a Lewis base.

(c) It can accept a pair of electrons, H^+ is a Lewis acid.

(d) It can accept a pair of electrons, BCl_3 is a Lewis acid.

Question 7.41: The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. what is its pH?

Answer:

Given,

The pH value of a soft drink

$$\left[H^+\right] = 3.8 \times 10\text{-}3M$$
$$= -\log\left[H^+\right] = -\log 3.8 \times 10^{-3}\ n$$
$$= -\log 3.8 - \log 10^{-3}$$
$$= -\log 3.8 + 3$$
$$= -0.58 + 3$$
$$= 2.4$$

As a result, the hydrogen ion concentration in the vinegar sample is 1.74×10^{-4} M.

Question 7.43: The ionization constant of HF, HCOOH and HCN at 298K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

Answer: We know that,

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

Given, K_a of HF $= 6.8 \times 10^{-4}$

Hence, K_b of its conjugate base F^-

$$= \frac{K_w}{K_a}$$
$$= \frac{10^{-14}}{6.8 \times 10^{-4}}$$
$$= 1.5 \times 10^{-11}$$

Given, K_a of HCOOH $= 1.8 \times 10^{-4}$

Therefore, K_b of its conjugate base $HCOO^-$

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

$$= \frac{10^{-14}}{1.8\times10^{-4}}$$

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

Given, K_a of HCN $= 4.8 \times 10^{-9}$ Hence, K_b of its conjugate base CN^-

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

$$= \frac{10^{-14}}{4.8\times10^{-9}}$$

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

Question 7.44: The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

Answer: Phenol Ionization

$$C_6H_3OH + H_2O \leftrightarrow C_6H_5O^- + H_3O^+$$

Initial conc	0.05	0	0
At equilibrium	0.05 - x	x	x

$$K_\alpha = \frac{\left[C_6H_5O^-\right]\left[H_3O^+\right]}{\left[C_6H_3OH\right]}$$

$$K_d = \frac{x\times x}{0.05\text{-}x}$$

x can be ignored in the denominator as the value of x is less.

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

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

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

Since $\left[H_3O^+\right] = \left[C_6H_3O^-\right]$

$$\left[C_6H_3O^-\right] = 2.2 \times 10^{-6} M$$

In the presence of $0.01\ M\ \ C_6H_5ONa$, let α be the degree of ionisation of phenol.

$$C_6H_5ONa \rightarrow C_6H_5O^- + Na^+$$

Conc. 0.1

Here,

$$C_6H_5OH+H_2O \leftrightarrow C_6H_5O^- + H_3O^+$$

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

$\left[C_6H_5OH\right] = 0.05 - 0.05\alpha;\ 0.05M$

$\left[C_6H_5O^-\right] = 0.01 + 0.05\alpha;\ 0.01M$

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

$$K0 = \frac{\left[C_6H_5O^-\right]\left[H_3O^+\right]}{\left[C_6H_5OH\right]}$$

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

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

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

Question 7.45: 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 solution 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.

Answer:

(i) Calculate the concentration of HS^- ion:

Case I (in the absence of HCl): Let the concentration of HS^- be x M.

$$H_2S \leftrightarrow H^+ + HS\text{-}$$

$C_1 \qquad 0.1 \qquad 0 \qquad 0$

$C_j \qquad 0.1 - x \quad x \qquad x$

Then, $K_{u_1} = \dfrac{\left[H^+\right]\left[HS^-\right]}{\left[H_2S\right]}$

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

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

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

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

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

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

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

In case II in the presence of HCl

In the presence of 0.1 M of HCl, let $\left[HS^-\right]$ be y M

$$\begin{array}{llll} \text{Then,} & H_2S \leftrightarrow & HS^- + & H^+ \\ \text{Ci} & 0.1 & 0 & 0 \\ \text{Cj} & 0.1\text{-}y & y & y \end{array}$$

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

$$K_{a_1} = \frac{[y](0.1+y)}{(0.1\text{-}y)} \qquad (\because\ 0.1 - y;\ 0.1M)$$

$$(\text{and } 0.1 + y;\ 0.1M)$$

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

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

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

Next to calculate $\left[S^{2-}\right]$

In case I in the presence of HCl

$$HS^- \leftrightarrow H^+ + S^{2-}$$

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

Let S^{2-} be X.

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

$$K_{u_2} = \frac{\left[H^+\right]\left[S^{2-}\right]}{\left[HS^-\right]}$$

$$K_{a_1} = \frac{\left(9.54 \times 10^{-5}\right)(X)}{9.54 \times 10^{-5}}$$

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

In case II in the presence of HCl

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

$\left[H^+\right] = 0.1M$ (From HCl, case II)

$S^{2-} = X'$

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

$1.2 \times 10^{-13} = \frac{(0.1)(X')}{9.1\times10^{-8}}$

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

$\frac{10.92\times10^{-21}}{0.1} = X'$

$X' = \frac{1.092\times10^{-20}}{0.1}$

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

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

Question 7.46: 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:

Method 1

1) $CH_3COOH \leftrightarrow CH_3COO^- + H^+ \quad K_a = 1.74 \times 10^{-5}$

2) $H_2O + H_2O \leftrightarrow H_3O^+ + OH^- \quad K_w = 1.0 \times 10^{-14}$

$K_a \gg K_w$

$$\begin{array}{lllll} & CH_3COOH+H_20 & \leftrightarrow CH_3COO^- & + H_3O^+ \\ C_i = & 0.05 & 0 & 0 \\ & 0.05-.05\alpha & 0.05\alpha & 0.05\alpha \end{array}$$

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

$= \frac{(.05\alpha)(0.05\alpha)}{.05(1 - \alpha)}$

$= \frac{.05\alpha^2}{1 - \alpha}$

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

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

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

$$D = b^2 - 4ac$$

$$= \left(1.74 \times 10^{-5}\right)^2 - 4(.05)\left(1.74 \times 10^{-5}\right)$$

$$= 3.02 \times 10^{-25} + .348 \times 10^{-5}$$

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

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

$$= \sqrt{\frac{34.8 \times 10^{-3} \times 10}{10}}$$

$$= \sqrt{3.48 \times 10^{-6}}$$

$$= CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

$$\frac{\alpha 1.86 \times 10^{-3}}{\left[CH_3COO^-\right]} = 0.05 \times 1.86 \times 10^{-3}$$

$$= \frac{0.93 \times 10^{-3}}{1000} = .000093$$

Method 2

Is Degree of dissociation

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

$c = 0.05$ M

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

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

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

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

$$\alpha = 1.8610^{-2}$$

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

Hence, the concentration of $CH_3COO^- = c.\alpha$

$= .05 \times 1.86 \times 10^{-2} =$

$.093 \times 10^{-2}$

$= .00093\text{M}$

Since $\left[\text{oAc}^{-}\right] = \left[\text{H}^{+}\right]$,

$\left[\text{H}^{+}\right] = .00093 = .093 \times 10^{-2}$.

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

$= \text{-log}\left(.093 \times 10^{-2}\right)$

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

As a result, the acetate ion concentration in the solution is $0.00093\ \text{M}$, and the pH is 3.03.

Question 7.47: It has been found that the pH of a $0.01\ \text{M}$ solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its $\text{p}K_a$.

Answer: Let's call the organic acid HA.

