THE UNIVERSITY OF ZAMBIA
SCHOOL OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY
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TERM 2
CHE1000: INTRODUCTION TO CHEMISTRY

Solved Examples:

EQUILIBRIUM

1. Write the expression for the equilibrium constants for the following reactions:

(a) $Br_{2(g)} + H_{2\,(g)} \rightleftharpoons 2HBr_{(g)}$ $$K_p = \frac{[HBr]^2}{[Br_2][H_2]}$$

(b) $CS_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2S_{(g)}$ $$K_p = \frac{[H_2S]^2[CH_4]}{[CS_2][H_2]^4}$$

(c) $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$ $$K_p = \frac{[H_2]}{[H_2O]}$$

2. Would either of the following reaction go almost completely to products?

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ $K_c = 3 \times 10^{-17}$

$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$ $K_c = 8 \times 10^{25}$

Explain.

Yes, the oxidation of sulphur dioxide would go almost to completion as equilibrium constant is high But the first one will not as the equilibrium constant is low.

3. A 6.0 L vessel contained 0.0222 mol of phosphorus trichloride, 0.0189 mol phosphorus pentachloride and 0.1044 mol 0f chlorine at 230 °C in an equilibrium mixture. Calculate the equilibrium constant K_c and K_p for the reaction.

$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

The reaction is $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

Equilibrium concentrations $\frac{0.0222}{6}$ $\frac{0.1044}{6}$ $\frac{0.0189}{6}$

0.0037 0.0174 0.00315

$$K_c = \frac{0.00315}{0.0037 \times 0.0174} = 48.9$$

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

$$= \mathbf{48.9}\ (\mathbf{0.08206(230 + 273)})^{-1}$$

$$= \mathbf{2.35} \times \mathbf{10^{-3}}$$

Note: **R = 0.08206 atm $\mathrm{mol^{-1}\ K^{-1}}$**

4. At 77 °C 2 mol of nitrosyl bromide, NOBr, in a 1.0 L flask were allowed to reach equilibrium according to following equation:

$$2NOBr \rightleftharpoons 2NO + Br_2$$

If the NOBr is 9.4% dissociated at this temperature calculate the equilibrium constant.

	2NOBr	$\rightleftharpoons$	**2NO + Br_2**
Initial concentration	**2**		**0 0**
Change	**- 2 x 9.4%**		**+9.4% +4.7%**
	2 – (2x 9.4/100)		**(2x 9.4/100) (2x 4.7/100)**

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$

$$= \frac{(0.188)^2(0.094)}{(1.812)^2} = 0.0010119 = 0.0010$$

5. Consider the equilibrium process :

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

At 700 °C the total pressure of the system is found to be 4.50 atm. If the equilibrium constant K_p is 1.52, calculate the equilibrium partial pressures of CO_2 and CO.

The equilibrium expression $\boldsymbol{K = \frac{(p_{CO})^2}{(p_{CO2})}}$

Total pressure = Pco + P $\mathbf{co_2}$ = 4.5 atm

Let us assume Pco = x

Then, Pco$_2$= (4.5-x) atm

$$K_p = \frac{P_{CO}{}^2}{P_{CO_2}} = \frac{x^2}{(4.50 - x)} = 1.52$$

x^2 + 1.52x - 6.84 =0

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-1.52 \pm \sqrt{(1.52)^2 - 4 \times 1 \times (-6.84)}}{2 \times 1} \\ &= \frac{-1.52 \pm \sqrt{29.6704}}{2} \\ &= \frac{-1.52 \pm 5.45}{2} \\ x &= 1.96 \\ &or \\ x &= -3.48 \end{aligned}$$

Only positive value has significance.

Hence, partial pressures are

Pco = 1.96 and Pco$_2$ = (4.50-1.96) = 2.54 atm

6. Consider the equilibrium:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)} \qquad H = 284kJ$$

What would be the effect on the position of equilibrium of

(a) increasing the total pressure on the system by decreasing its volume;
Increase in pressure favours the forward reaction as it decreases the number of moles. More O_3 is produced. OR Equilibrium shifts to right.

