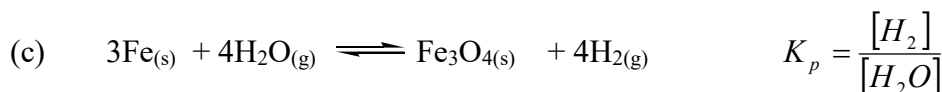
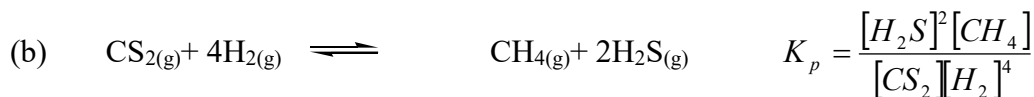
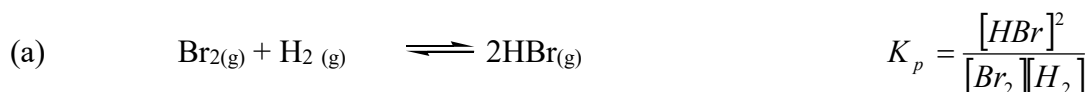


**THE UNIVERSITY OF ZAMBIA**  
**SCHOOL OF NATURAL SCIENCES**  
**DEPARTMENT OF CHEMISTRY**  
**ACADEMIC YEAR 2019/20**  
**TERM 2**  
**CHE1000: INTRODUCTION TO CHEMISTRY**

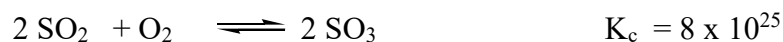
**Solved Examples:**

**EQUILIBRIUM**

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



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



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 of chlorine at 230 °C in an equilibrium mixture. Calculate the equilibrium constant  $K_c$  and  $K_p$  for the reaction.



|                                   |   |
|-----------------------------------|---|
| <b>The reaction is</b>            | $\text{PCl}_{3(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{PCl}_{5(g)}$ |
| <b>Equilibrium concentrations</b> | $\frac{0.0222}{6} \qquad \frac{0.1044}{6} \qquad \frac{0.0189}{6}$          |
|                                   | <b>0.0037      0.0174      0.00315</b>                                      |

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

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

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

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

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

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:



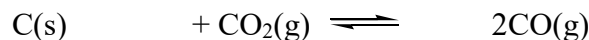
If the NOBr is 9.4% dissociated at this temperature calculate the equilibrium constant.

|                              |                          |                      |   |
|------------------------------|--------------------------|----------------------|---|
|                              | <b>2NOBr</b>             | $\rightleftharpoons$ | <b>2NO + Br<sub>2</sub></b>                   |
| <b>Initial concentration</b> | 2                        |                      | 0    0  |
| <b>Change</b>                | - 2 x 9.4%               |                      | +9.4% +4.7%                                   |
|                              | $2 - (2 \times 9.4/100)$ |                      | $(2 \times 9.4/100) \quad (2 \times 4.7/100)$ |

$$K_c = \frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2}$$

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

5. Consider the equilibrium process :



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  $\text{CO}_2$  and  $\text{CO}$ .

**The equilibrium expression**  $K = \frac{(p_{\text{CO}})^2}{(p_{\text{CO}_2})}$

**Total pressure =  $P_{\text{CO}} + P_{\text{CO}_2} = 4.5 \text{ atm}$**

Let us assume  $P_{CO} = x$

Then,  $P_{CO_2} = (4.5 - x)$  atm

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

$$x^2 + 1.52x - 6.84 = 0$$

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

$$x = 1.96$$

or

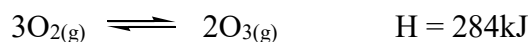
$$x = -3.48$$

Only positive value has significance.

Hence, partial pressures are

$$P_{CO} = 1.96 \text{ and } P_{CO_2} = (4.50 - 1.96) = 2.54 \text{ atm}$$

6. Consider the equilibrium:



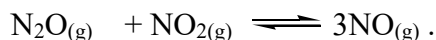
What would be the effect on the position of equilibrium of

- (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<sub>3</sub> is produced. OR Equilibrium shifts to right.**
- (b) adding O<sub>2</sub> 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  $K_c = 1.4 \times 10^{-10}$  for the reaction



If 0.200 mol of  $\text{N}_2\text{O}$  and 0.400 mol of  $\text{NO}_2$  are placed in a 4.00 L container, what would the concentration of  $\text{NO}$  be if this equilibrium were established?