$\text{HA} \leftrightarrow \text{H}^{+} + \text{A}^{-}$

Concentration of $\text{HA} = 0.01\ \text{M pH}$

$= 4.15$

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

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

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

Then,

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

$[\text{HA}] = 0.01$

Then,

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

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

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

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

$\text{p}K_a = 6.3001$

Question 7.48: Assuming complete dissociation, calculate the pH of the following solutions:

(i) 0.003 M HCl

(ii) 0.005 M NaOH

(iii) 0.002 M HBr

(iv) 0.002 M KOH

Answer: (i) 0.003 M HCl

$$H_2O+HCl \leftrightarrow H_3O^+ + Cl^-$$

As HCl is completely ionized

$$\left[H_3O^+\right] = [HCl].$$

$$=[H_3O+] \quad = 0.003$$

Now,

$$pH=-\log\left[H_3O^+\right]=-\log(0.003)$$

$$=2.52$$

Therefore, the pH of the solution is 2.52.

(ii) 0.005 M NaOH:

$$NaOH_{(aq)} \leftrightarrow Na^+_{(aq)} + HO^-_{(aq)}$$

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

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

$$=pOH = -\log HO^- = -\log(.005)$$

$$=pOH = 2.30$$

$$\therefore pH = 14 - 2.30$$

$$= 11.70$$

(iii) 0.002 M HBr

$$HBr + H2O \leftrightarrow H_3O^+ + Br^-$$

$$\left[H_3O^+\right] = [HBr]$$

$$= \left[H_3O^+\right] = .002$$

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

$$= -\log(0.002) = 2.69$$

(iv) 0.002 M KOH

$$KOH_{(aq)} \leftrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$\left[OH^-\right] = [KOH]$$

$$= \left[OH^-\right] = .002$$

$$\text{Now, pOH} = -\log\left[OH^-\right] = 2.69$$

$$\therefore\ pH = 14 - 2.69 = 11.31$$

Question 7.49: Calculate the pH of the following solutions:

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

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

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

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

Answer:

To make 2 L of solution from 2g of $TIOH$ dissolved in water:

$$TlOH_{(aq)} = \frac{2}{2}\ g/L$$

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

$$TIOH_{(aq)} \leftrightarrow TI^+_{(aq)} + OH^-_{(aq)}$$

$$\left[OH^-_{(aq)}\right] = TlOH_{(aq)} = \frac{1}{221}\ M$$

$$K_w = \left[H^+\right]\left[OH^-\right]$$

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

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

$$pH = -\log\left[H+\right] =$$

$$-\log 221 \times 10^{-14}$$

$$= -\log 2.21 \times 10^{-12}$$

$$= 11.6$$

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

$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-$

$\left[Ca(OH)_2\right] = 0.3 \times \dfrac{1000}{500} = 0.6M$

$\left[OH^-_{(aq)}\right] = 2 \times \left[Ca(OH)_{2aq}\right] = 2 \times 0.6$

$= 1.2M$

$\left[H^+\right] = \dfrac{K_w}{\left[OH^-_{aq}\right]}$

$= \dfrac{10\text{-}14}{1.2}\ M$

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

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

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

$=(-0.902 + 13)$

$=12.098$

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

$13.6 \times 1\ mL = M_2 \times 1000\ mL$

Before solution After solution

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

$= 1.36 \times 10^{-2}\ \left[H^+\right] = 1.36 \times 10^{-2}\ pH = -\log\left(1.36 \times 10^{-2}\right)$

$=(-0.1335 + 2) = 1.866...\ 1.87$

Question 7.50: The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

Answer:

Degree of ionization, $\alpha = 0.132$

Concentration, $c = 0.1\ M$

Therefore, the concentration of $H_3O^+ = c.\alpha$

$= 0.1 \times 0.132$

$= 0.0132$

$$pH = -\log H^+$$
$$= -\log(0.0132)$$
$$= 1.879 : 1.88$$

Now,

$$K_a = C\alpha^2$$
$$= 0.1 \times (0.132)^2$$
$$K_a = .0017$$
$$pK_a = 2.75$$

Question 7.51: The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

Answer:

Degree of ionization, $\alpha = 0.132$

Concentration, $c = 0.1\ M$

Therefore, the concentration of $H_3O^+ = c.\alpha$

$$= 0.1 \times 0.132$$
$$= 0.0132$$

$$pH = -\log H^+$$
$$= -\log(0.0132)$$
$$= 1.879 : 1.88$$

Now,

$$K_a = C\alpha^2$$
$$= 0.1 \times (0.132)^2$$
$$K_a = .0017$$
$$pK_a = 2.75$$

Question 7.52: What is the 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:

$$K_b = 4.27 \times 10^{-10}$$
$$c = 0.001M\ pH = ?$$
$$\alpha = ?$$

$k_b = c\alpha^2$

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

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

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

Then, $\left[\text{ anion }\right] = c\alpha = .001 \times 65.34 \times 10^{-5}$

$= \text{-}065 \times 10^{-5}$

$\text{pOH} = -\log(.065\times10^{-5})$

$= 6.187$

$\text{pH} = 7.813$

Now,

$K_a \times K_h = K_w$

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

$$K_a = \frac{10^{-14}}{4.27\times10^{-10}} = 2.34 \times 10^{-5}$$

As a result, the ionisation constant of aniline's conjugate acid is 2.34×10^{-5}.

Question 7.53: Calculate the degree of ionization of $0.05\ \text{M}$ acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains

(a) $0.01\ \text{M}$

(b) $0.1\ \text{M in HCl}$ **?**

Answer:

$c = 0.05\text{M}$

$\text{pK}_a = 4.74$

$\text{pK}_a = -\log\left(K_a\right)$

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

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

$$\alpha = \sqrt{\frac{1.82\times10^{-5}}{5\times10^{-2}}} = 1.908 \times 10^{-2}$$

The concentration of H+ ions in a solution increases when HCl is added. As a result, the equilibrium will move backward, resulting in a decrease in acetic acid dissociation.

Case I- When using $0.01\ \text{M HCl}$. Let x represent the amount of acetic acid dissociated after HCl was added.

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

Because only a little amount of acetic acid will dissociate, the values $0.05 - x$ and $0.01 + x$ can be assumed to equal 0.05 and 0.01 respectively.

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

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

$$x = \frac{1.82\times10^{-5}\times0.05}{0.01}$$

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

Now,

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

$$= \frac{1.82\times10^{-3}\times0.05}{0.05}$$

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

Case II: When using 0.1 M HCl.

In this scenario, let X be the amount of acetic acid dissociated. The concentrations of various species participating in the reaction, as in the first scenario, are:

$$\left[CH_3COOH\right] = 0.05 - X; 0.05M$$

$$\left[CH_3COO^-\right] = X$$

$$\left[H^+\right] = 0.1 + X; 0.1M$$

$$K_0 = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

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

$$x = \frac{1.82\times10^{-5}\times0.05}{0.1}$$

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

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

$$= \frac{1.82\times10^{-4}\times0.05}{0.05}$$

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

Question 7.54: The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?