(b) adding O_2 to the system;
If the concentration of oxygen is increased the equilibrium is disturbed. System tries achieves new equilibrium by using up more oxygen Or OR Equilibrium shifts to right.

(c) decreasing the temperature?

The reaction is endothermic so decreasing the temperature shifts the equilibrium to left.

7. At 200 °C $K_c = 1.4\text{x}10^{-10}$ for the reaction

$$N_2O_{(g)} + NO_{2(g)} \rightleftharpoons 3NO_{(g)} .$$

If 0.200 mol of N_2O and 0.400 mol of NO_2 are placed in a 4.00 L container, what would the concentration of NO be if this equilibrium were established?

The reaction is	$\mathbf{N_2O_{(g)}}$	+	$\mathbf{NO_{2(g)}}$	$\rightleftharpoons$	$\mathbf{3NO_{(g)}}$ **.**
Initial concentration	$\frac{0.200}{4}$		$\frac{0.400}{4}$		**0**
	0.0500		**0.100**		**0**
Change	**- x**		**- x**		**3x**
Equilibrium concentration	**(0.0500-x)**		**(0.100-x)**		**3x**

$$K_c = \frac{(3x)^3}{(0.0500 - x)(0.100 - x)} = 1.4 \times 10^{-10}$$

$$9x^3 = 1.4 \times 10^{-10} \times (0.05 - x)(0.1 - x)$$

Assume x is small as compared to 0.1 and 0.05.

Then $x^3 = (1.4 \text{ x } 10^{-10} \text{ x } 0.05 \text{ x } 0.1) /9$

$x = 8.88 \text{ x } 10^{-5}$ mol dm^{-3}

8. At 25 °C Kc = 0.145 for the following reaction in the solvent CCl_4.

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

A solution was prepared with the following initial concentrations:

[BrCl] = 0.0400 mol dm^{-3}, [Cl_2] = 0.0200 mol dm^{-3}, [Br_2] = 0.0300 mol dm^{-3}. What will be their equilibrium concentration?

From the concentration Q =(0.03 x 0.02)/$(0.04)^2$ =0.375

Q is greater than equilibrium constant. Hence, the reaction would proceed in reverse direction or we can say concentration of BrCl would increase and of clorine and bromine decrease.

The reaction is	**$2BrCl \rightleftharpoons$**	**Br_2**	**+**	**Cl_2**
Initial concentration	**0.0400 M,**	**0.0300 M**		**0.0200 M.**
Change	**2x**		**x**	**x**
Equilibrium concentration	**(0.04 +2x)**	**(0.03 -x)**		**(0.02-x)**

$$K = 0.145 = \frac{(0.03\ - x)\,(0.02 - x)}{(0.04 + 2x)^2}$$

$$0.145(\ 0.04 + 2x)^2 = 0.0006 -\ 0.05\ x + x^2$$

$$0.145(0.0016+4x^2 + 0.16x)= 0.0006 - 0.05\ x + x^2$$

$$0.58\ x^2 + 0.000232 +0.0232\ x = 0.0006 - 0.05\ x + x^2$$

$$0.42x^2 -0.0732\ x + 0.000368 = 0$$

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

$$= \frac{-(-0.0732) \pm \sqrt{(-0.0732)^2 - 4 \times 0.42 \times (0.000368)}}{2 \times 0.42}$$