Answer:

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

$c = 0.02\text{M}$

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

$$= \sqrt{\frac{5.4\times10^{-4}}{0.02}}$$

$= 0.1643$

When 0.1 M in NaOH is added to the solution, it undergoes full ionisation because NaOH is a strong base.

$$\begin{array}{lcl} \text{NaOH}_{(aq)} \leftrightarrow & \text{Na}^{+}_{(aq)} & +\text{OH}^{-}_{(aq)} \\ & 0.1\text{ M} & 0.1\text{ M} \end{array}$$

$$\begin{array}{lllllll} (\text{CH}_3)_2\text{ NH} & + & \text{H}_2\text{O} & \leftrightarrow & (\text{CH}_3)_2\text{ NH}_2^+ & + & \text{OH} \\ (0.02 - x) & & & & x & & x \\ ;\ 0.02\text{M} & & & & & & ;0.1\text{ M} \end{array}$$

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

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

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

$$5.4 \times 10^{-4} = \frac{x\times0.1}{0.02}$$

$x = 0.0054$

It signifies that 0.54 percent of dimethylamine will dissociate in the presence of 0.1 M in NaOH.

Question 7.55: Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a)Human muscle-fluid, 6.83

(b)Human stomach fluid, 1.2

(c) Human blood, 7.38

(d)Human saliva, 6.4

Answer:

(a) Human muscle fluid 6.83:

$$\mathrm{pH} = 6.83\ \mathrm{pH} = -\log\left[\mathrm{H}^{+}\right]$$

$$6.83 = -\log\left[\mathrm{H}^{+}\right]$$

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

(b) Human stomach fluid, 1.2:

$$\mathrm{pH} = 1.2$$

$$1.2 = -\log\left[\mathrm{H}^{+}\right]$$

$$\left[\mathrm{H}^{+}\right] = 0.063$$

(c) Human blood, 7.38:

$$\mathrm{pH} = 7.38 = -\log\left[\mathrm{H}^{+}\right]$$

$$\left[\mathrm{H}+\right] = 4.17 \times 10^{-8}\ \mathrm{M}$$

(d) Human saliva, 6.4:

$$\mathrm{pH} = 6.4$$

$$6.4 = -\log\left[\mathrm{H}^{+}\right]$$

$$\left[\mathrm{H}^{+}\right] = 3.98 \times 10^{-7}$$

Question 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.

Answer: The concentration of hydrogen ions in the given substances can be estimated using the following formula: $-\log\left[\mathrm{H}^{+}\right] = \mathrm{pH}$

(i) pH of milk = 6.8

Since, $\mathrm{pH} = -\log\left[\mathrm{H}^{+}\right]$

$$6.8 = -\log\left[\mathrm{H}^{+}\right] \log$$

$$\left[\mathrm{H}^{+}\right] = -6.8$$

$$\left[\mathrm{H}^{+}\right] = \mathrm{anitlog}(-6.8)$$

$$= 1.5 \times 19^{-7}\ \mathrm{M}$$

(ii) pH of black coffee

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

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

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

$\left[\text{H}^+\right] = \text{anitlog}(-5.0)$

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

(iii) pH of tomato juice = 4.2

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

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

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

$\left[\text{H}^+\right] = \text{anitlog}(-4.2)$

$= 6.31\times10^{-5}\ \text{M}$

(iv) pH of lemon juice = 2.2

$\text{Since, pH} = -\log\left[\text{H}^+\right]\ 2.2$

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

$\left[\text{H}^+\right] = \text{anitlog}(-2.2)$

$= 6.31\times10^{-3}\ \text{M}$

(v) pH of egg white

Question 7.57: If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen, and hydroxyl ions. What is its pH ?

Answer:

$$\left[\text{KOH}_{\text{aq}}\right] = \frac{0.561}{\frac{1}{5}}\ \text{g/L}$$

$= 2.805\ \text{g/L}$

$$= 2.805 \times \frac{1}{56.11}\ \text{M}$$

$= .05\text{M}$

$$KOH_{(aq)} \leftrightarrow K^{+}_{(aq)} + OH^{-}_{(aq)}$$

$$\left[OH^{-}\right] = .05M = \left[K^{+}\right]$$

$$\left[H^{+}\right]\left[H^{-}\right] = K_w$$

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

$$= \frac{10^{-14}}{0.05} = 2 \times 10^{-13} M$$

$$\therefore pH = 12.70$$

Question 7.58: The solubility of $Sr\left(OH\right)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

Answer:

Solubility of $Sr\left(OH\right)_2$ = 19.23 g/L

Then, concentration of $Sr\left(OH\right)_2$

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

$$= 0.1581M$$

$$Sr\left(OH\right)_{2(aq)} \; Sr^{2+}_{(aq)} + 2\left(OH^{-}\right)_{(aq)}$$

$$\Rightarrow \left[Sr^{2+}\right] = 0.1581M$$

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

Now,

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

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

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

$$\therefore\ pH = 13.495;\ 13.50$$

Question 7.59: The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

Answer: Propanoic acid's degree of ionisation should be.

Then, using HA to represent propionic acid, we get:

$$HA + H_2O \quad \leftrightarrow \quad H_3O^+ \quad + \quad A^-$$

$$(.05 - 0.0\alpha) \approx \quad .05\alpha \quad .05\alpha$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{(.05\alpha)(.05\alpha)}{0.05} = .05\alpha^2$$

$$\alpha = \sqrt{\frac{Ka}{.05}} = 1.63 \times 10^{-2}$$

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

$$= K_b.15 \times 10^{-4} M$$

$$\therefore pH = 3.09$$

Let' be the degree of ionisation in the presence of $0.1M\ HCl$.

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

$$[A^-] = 005\alpha'$$

$$[HA] = .05$$

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

$$\alpha' = 1.32 \times 10^{-3} = .01 \times \alpha'$$

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

Question 7.60: The pH of 0.1M solution of cyanic acid $(HCNO)$ is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Answer:

$$c = 0.1\ M$$

$$pH = 2.34$$

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

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

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

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

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

$$\frac{4.5\times10^{-3}}{0.1} = \alpha$$

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

Then, $K_a = c\alpha^2$

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

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

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

Question 7.61: The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and its degree of hydrolysis.

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

$NO^{-2} + H_2O \leftrightarrow HNO_2 + OH^-$

$$K_h = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5\times10^{-4}} = .22 \times 10^{-10}$$

If x moles of salt are hydrolyzed, the concentration of various species in the solution will be as follows:

$[NO_2^-] = .04 - x; 0.04$

$[HNO_2] = x$

$[OH^-] = x$

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

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

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

$$\Rightarrow \left[OH^-\right] = 0.093 \times 10^{-5} M$$

$$\left[H_3O^-\right] = \frac{10^{-14}}{.093\times10^{-5}} = 10.75 \times 10^{-9} M$$

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

$$= 7.96$$

As a result, the degree of hydrolysis

$$= \frac{x}{0.04} = \frac{.093\times10^{-5}}{.04}$$

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

Question 7.62: A 0.02 M solution of pyridinium hydrochloride has $pH = 3.44$. Calculate the ionization constant of pyridine.

Answer:

$pH = 3.44$

We know that,

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

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

Then, $K_h = \frac{\left(3.63\times10^{-4}\right)^2}{0.02}$ $(\because$ concentration $= 0.02M)$

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

Now,

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

$$\Rightarrow K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6\times10^{-6}}$$

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

Question 7.63: Predict if the solutions of the following salts are neutral, acidic or basic:
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

Answer: (i) NaCl

$$\begin{array}{lllll} NaCl+H_2O & \leftrightarrow & NaOH & + & HCl \\ & & \text{Strong base} & & \text{Strong base} \end{array}$$

As a result, it's a neutral solution.

(ii) KBr

$$\begin{array}{lllll} KBr + H_2O & \leftrightarrow & KOH & + & HBr \\ & & \text{Strong base} & & \text{Strong acid} \end{array}$$

As a result, it's a solution that's neither good nor bad.

(iii) NaCN

$$\begin{array}{lllll} NaCN + H_2O & \leftrightarrow & HCN & + & NaOH \\ & & \text{Weak acid} & & \text{Strong base} \end{array}$$

(iv) NH_4NO_3

$$\begin{array}{lllll} NH_4NO_3 + H_2O & \leftrightarrow & NH_4OH & + & HNO_3 \\ & & \text{Weak acid} & & \text{Strong base} \end{array}$$

As a result, the solution is acidic

(v) $NaNO_2$

$$\begin{array}{lllll} NaNO_2 + H_2O & \leftrightarrow & NaOH & + & HNO_3 \\ & & \text{Strong base} & & \text{Weak acid} \end{array}$$

Hence, the solution is basic

(vi) KF

$$\begin{array}{lllll} KF + H_2O & \leftrightarrow & KOH & + & HF \\ & & \text{Strong base} & & \text{Weak acid} \end{array}$$

Hence, the solution is basic

Question 7.64: The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

Answer:

Given,

K_a for $ClCH_2COOH$ is 1.35×10^{-3} .

$K_a = c\alpha^2$

$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.35\times10^{-3}}{0.1}}$

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

$= 0.116$

$\therefore \left[H^+\right] = c\alpha = 0.1 \times 0.116$

$= .0116$

$\therefore\ pH = -\log\left[H^-\right] = 1.94$

$ClCH_2COONa$ is the salt of a weak acid i.e., $ClCH_2COOH$ and a strong base i.e., $NaOH$.

$ClCH_2COO^- + H_2O \leftrightarrow ClCH_2COOH + OH^-$

$K_b = \frac{\left[ClCH_2COOH\right]\left[OH^-\right]}{\left[ClCH_2COO\text{-}\right]}$

$K_h = \frac{Kv}{Ka}$

$Kb = \frac{10^{-14}}{1{,}35\times10^{-3}}$

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

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

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

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

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

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

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

$\therefore \left[H^+\right] = \frac{Kw}{0.86\times10^{-6}} = \frac{10^{-14}}{0.86\times10^{-6}}$

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

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

$= 7.94$

Question 7.65: Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Ans

Ionic product

$K_w = \left[H^+\right]\left[OH^-\right]$

Let $\left[H^+\right] = x.$

Since $\left[H^+\right] = \left[OH^-\right]$, $Kw = x^2$.

$= K_w$ at 310 K is 2.7×10^{-14} .

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

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

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

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

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

$= 6.78$

As a result, neutral water has a pH of 6.78.

Question 7.66: Calculate the pH of the resultant mixtures:

a) 10 mL of $0.2M\ Ca(OH)_2$ + 25 mL of 0.1M HCl

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

c) 10 mL of $0.1M\ H_2SO_4$ + 10 mL of 0.1M KOH

Answer:

$$\text{Moles of } H_3O^+ = \frac{25 \times 0.1}{1000} = .0025 \text{ mol}$$

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

Excess of $OH^- = .0015$ mol

$$\left[OH^-\right] = \frac{.0015}{35\times10^{-3}} \text{ mol/L} = .0428$$

$pOH = -\log\left[OH\right]$

$= 1.36$

$pH = 14 - 1.36$

$= 12.63$ (not matched)

(b)

$$\text{Moles of } H_3O^+ = \frac{2\times10\times0.01}{1000} = .0002 \text{ mol}$$

$$\text{Moles of } OH^- = \frac{2\times10\times.01}{1000} = .0002 \text{ mol}$$

Excess of $H_3O^+ = .001$ mol

$$\text{Thus, } \left[H_3O^+\right] = \frac{.001}{20\times10^{-3}} = \frac{10^{-3}}{20\times10^{-3}} = .05$$

$$\therefore \text{pH} = -\log(0.05) = 1.30$$

It is a neutral solution and pH is 7

Question 7.67: Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9 (page 221). Also determine the molarities of individual ions.

Answer:

(1) Silver chromate:

$Ag_2CrO_4 \leftrightarrow 2Ag^+ + CrO_4^{2-}$

Then,

$K_{sp} = \left[Ag^+\right]^2 \left[CrO_4^{2-}\right]$ Let the solubility of Ag_2CrO_4 be s.

$= \left[Ag^+\right] 2s$ and $\left[CrO_4^{2-}\right] = s$

Then,

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

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

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

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

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

Molarity of CrO_4^{2+} $= s = 0.65 \times 10^{-4}$ M

(2) Barium chromate:

$BaCrO_4 \leftrightarrow Ba^{2+} + CrO_4^{2-}$

Then, $K_{sp} = \left[Ba^{2+}\right] \left[CrO_4^{2-}\right]$

Let the solubility of $BaCrO_4$ be s

$\left[Ba^{2+}\right] = s$

$\left[CrO_4^{2-}\right] = s$

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

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

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

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

(3) Ferric hydroxide:

$Fe(OH)_3 \leftrightarrow Fe^{2+} + 3OH^-$

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

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

Thus, $\left[Fe^{3+}\right] = s$ and $\left[OH^-\right] = 3s \Rightarrow K_{sp} = s.(3s)^3$

$= s.27s^3$

$K_{sp} = 27s^4$

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

$.037 \times 10^{-38} = s^4$

$.00037 \times 10^{-36} = s^4$

$\Rightarrow 1.39 \times 10^{-10} M = S$

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

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

(4) Lead chloride:

$PbCl_2 \leftrightarrow Pb^{2+} + 2Cl^-$

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

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

$\left[PB^{2+}\right] = s$ and $\left[Cl^-\right] = 2s$

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

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

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

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

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

(5) Mercurous iodide:

$Hg_2I_2 \leftrightarrow Hg2+ + 2I^-$

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

Let s be the solubility of Hg_2I_2.

Þ $\left[Hg_2^{2+}\right] = s$ and $\left[I^-\right] = 2s$

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

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

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

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

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

Molarity of $Hg_2^{2+} = s = 2.24 \times 10^{-10}M$

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

Question 7.68: 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:

s can be the solubility of Ag_2CrO_4

Then, $Ag_2CrO_4 \leftrightarrow Ag^{2+} + 2CrO_4^-$

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

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

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

Let s' be the solubility of AgBr.