$$= \frac{0.0732 \pm \sqrt{0.00536 - 0.00061824}}{0.84}$$

$$= \frac{0.0732 \pm 0.0688}{0.84}$$

$$x = 0.169$$

$$or$$

$$x = 0.00523$$

Second value is the correct value. Hence, concentrations are

[BrCl] =0.04-(2 x 0.00523)=0.05046 mol dm^{-3}

[Cl_2]= 0.02- 0.00523= 0.01477 moldm^{-3}

$[Br_2] = 0.03 - 0.00523 = 0.02477$ mol dm^{-3}

ACID BASE EQUILIBRIUM

1. Write equations that show HSO_4^- acting as both as acid and a base.

As a base $\boldsymbol{HSO_4^- + H_2O \leftrightarrow H_2SO_4 + OH^-}$

As a Acid $\boldsymbol{HSO_4^- + H^+ \leftrightarrow SO_4^{2-} + H^+}$

2. What are the conjugate acids and bases of the following?

(a) OH^- (b) H_2O (c) HCO_3^- (d) NH_3

Species	Acid	Base
OH^-	**H_2O**	**O^{2-}**
H_2O	**H_3O^+**	**OH^-**
HCO_3^-	**H_2CO_3**	**CO_3^{2-}**
NH_3	**NH_4^+**	**NH_2^-**

3. Identify and label the Bronsted acid, its conjugate base, the Bronsted base and its conjugate acid in the following equations.

(a) $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

(acid) (base) Conj. A (conj. B)

(b) $H_2PO_4^-(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HPO_4^{2-}(aq)$

(acid) (base) (conj. A) (conj. B)

(c) $NH_4^+(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NH_3(aq)$

(acid) (base) (conj. A) (conj. B)

(d) $NH_4^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + NH_3(aq)$

(acid) (base) (conj. A) (conj. B)

5. What are the concentrations of HCl, H_3O^+, and Cl^-, respectively, in a solution of 0.10 mol dm^{-3} HCl?

   [HCl] = 0.00 mol dm^{-3}; [H_3O^+] = [Cl^-] = 0.10 mol dm^{-3}

   Because it is a strong acid, therefore completely dissociated.

6. What are the major species present in 0.10 mol dm^{-3} solutions of each of the acids, HNO_3, and HNO_2 acids?

   major species in Strong Acid : $HNO_3 = H_3O^+$ & NO_3^-;
   major species in weak acids $HNO_2 = HNO_2$

7. What are amphoteric species? Give an example of one and write its ionization reaction.

   Exhibit properties of acids and bases e.g. HSO_4^-

   As an acid: $HSO_4^- \rightarrow H^+ + SO_4^{2-}$

   As a base: $HSO_4^- + H_2O \rightarrow H_2SO_4 + OH^-$

8. Given the K_a values (in parentheses) for the following acids:

   HCl (K_a is very large); HF ($K_a = 7.2 \times 10^{-4}$); HCN ($K_a = 6.2 \times 10^{-10}$); HNO_2 ($K_a = 4.0 \times 10^{-4}$); CH_3COOH ($K_a = 1.8 \times 10^{-5}$), and C_6H_5COOH ($K_a = 6.3 \times 10^{-5}$).

   (a) Rank (or list) these acids in order of decreasing strength (strongest first).
   HCl (K_a is very large); HF ($K_a = 7.2 \times 10^{-4}$); HNO_2 ($K_a = 4.0 \times 10^{-4}$); C_6H_5COOH ($K_a = 6.3 \times 10^{-5}$); CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and HCN ($K_a = 6.2 \times 10^{-10}$);

   (b) List their conjugate bases in order of increasing strength (weakest base first) and write the K_b value for each conjugate bases. ($K_w = 1.0 \times 10^{-14}$)
   Cl^- (K_b is very small); F^- ($K_b = 1.39 \times 10^{-11}$); HNO_2 ($K_b = 2.50 \times 10^{-11}$); C_6H_5COOH ($K_b = 1.59 \times 10^{-10}$); CH_3COOH ($K_b = 5.56 \times 10^{-10}$) and HCN ($K_b = 1.6 \times 10^{-5}$);

10. Explain why the equilibrium constant for the ionization of an acid in aqueous solution can be used as a measure of the strength of an acid.

    At a given concentration, stronger acids produce greater concentrations of hydronium ion. K_a involves the ratio of hydronium ion concentration to acid concentration; it increases in proportion to the increasing ability of an acid to produce more hydronium ion.