$AgBr_{(s)} \leftrightarrow Ag^+ + Br^-$

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

$\therefore$ s 0 $= 7.07 \times 10^{-7}M$

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

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

Question 7.69: Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

Answer: When equal volumes of sodium iodate and cupric chlorate solutions are combined, their molar concentrations are lowered to half, or 0.001 M. Then

$\mathrm{NaIO_3 \leftrightarrow \quad Na^+ + 10_3^-}$

0.001M $\qquad$ 0.001M

$\mathrm{Cu\ (ClO_3)_2 \leftrightarrow Cu^{2+} + 2ClO_3^-}$

0.001M $\qquad$ 0.001M

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

$\mathrm{Cu\ (10_3)_2 \ \rightarrow Cu^{2+}_{(aq)} + 210_3^-(aq)}$

Ionic product of copper iodate:

$= \left[\mathrm{Cu^{2+}}\right] \left[\mathrm{10_3^-}\ \right]$

$= (0.001)(0.001)^2$

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

As the ionic product $\left(1 \times 10^{-9}\right)$ is less than $\mathrm{K_{sp}}$ $\left(7.4 \times 10^{-8}\right)$, precipitation shall not occur

Question 7.70: The ionization constant of benzoic acid is 6.46×10^{-5} and $\mathrm{K_{sp}}$ for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of $\mathrm{pH}\ 3.19$ compared to its solubility in pure water?

Answer:

Since $\mathrm{pH} = 3.19$

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

$\mathrm{C_6H_3COOH + H_2O \leftrightarrow C_6H_3COO^- + H_3O}$

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

$$\frac{\left[\mathrm{C_6H_3COOH}\right]}{\left[\mathrm{C_6H_3COO^-}\right]} = \frac{\left[\mathrm{H_3O^+}\right]}{\mathrm{K_a}} = \frac{6.46\times10^{-4}}{6.46\times10^{-3}} = 10$$

Let the solubility of $\mathrm{C_6H_5COOAg}$ be $\mathrm{x\ mol/L}$. Then,

$$\left[Ag^{+}\right] = x$$

$$\left[C_6H_5COOH\right] + \left[C_6H_5COO^{-}\right] = x$$

$$10\left[C_6H_3COO^{-}\right] + \left[C_6H_5COO^{-}\right] = x$$

$$\left[C_6H_3COO^{-}\right] = \frac{x}{11}$$

$$K_{sp}\ \left[Ag^{+}\right]\left[C_6H_5COO^{-}\right]$$

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

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

Hence, C_6H_5COOAg is approximately 3.317 times more soluble in a low pH solution.

Question 7.71: 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, $K_{sp} = 6.3 \times 10^{-18}$).

Answer: Let each solution's maximum concentration be x mol/L. After mixing, the volume of each solution's concentrations will be lowered to half, or $x/2$.

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

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

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

$$FeS_{(t)} \leftrightarrow Fe^{2+}_{(aq)} + S^{2-}_{(aq)}$$

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

$$6.3 \times 10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right) \quad \frac{x^2}{4} = 6.3 \times 10^{-18}$$

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

There will be no precipitation of iron sulphide if the concentrations of both solutions are equal to or less than 5.02×10^{-9} M.

Question 7.72: 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}).

Answer:

$CaSO_4(s) \leftrightarrow Ca^{2+}_{(aq)} + SO_4^{2-}$

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

Let the solubility of $CaSO_4$ be s.

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

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

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

Molecular mass of $CaSO_4 = 136$ g/mol

Solubility of $CaSO_4$ in gram/L

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

$= 0.41$ g/L

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

As a result, to dissolve 1g of $CaSO_4$, we'll need

$= \frac{1}{0.41}$ L= 2.44L

Question 7.73: The concentration of sulphide ion in $0.1M\ HCl$ 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: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions' precipitation will take place?

Answer: Given,

K_{sp} for FeS = 6.3×10^{-18} , MnS = 2.5×10^{-13} , ZnS = 1.6×10^{-24} , CdS = 8.0×10^{-27}

Answer: The computed ionic product must surpass the K_{sp} value for precipitation to occur.

Before you start mixing:

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

volume=10mL Volume=5mL

After mixing

$\left[s^{2-}\right]=?$ $\left[M^{2+}\right]$

volume = $(10 + 5)$ = 15 mL volume = 15 mL

$$\left[S^{2-}\right]=\frac{1.0\times10^{-19}\times10}{15} = 6.67 \times 10^{-20}M$$

$$\left[M^{2+}\right]=\frac{0.04\times5}{15} = 1.33 \times 10^{-2}M$$

Ionic product = $\left[M^{2+}\right]\left[S^{2-}\right]$

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

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

The K_{sp} of ZnS and CdS are exceeded by this ionic product. Precipitation will occur in $CdCl_2$ and $ZnCl_2$ solutions as a result.

Example Exercises

Problem 7.1 The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K.
$\left[N_2\right] = 1.5 \times 10^{-2}M$. $\left[H_2\right] = 3.0 \times 10^{-2}$ M and $\left[NH_3\right] = 1.2 \times 10^{-2}M$. **Calculate equilibrium constant.**

Answer: The equilibrium constant for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as,

$$K_c = \frac{\left[NH_3(g)\right]^2}{\left[N_2(g)\right]\left[H_2(g)\right]^3}$$

$$= \frac{\left(1.2 \times 10^{-2}\right)^2}{\left(1.5 \times 10^{-2}\right)\left(3.0 \times 10^{-2}\right)^3}$$

$= 0.106 \times 104 = 1.06 \times 10^3$

Problem 7.2 At equilibrium, the concentrations of $N_2 = 3.0 \times 10^{-3}M$, $O_2 = 4.2 \times 10^{-3}M$ and $NO = 2.8 \times 10^{-3}M$ in a sealed vessel at 800K. What will be Kc for the reaction
$N_2(g) + O_2(g)\ 2NO(g)$

Answer: For the reaction equilibrium constant, K_c can be written as,

$$Kc = \frac{[NO]_2}{[N_2]\,[O_2]}$$

$$= \frac{(2.8 \times 10^{-3}M)^2}{(3.0 \times 10^{-3}M)\,(4.2 \times 10^{-3}M)}$$

=0.622

Problem 7.3 PCl_5 , PCl_3 and Cl_2 **are at equilibrium at 500 K and having concentration** 1.59M PCl_3, 1.59M Cl_2 and 1.41 M PCl_5 .

Calculate K_c **for the reaction,** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Answer: For the for mentioned reaction, the equilibrium constant K_c can be expressed as,

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{(1.59)^2}{(1.41)} = 1.79$$

Problem 7.4 The value of $K_c = 4.24$ at 800K **for the reaction,** $CO(g) + H_2O(g) \rightleftharpoons CO_2\ (g) + H_2(g)$ **Calculate equilibrium concentrations of** CO_2 , H_2 , CO and H_2O at 800 K**, if only** CO **and** H_2O **are present initially at concentrations of 0.10M each.**

Answer: For the reaction,

$CO(g) + H_2O\ (g) \rightleftharpoons CO_2(g) + H_2(g)$

Initial concentration

0.1 0.1 0 0

At equilibrium

(0.1-x)M (0.1-x)M xM xM

Let x mole per litre of each of the product be formed. where x is the amount of CO_2 and H_2 at equilibrium. Hence, equilibrium constant can be

$K_c = x^2/(0.1 - x)^2 = 4.24$

$x^2 = 4.24\ (0.01 + x^2 - 0.2x)$

$x^2 = 0.0424 + 4.24x^2 - 0.848x$

$3.24x^2 - 0.848x + 0.0424 = 0$

a = 3.24, b = -0.848, c = 0.0424

For quadratic equation $ax^2 + bx + c = 0$,

$$x = \frac{\left(-b \pm \sqrt{b^2-4ac}\right)}{2a}$$

$$x = 0.848 \pm \sqrt{(0.848)^2} - 4(3.24)(0.0424)/(3.24\times2)$$

$$x = (0.848 \pm 0.4118)/6.48$$

$$x_1 = (0.848 - 0.4118)/6.48 = 0.067$$

$$x_2 = (0.848 + 0.4118)/6.48 = 0.194$$

The value 0.194 should be ignored since it will result in a reactant concentration that is higher than the initial concentration. As a result, the equilibrium concentrations are as follows:

$$[CO_2] = [H_2] = x = 0.067M$$

$$[CO] = [H_2O] = 0.1 - 0.067 = 0.033M$$

Problem 7.5 For the equilibrium, $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Answer: As we know that

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

From the given equation

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

$$K_p = 3.75 \times 10^{-6} \ (0.0831 \times 1069)$$

$$K_p = 0.033$$

Problem 7.6 The value of K_p for the reaction, $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ is 3.0 at 1000 K. If initially $PCO_2 = 0.48$ bar and $PCO = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2 .