12. Explain why the ionization constant for H_2SO_4 is larger than the ionization constant for H_2SO_3.

The oxidation state for sulfur (+6) in H_2SO_4 is greater the oxidation state for sulfur (+4) in H_2SO_3. In general, a higher oxidation state on the central atom leads to a stronger acid because electrons are pulled more strongly to it, making the H^+ release easier.

13. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.
HI releases the hydronium ion more easily than does HF, partially because of the decreasing electronegativity difference from F to I.

14. Calculate the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

$K_w = K_a \times K_b$ and $K_a = K_w/K_b$ i.e. $K_a = 1 \times 10^{-14}/4.4 \times 10^{-4} = 2.3 \times 10^{-11}$

15. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH and pOH for pure water at 40 °C.

$K_w = [H_3O^+][OH^-] = 2.9 \times 10^{-14}$

$[H_3O^+] = [OH^-] = \sqrt{(2.9 \times 10^{-14})} = 1.70 \times 10^{-7}$ M

pH = pOH = $-\log(1.70 \times 10^{-7}) = 6.77$

16. Determine K_b for acetate ion, $CH_3CO_2^-$ in a 0.10 M solution, the base is 0.0075 % ionized.
Reaction equation: $CH_3CO_2^-{}_{(aq)} + H_2O_{(l)} = CH_3CO_2H_{(aq)} + OH^-{}_{(aq)}$

$K_b = [CH_3CO_2H][OH^-]/[CH_3CO_2^-]$

$[CH_3CO_2H] = [OH^-] = (7.5 \times 10^{-5})(0.10) = 7.5 \times 10^{-6}$ M

$[CH_3CO_2^-] = 0.10 - 1.75 \times 10^{-6} = 0.10$ M

$K_b = (7.5 \times 10^{-6})^2/0.10 = 5.6 \times 10^{-10}$

17. Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings. What is the concentration of the hydronium ion in a 0.534 M solution of formic acid? (K_a Formic acid = 1.8×10^{-4})

$HCO_2H \rightarrow H^+ + HCO_2^-$

Initial mol	**0.534**	**0**	**0**
Change	**-x**	**+x**	**+x**
Equilibrium	**0.534 – x**	**x**	**x**

$K_a = [H^+][HCO_2^-]/ [HCO_2H]$

$x^2/0.534 - x = 1.8 \times 10^{-4}$ Ignore x since Ka is small, extent of ionization is small.and solve for x

$x = [H^+] = 9.8 \times 10^{-3}$ M

18. Calculate the concentration of all species and the pH of a solution of a 0.05 M CH_3COONa. (K_a $CH_3COOH = 1.8 \times 10^{-5}$)

pH and concentration of ions in a solution of a salt of a weak acid and strong base

$$CH_3COONa. \rightarrow Na^+. + CH_3COO^-$$

$$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$$

Initial mols	**0.05**	**----**	**0**	**0**
Change	**-x**	**----**	**+x**	**+x**
Equilibrium	**0.05 – x**	**----**	**x**	**x**

$K_b = [OH^-][CH_3COOH]/[CH_3COO^-]$

$K_b = K_w/K_a = 1.00 \times 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}$

$x^2/0.05\text{-}x = 5.56 \times 10^{-10}$ Ignore x, extent of hydrolysis is small since K_b is small

Solve for $x =[OH^-] = 5.27 \times 10^{-6}$ M and pOH = 5.28
pH = 14.00 – 5.28 = 8.72
$[Na^+] = 0.05$ M
$[OH^-] = [CH_3COO^-] = 5.27 \times 10^{-6}$ M
$[CH_3COOH] = 0.05 - 5.27 \times 10^{-6} \sim 0.05$ M

19. For H_3PO_4, $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$ and $K_{a3} = 3.6 \times 10^{-13}$, calcualte the $[H^+]$, $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.100 M solution of H_3PO_4.