Answer: In the given reaction, let ‘x’ be the decrease in pressure of CO_2, then

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial pressure	$PCO_2 = 0.48$ bar	0
At Equilibrium	(0.48-x)bar	2x bar

$$K_p = \frac{p^2_{CO}}{p_{CO_2}}$$

$K_p = (2x)^2/(0.48 - x) = 3$

$4x^2 = 3(0.48 - x)$

$4x^2 = 1.44 - x$

$4x2 + 3x - 1.44 = 0$

$a = 4, b = 3, c = -1.44$

$$x = \frac{\left(-b \pm \sqrt{b^2 - 4ac}\right)}{2a} =$$

$$\left[-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}\right]/2 \times 4$$

$= (-3 \pm 5.66)/8$

$= (-3 + 5.66)/8$

(as value of x cannot be negative hence we neglect that value)

$x = 2.66/8 = 0.33$

The equilibrium partial pressures are

$p_{CO_2} = 2x = 2 \times 0.33 = 0.66$ bar

$p_{CO_2} = 0.48 - x = 0.48 - 0.33 = 0.15$ bar

Problem 7.7 The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

Answer: The reaction quotient Q_c is calculated as follows:

$Q_c = [B][C]/[A]^2$

as $[A] = [B] = [C] = 3 \times 10^{-4}M$

$Q_c = (3 \times 10^{-4})(3 \times 10^{-4})/(3 \times 10^{-4})^2 = 1$

as $Q_c > K_c$

As a result, the reaction will go in the opposite direction.

Problem 7.8 13.8g of N_2O_4 **was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ The total pressure at equilbrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressure at equilibrium.**

Answer:

We know $pV = nRT$

Total volume $\left(V\right) = 1\text{ L}$

Molecular mass of $N_2O_4 = 92\text{ g}$

Number of moles $= 13.8\text{g}/92\text{ g} = 0.15$ of the gas (n)

Gas constant (R) $= 0.083\text{ bar L mol}^{-1}\text{K}^{-1}$

Temperature $\left(T\right) = 400\text{ K}$

$$pV = nRT$$
$$p \times 1\text{L} = 0.15\text{ mol} \times 0.083\text{ bar L mol}^{-1}\text{K}^{-1} \times 400\text{ K}$$
$$p = 4.98\text{ bar}$$

	$N_2O_4\left(g\right) \rightleftharpoons$	$2NO_2\left(g\right)$
Initial pressure	0.48 bar	0
At Equilibrium	(0.48-x)bar	2x bar

$$p_{\text{total}} \text{ at equilibrium} = p_{N_2O_4} + p_{NO_2}$$
$$9.15 = \left(4.98 - x\right) + 2x$$
$$9.15 = 4.98 + x$$
$$x = 9.15 - 4.98 = 4.17\text{ bar}$$

At equilibrium the partial pressures are

$$p_{N_2O_4} = 4.98 - 4.17 = 0.81\text{bar}$$
$$p_{NO_2} = 2x = 2 \times 4.17 = 8.34\text{ bar}$$

$$K_p = \left(p_{NO_2}\right)^2 / p_{N_2O_2}$$
$$= \left(8.34\right)2/0.81 = 85.87$$
$$K_p = K_c\left(RT\right)^{\Delta n}$$
$$85.87 = K_c\left(0.083 \times 400\right)^1$$
$$K_c = 2.586 = 2.6$$

Problem 7.9 3.00 mol of PCl_5 **kept in 1L closed reaction vessel could attain equilibrium at 380K. Calculate composition of the mixture at equilibrium.** $K_c = 1.80$

Answer:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial concentration:	3.0	0	0
At equilibrium	(3-x)	x	x

Allow x mol of PCl_5 per litre to dissociate.

$$K_c = [PCl_3][Cl_2]/[PCl_5]$$

$$1.8 = x^2/(3-x)$$

$$x^2 + 1.8x - 5.4 = 0$$

$$x = \left[-1.8 \pm \sqrt{(1.8)2 - 4(-5.4)}\right]/2$$

$$x = \left[-1.8 \pm \sqrt{3.24 + 21.6}\right]/2$$

$$x = [-1.8 \pm 4.98]/2$$

$$x = [-1.8 + 4.98]/2 = 1.59$$

$$[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41\ M$$

$$[PCl_3] = [Cl_2] = x = 1.59\ M$$

Problem 7.10 The value of ΔG^{-} for the phosphorylation of glucose in glycolysis is $13.8\ kJ/mol$. Find the value of K_c at 298 K.

Answer:

$$\Delta G^{-} = 13.8\ kJ/mol = 13.8 \times 103 J/mol$$

$$\text{Also, } \Delta G^{-} = -RT\ lnK_c$$

$$\text{Hence, } \ln K_c = -13.8 \times 103 J/mol$$

$$(8.314\ J\ mol -1K -1 \times 298\ K)$$

$$\ln K_c = -5.569\ K_c = e^{-5.569}$$

$$K_c = 3.81 \times 10^{-3}$$

Problem 7.11 Hydrolysis of sucrose gives, $\text{Sucrose} + H_2O \rightleftharpoons \text{Glucose} + \text{Fructose}$ **Equilibrium constant K_c for the reaction is** 2×1013 at $300K$**. Calculate ΔG^{-} at 300K.**

Answer:

$$\Delta G^{-} = -RT\ lnKc$$

$$\Delta G^{-} = -8.314 J\ mol^{-1} K^{-1} \times 300K \times \ln(2 \times 1013)$$

$$\Delta G^{-} = -7.64 \times 104\ J\ mol^{-1}$$

Problem 7.12 What will be the conjugate bases for the following Brönsted acids:
HF, H_2SO_4 and HCO_3^- **?**

Answer: In each case, the conjugate bases should be one proton less, hence the appropriate conjugate bases are: F^- , HSO_4^- and CO_3^{2-} correspondingly.

Problem 7.13 Write the conjugate acids for the following Brönsted bases:
NH_2^- , NH_3 and $HCOO^-$.

Answer: In each scenario, the conjugate acid should have an extra proton, therefore the appropriate conjugate acids are NH_2^- , NH_3 and $HCOO^-$., respectively.