Consider the dissociation of the first proton only in calculating $[H^+]$ since $K_{a1}/K_{a2} = 7.5 \times 10^{-3}/6.3 \times 10^{-8} = 119047$ i.e. much greater than 20

$H_3PO_4 \leftrightarrows H^+ + H_2PO_4^-$ $K_{a1} = [H^+][H_2PO_4^-]/[H_3PO_4]$

Setup the equation $x^2/0.100\text{-}x = 7.5 \times 10^{-3}$ and solve for x using the quadratic formular $[H^+] = [H_2PO_4^-] = 0.024$ M and $[H_3PO_4] = 0.076$ M

From the second dissociation

$H_2PO_4^- \leftrightarrows H^+ + HPO_4^{2-}$ and $K_{a2} = [H^+][HPO_4^{2-}]/[H_2PO_4^-]$

Since $[H^+] = [H_2PO_4^{2-}]$ implies $[HPO_4^{2-}] = K_{a2} = 6.3 \times 10^{-8}$ M

From the third ionization

$HPO_4^{2-} \leftrightarrows H^+ + PO_4^{3-}$ $K_{a3} = [H^+][PO_4^{3-}]/[HPO_4^{2-}]$

Substitute $[H^+] = 0.024$ M , $[HPO_4^{2-}] = 6.3 \times 10^{-8}$ M and $K_{a3} = 3.6 \times 10^{-13}$ into above equation and solve for the unknown

$[PO_4^{3-}] = 9.4 \times 10^{-19}$ M

20. A buffer solution is prepared from equal volumes of 0.200 M acetic acid and 0.600 M sodium acetate. K_a $CH_3COOH = 1.8 \times 10^{-5}$.

(a) What is the pH of the solution?

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

$pH = pK_a + \log [CH_3COO^-]/[CH_3COOH]$ $pK_a = 4.74$

$4.74 + \log (0.300)/(0.100)$

$4.74 + 0.48 =$ **5.22**

(b) What is the pH of a solution that results when 3.00 mL of 0.034 M HCl is added to 0.2000 L of the original buffer?

	CH_3COO^-	**+ H^+**	**$\rightarrow CH_3COOH$**
Initial mmol	**20**	**0.102**	**60**
After reaction	**19.898**	**0**	**60.102**

$pH = 4.74 + \log (60.102)/(19.898) = 4.74 + 0.48 = 5.22$

21. Determine the pH at the following points in the titration of 20.0 mL of 0.100 M $HClO_4$, a strong acid with 0.200 M KOH a strong base: 0.00, 5.00, 10.00 and 15.00 mL of base added.

$H^+ + OH^- \rightarrow H_2O$ $V_e = (20.0 \text{ mL} \times 0.100 \text{ M})/0.200 \text{ M} = 10.00 \text{ mL}$

(i) Before addition of base i.e. 0 mL KOH pH of a strong acid

$pH = -\log[H^+] = -\log(0.1) =$ **1.00**

(ii) After 5.00 mL acid is in excess by 1 mmole and $[H^+] = 1.00\text{mmol}/25.00\text{ mL} = 0.04$ M and $pH = -\log 0.04 =$ **1.40**

(iii) At $V_e = 10.00$ mL all H^+ and OH^- ions are consumed but will be in equal concentration from self ionization of water $x^2 = K_w$ and $x = [H^+]$ = SQR(1.00 x 10^{-14}) = 1.00 x 10^{-7} M **pH = 7.00**

(iv) After adding 15.00 mL of KOH, base is in excess by 1.00 mmol and $[OH^-]$ = 1.00 mmol/35.00 mL = 0.0286 M and pOH = 1.54 i.e. pH = 14.00 – 1.54 = **12.46**

SOLUBILITY EQUILIBRIUM

1. Given the solubility product of calcium sulphate, $CaSO_4$ at 25 °C is

2.4 x 10^{-5} $mol^2 dm^{-6}$, calculate the solubility at this temperature.

Reaction equation for dissociation is

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

x x

$$Ksp = [Ca^{2+}][SO_4^{2-}] = x^2$$

$$2.4 \times 10^{-5} = x^2$$

$$x = 0.004899 = 0.049\ moldm^{-3}$$

2. If the solubility of lead fluoride, PbF_2, is 0.64 g dm^{-3}, what is the value of solubility product?

Reaction equation for dissociation is

$$PbF_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2F^-{}_{(aq)}$$

x 2x

$$\text{Molar solubility} = 0.64\ g\ dm^{-3}/\{207.2+2(19.00)\}g\ mol^{-1}$$

$$= 0.0026\ mol\ dm^{-3}$$

$$Ksp = [Pb^{2+}][F^-]^2 = 4x^3 = 4(0.0026)^3 = 7.0 \times 10^{-8}\ (moldm^{-3})^3$$

3. Calculate the solubility of MnS in

(a) water

Reaction equation for dissociation is

$\mathbf{MnS_{(s)} \rightleftharpoons Mn^{2+}_{(aq)} + S^{2-}_{(aq)}}$

x x

$\mathbf{Ksp = [Mn^{2+}][S^{2-}] = x^2}$

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

$\mathbf{x = 5.0 \times 10^{-7}\ moldm^{-3}}$

(b) in a 1.0 x 10^{-2} mol dm^{-3} solution of sulphide ion.

K_{sp} (MnS) = 2.5 x 10-^{13} mol^2 dm^{-6}.

Reaction equation for dissociation is

$\mathbf{MnS_{(s)} \rightleftharpoons Mn^{2+}_{(aq)} + S^{2-}_{(aq)}}$

x (0.01+ x)

But x is very small as compared to 0.01, therefore (0.01+ x) ≈ 0.001

$\mathbf{Ksp = [Mn^{2+}][S^{2-}] = x(0.01)}$

$\mathbf{2.5 \times 10^{-13} = x\ (0.01)}$

$\mathbf{x = 2.5 \times 10^{-11}\ mol\ dm^{-3}}$

4. why, when hydrogen sulphide is passed into an acidic solution containing Cu^{2+} ions and Fe^{2+} ions, CuS is precipitated but FeS is not precipitated.

K_{sp} (CuS) = 6 x 10-^{36} mol^2 dm^{-6}. K_{sp} (FeS) = 6 x 10-^{18} mol^2 dm^{-6}.

Hydrogen sulphide ionises as follows

$\mathbf{H_2S_{(s)} \rightleftharpoons 2H^{+}_{(aq)} + S^{2-}_{(aq)}}$ **and hydrochloric acid**

$\mathbf{HCl_{(aq)} \rightleftharpoons H^{+}_{(aq)} + Cl^{-}_{(aq)}}$

Hydrogen sulphide is a weak acid hence dissociates partially, the dissociation of hydrogen sulphide is further suppressed due to common ion (hydrogen ion).

Hence lower sulphide ion concentration.

Precipitation occurs when the product of ionic concentration exceeds solubility product. CuS has lower solubility product as compared to FeS therefore only CuS precipitates.

5. Explain the following observations:

(a) the solubility of $PbCl_2$ in water decreases on the addition of dilute hydrochloric acid and increases on the addition of concentrated hydrochloric acid.

$PbCl_2$ and HCl dissociates in water as follows:

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + Cl^-_{(aq)}$

$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$

In presence of dilute hydrochloric acid due to common ion (Chloride ion) effect equilibrium shifts to left. Or the solubility decreases.

In presence of concentrated hydrochloric acid lead forms a complex ion $[PbCl_4]^{2-}$. Due to complex formation equilibrium shifts to right or solubility increases.

(b) The addition of aqueous ammonia to magnesium sulphate gives a white precipitate which is soluble in aqueous ammonium chloride.

On addition of aqueous ammonia to magnesium sulphate as soon as the ionic product exceeds the solubility product the white precipitate of magnesium hydroxide appears. Dissociation equations are as follows:

$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

$MgSO_{4(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$

On addition of ammonium chloride for reaction equilibrium shifts to left due to common ion effect hence, the ammonium ion concentration decreases. Or the ionic product decreases . The solubility product is greater than ionic product , Hence on addition of ammonium chloride precipitate is soluble.