Problem 7.14 The species: H_2O, HCO_3^- , HSO_4^- and NH_3 **can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.**

Answer: The following table has the answer:

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

Problem 7.15 Classify the following species into Lewis acids and Lewis bases and show how these act as such:

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

Answer:

(a) It can contribute an electron lone pair $\left(OH^-\right)$, the hydroxyl ion is a Lewis base.

(b) It can donate any of its four electron lone pairs, the fluoride ion behaves as a Lewis base.

(c) It may accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion, a proton is a Lewis acid.

(d) BCl_3 can accept a lone pair of electrons from species such as ammonia or amine molecules, making it a Lewis acid.

Problem 7.16 The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. what is its pH ?

Answer:

$$pH = -\log\left[3.8 \times 10^{-3}\right]$$
$$= -\left\{\log[3.8] + \log\left[10^{-3}\right]\right\}$$
$$= -\left\{(0.58) + (-3.0)\right\} = -\left\{-2.42\right\} = 2.42$$

As a result, the pH of the soft drink is 2.42, indicating that it is acidic.

Problem 7.17 Calculate pH of a 1.0×10^{-8} M solution of HCl.

Answer:

$$2H_2O\ (l) \rightleftharpoons H_3O^+(aq) + OH^-\ (aq)$$
$$K_w = \left[OH^-\right]\left[H_3O^+\right]$$
$$= 10^{-14}$$
$$\text{Let, } x = \left[OH^-\right] = \left[H_3O^+\right] \text{ from } H_2O$$

The H_3O^+ concentration is produced I by ionisation of dissolved HCl, i.e.

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-\ (aq),$$

and (ii) from H_2O ionisation. Both sources of H_3O^+ must be considered in these extremely dilute solutions.

$$\left[H_3O^+\right] = 10^{-8} + x$$
$$K_w = \left(10^{-8} + x\right)(x) = 10^{-14}$$
$$\text{or } x^2 + 10^{-8}\ x - 10^{-14} = 0$$
$$\left[OH^-\right] = x = 9.5 \times 10^{-8}$$

So, pOH = 7.02 and pH = 6.98

Problem 7.18 The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present $\left(H_3O^+, F^- \text{ and } HF\right)$ in the solution and its pH.

Answer: Proton transfer reactions include the following:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

$K_a = 3.2 \times 10^{-4}$

2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$K_w = 1.0 \times 10^{-14}$

As $K_a >> K_w$, $[1]$ is the principle reaction

	HF	$+$	H_2O	$\rightleftharpoons$	H_3O^+	$+$	F^-
Initial conc,(M)	0.02				0		0
Change(M)	-0.02				$+0.02\alpha$		$+0.02\alpha$
Equilibrium conc(M)	$0.02 - 0.02\alpha$				0.02α		0.02α

When equilibrium concentrations are substituted for primary reaction in the equilibrium reaction, the following results are obtained:

$$K_a = (0.02\alpha)\ 2 / (0.02 - 0.02\alpha)$$

$$= 0.02\ \alpha\ 2 / (1 - \alpha) = 3.2 \times 10^{-4}$$

The following quadratic equation is obtained:

$$\alpha\ 2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0$$

It is possible to solve the quadratic equation in, and the two roots are:

$$\alpha = +\ 0.12 \text{ and } -0.12$$

Because the negative root is unacceptable,

$$\alpha = 0.12$$

The degree of ionization, $\alpha = 0.12$, then equilibrium concentrations of other species viz., HF, F^- and H_3O^+ are given by:

$$\left[H_3O^+\right] = \left[F^-\right] = c\alpha = 0.02 \times 0.12 = 2.4 \times 10^{-3}\ M$$

$$[HF] = c(1 - \alpha) = 0.02\ (1 - 0.12) = 17.6 \times 10^{-3}\ M$$

$$pH = -\log[H+] = -\log\left(2.4 \times 10^{-3}\right) = 2.62$$

Problem 7.19 The pH of 0.1M **monobasic acid is 4.50. Calculate the concentration of species** H^+ , A^- and HA **at equilibrium. Also, determine the value of** Ka and pKa **of the monobasic acid.**

Answer:

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

Therefore, $\left[H^+\right] = 10 - pH = 10^{-4.50} = 3.16 \times 10^{-5}$

$\left[H^+\right] = \left[A^-\right] = 3.16 \times 10^{-5}$

Thus, $Ka = \left[H^+\right]\left[A^-\right] / [HA]$

$[HA]_{eqlbm} = 0.1 - \left(3.16 \times 10^{-5}\right) /0.1$

$K_a = \left(3.16 \times 10^{-5}\right) 2 / 0.1 = 1.0 \times 10^{-8}$

$pK_a = -\log\left(10^{-8}\right) = 8$

Another effective way for determining the strength of a weak acid is "percent dissociation," which is expressed as: Dissociation percentage

$$= [HA]_{dissociated} / [HA]_{initial} \times 100\% \ (7.32)$$

Problem 7.20 Calculate the pH of $0.08M$ **solution of hypochlorous acid,** $HOCl$**. The ionization constant of the acid is** 2.5×10^{-5}**. Determine the percent dissociation of** $HOCl$**.**

Answer:

$$HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^+\ (aq) + ClO^-\ (aq)$$

Initial conc,(M) 0.08 0 0

Change to reach equilibrium concentration(M)

-x +x +x

equilibrium concentration(M)

0.08-x x x

$K_a = \left\{\left[H_3O^+\right]\left[ClO^-\right] / [HOCl]\right\} = x2 / (0.08 - x)$

As we know that $x << 0.08$, thus,

$0.08\text{-}x \simeq 0.8$

$x^2 / 0.08 = 2.5 \times 10^{-5}$

$x^2 = 2.0 \times 10^{-6}$, thus , $x = 1.41 \times 10^{-2}$

$\left[H^+\right] = 1.41 \times 10^{-3}$ M.

Therefore

Percent dissociation

$$= \left\{[\mathrm{HOCl}]_{\mathrm{dissociated}} \;/\; [\mathrm{HOCl}]_{\mathrm{initial}}\right\} \times 100$$

$$= 1.41 \times 10^{-3} \times 102/\ 0.08 = 1.76\ \%.$$

$$\mathrm{pH} = -\log\left(1.41 \times 10^{-3}\right) = 2.85.$$

Problem 7.21 The pH of $0.004\ \mathrm{M}$ hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b .

Answer: $NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$

The hydrogen ion concentration can be calculated using the pH. We can compute the concentration of hydroxyl ions by knowing the concentration of hydrogen ions and the ionic product of water. As a result, we have

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

$$= \mathrm{antilog}\ (-9.7) = 1.67 \times 10^{-10}$$

$$[\mathrm{OH-}] = K_w\ /\ [\mathrm{H}^+] = 1 \times 10^{-14} / \ 1.67 \times 10^{-10} = 5.98 \times 10^{-5}$$

The hydrazinium ion corresponding to the hydroxyl ion has the same concentration as the hydroxyl ion. Because both ions have very low concentrations, the concentration of the undissociated base can be assumed to be $0.004\ \mathrm{M}$.

$$K_b = [NH_2NH_3^+][OH^-]\ /\ [NH_2NH_2]$$

$$= \left(5.98 \times 10^{-5}\right)^2\ /\ 0.004 = 8.96 \times 10^{-7}$$

$$\mathrm{pKb} = -\log\mathrm{Kb} = -\log\left(8.96 \times 10^{-7}\right) = 6.04.$$

Problem 7.22 Calculate the pH of the solution in which $0.2\ \mathrm{M}\ NH_4Cl$ and $0.1\mathrm{M}\ NH_3$ are present. The pK_b of ammonia solution is 4.75.

Answer: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH$

Constant ionization of NH_3

$$K_b = \mathrm{antilog}\ (-pK_b)\ \text{i.e}$$

$$K_b = 10^{-4.75} = 1.77 \times 10^{-5}\ \mathrm{M}$$

	NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH
Initial concentration(M)	0.10				0.20		0
Change to reach equilibrium (M)							
	-x				+x		+x
At equilibrium(M)							
	0.10-x				0.20+x		x

$$K_b = \left[NH_4^+\right]\left[OH^-\right] / \left[NH_3\right]$$

$$= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$$

Since K_b is small, x can be neglected in comparison to 0.1M and 0.2M. Thus,

$$\left[OH^-\right] = x = 0.88 \times 10^{-5}$$

Therefore, $\left[H^+\right] = 1.12 \times 10^{-9}$

$$pH = -\log\left[H^+\right] = 8.95.$$

Problem 7.23 Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 7.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

Answer: Equation is used to illustrate the ionisation of NH_3 in water.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH$$

The hydroxyl ion concentration is calculated using equation (7.33).

$$\left[OH^-\right] = c\,\alpha = 0.05\,\alpha$$

$$K_b = 0.05\,\alpha^2 / (1 - \alpha)$$

Because the value of is tiny, the quadratic equation can be simplified by ignoring in the denominator on the right hand side of the equation in comparison to 1.

$$K_b = c\,\alpha^2 \text{ or } \alpha = \sqrt{\left(1.77 \times 10^{-5} / 0.05\right)}$$

$$= 0.018. \left[OH^-\right] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4} M.$$

$$\left[H^+\right] = K_w / \left[OH^-\right] = 10^{-14} / \left(9.4 \times 10^{-4}\right)$$

$$= 1.06 \times 10^{-11}$$

$$pH = -\log\left(1.06 \times 10^{-11}\right) = 10.97$$

Now, using the conjugate acid-base pair relation,

$$K_a \times K_b = K_w$$

using the value of K_b of NH3 from Table 7.7. We can determine the concentration of conjugate acid NH_4^+

$K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5}$
$= 5.64 \times 10^{-10}$

Problem 7.24 Calculate the pH **of a** $0.10M$ **ammonia solution. Calculate the** pH **after** $50.0\ mL$ **of this solution is treated with** $25.0\ mL$ of $0.10M\ HCl$**. The dissociation constant of ammonia,** $K_b = 1.77 \times 10^{-5}$

Answer:

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$K_b = [NH_4^+][OH^-] / [NH_3] = 1.77 \times 10^{-5}$
Before neutralization, $[NH_4^+] = [OH^-] = x$
$[NH_3] = 0.10 - x / 0.10$
$x^2 / 0.10 = 1.77 \times 10^{-5}$
Thus, $x = 1.33 \times 10^{-3} = [OH^-]$
Therefore, $[H+] = K_w / [OH^-] = 10^{-14} / (1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$
$pH = -\log(7.5 \times 10^{-12}) = 11.12$

On addition of $25\ mL$ of $0.1M\ HCl$ solution $(i.e., 2.5\ mmol\ of\ HCl)$ to $50\ mL$ of $0.1M$ ammonia solution $(i.e., 5\ mmol\ of\ NH_3)$, $2.5\ mmol$ of ammonia molecules are neutralized. The resulting $75\ mL$ solution contains the remaining unneutralized $2.5\ mmol$ of NH_3 molecules and $2.5\ mmol$ of NH_4^+.

	NH_3	+ HCl	$\rightarrow$ NH_4^+	+ Cl^-
	2.5	2.5	0	0
At equilibrium	0	0	2.5	2.5

The resulting 75 mL of solution contains $2.5\ mmol$ of NH_4^+. ions $(i.e., 0.033\ M)$ and $2.5\ mmol$ $(i.e., 0.033\ M)$ of unneutralized NH_3 molecules. This NH3 exists in the following equilibrium:

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
0.033-y y y
where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains $2.5\ \text{m mol NH}_4^+$ ions $\left(\text{i.e., } 0.033\ \text{M}\right)$, thus total concentration of NH_4^+ ions is given as:

$\left[NH_4^+\right] = 0.033 + y$

As y is small, $\left[NH_4OH\right]$; 0.033 M and

$\left[NH_4^+\right]$;0.033M.

We know,

$Kb = \left[NH_4^+\right]\left[OH^-\right] / \left[NH_4OH\right]$

$= y\left(0.033\right)/\left(0.033\right) = 1.77 \times 10^{-5}\ \text{M}$

Thus, $y = 1.77 \times 10^{-5} = \left[OH^-\right]\ \left[H^+\right] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$

Hence, pH = 9.24

Problem 7.25 The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Answer:

$pH = 7 + ½\ \left[pK_a - pK_b\right]$

$= 7 + ½\ \left[4.76 - 4.75\right]$

$= 7 + ½\ \left[0.01\right] = 7 + 0.005 = 7.005$

Problem 7.26 Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$.

Answer:

$A_2X_3 \rightarrow 2A^{3+} + 3X^{2-}$

$K_{sp} = \left[A^{3+}\right]^2\ \left[X^{2-}\right]^3 = 1.1 \times 10^{-23}$

If S = solubility of A_2X_3 , then

$\left[A^{3+}\right] = 2S;\ \left[X^{2-}\right] = 3S$

therefore, $K_{sp} = \left(2S\right)^2\ \left(3S\right)^3 = 108S^5 = 1.1 \times 10^{-23}$

thus, $S^5 = 1 \times 10^{-25}$

$S = 1.0 \times 10^{-5}$ mol/L.

Problem 7.27 The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Answer:

$AgCN \rightleftharpoons Ag^{+} + CN^{-}$

$K_{sp} = [Ag^{+}][CN^{-}] = 6 \times 10^{-17}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^{-}$

$K_{sp} = [Ni^{2+}][OH^{-}]2 = 2 \times 10^{-15}$

Let $[Ag^{+}] = S_1$, then $[CN^{-}] = S1$

Let $[Ni^{2+}] = S_2$, then $[OH^{-}] = 2S_2$

$S_1^2 = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$

$(S_2)(2S_2)2 = 2 \times 10^{-15}$, $S_2 = 0.58 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

Problem 7.28 Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}. Solution Let the solubility of $Ni(OH)_2$ be equal to S.

Answer: Dissolution of S mol/L of $Ni(OH)_2$ provides S mol/L of Ni^{2+} and 2S mol/L of OH^{-}, but the total concentration of $OH^{-} = (0.10 + 2S)$ mol/L because the solution already contains 0.10 mol/L of OH^{-} from NaOH.

$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}][OH^{-}]2 = (S)(0.10 + 2S)^2$

K_{sp} is small $2S << 0.10$

thus, $(0.10 + 2S) \approx 0.10$ Hence, $2.0 \times 10^{-15} = S(0.10)^2$

$S = 2.0 \times 10^{-13}$ M $= [Ni^{2+}]$