|                                  |                            |   |                    |                      |                    |   |
|----------------------------------|----------------------------|---|--------------------|----------------------|--------------------|---|
| <b>The reaction is</b>           | $\text{N}_2\text{O}_{(g)}$ | + | $\text{NO}_{2(g)}$ | $\rightleftharpoons$ | $3\text{NO}_{(g)}$ | . |
| <b>Initial concentration</b>     | $\frac{0.200}{4}$          |   | $\frac{0.400}{4}$  |                      | <b>0</b>           |   |
|                                  | <b>0.0500</b>              |   | <b>0.100</b>       |                      | <b>0</b>           |   |
| <b>Change</b>                    | <b>- x</b>                 |   | <b>- x</b>         |                      | <b>3x</b>          |   |
| <b>Equilibrium concentration</b> | <b>(0.0500-x)</b>          |   | <b>(0.100-x)</b>   |                      | <b>3x</b>          |   |

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

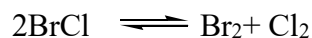
$$9x^3 = 1.4 \times 10^{-10} \times (0.05 - x)(0.1 - x)$$

**Assume x is small as compared to 0.1 and 0.05.**

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

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

8. At 25 °C  $K_c = 0.145$  for the following reaction in the solvent  $\text{CCl}_4$ .



A solution was prepared with the following initial concentrations:

$[\text{BrCl}] = 0.0400 \text{ mol dm}^{-3}$ ,  $[\text{Cl}_2] = 0.0200 \text{ mol dm}^{-3}$ ,  $[\text{Br}_2] = 0.0300 \text{ mol dm}^{-3}$ . What will be their equilibrium concentration?

**From the concentration  $Q = (0.03 \times 0.02) / (0.04)^2 = 0.375$**

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 chlorine and bromine decrease.

|                           |   |            |               |
|---------------------------|---|------------|---------------|
| The reaction is           | $2\text{BrCl} \rightleftharpoons \text{Br}_2$ | +          | $\text{Cl}_2$ |
| 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)    |

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

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

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

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

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

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

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

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

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

$$x = 0.169$$

or

$$x = 0.00523$$

Second value is the correct value. Hence, concentrations are

$$[\text{BrCl}] = 0.04 - (2 \times 0.00523) = 0.05046 \text{ mol dm}^{-3}$$

$$[\text{Cl}_2] = 0.02 - 0.00523 = 0.01477 \text{ mol dm}^{-3}$$

$$[\text{Br}_2] = 0.03 - 0.00523 = 0.02477 \text{ mol dm}^{-3}$$

### ACID BASE EQUILIBRIUM

1. Write equations that show  $\text{HSO}_4^-$  acting as both as acid and a base.

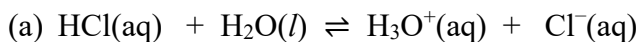


2. What are the conjugate acids and bases of the following?

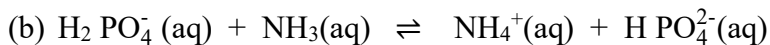


| Species              | Acid                    | Base               |
|----------------------|-------------------------|--------------------|
| $\text{OH}^-$        | $\text{H}_2\text{O}$    | $\text{O}^{2-}$    |
| $\text{H}_2\text{O}$ | $\text{H}_3\text{O}^+$  | $\text{OH}^-$      |
| $\text{HCO}_3^-$     | $\text{H}_2\text{CO}_3$ | $\text{CO}_3^{2-}$ |
| $\text{NH}_3$        | $\text{NH}_4^+$         | $\text{NH}_2^-$    |

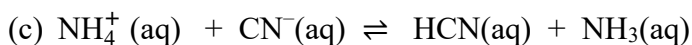
3. Identify and label the Bronsted acid, its conjugate base, the Bronsted base and its conjugate acid in the following equations.



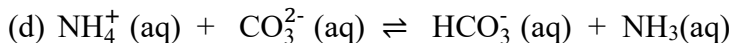
**(acid)          (base)          Conj. A          (conj. B)**



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



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



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

5. What are the concentrations of HCl, H<sub>3</sub>O<sup>+</sup>, and Cl<sup>-</sup>, respectively, in a solution of 0.10 mol dm<sup>-3</sup> HCl?



Because it is a strong acid, therefore completely dissociated.

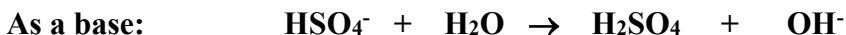
6. What are the major species present in 0.10 mol dm<sup>-3</sup> solutions of each of the acids, HNO<sub>3</sub>, and HNO<sub>2</sub> acids?

**major species in Strong Acid : HNO<sub>3</sub> = H<sub>3</sub>O<sup>+</sup> & NO<sub>3</sub><sup>-</sup>;**

**major species in weak acids HNO<sub>2</sub> = HNO<sub>2</sub>**

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

**Exhibit properties of acids and bases e.g. HSO<sub>4</sub><sup>-</sup>**



8. Given the K<sub>a</sub> values (in parentheses) for the following acids:

HCl (K<sub>a</sub> is very large); HF (K<sub>a</sub> = 7.2 x 10<sup>-4</sup>); HCN (K<sub>a</sub> = 6.2 x 10<sup>-10</sup>); HNO<sub>2</sub> (K<sub>a</sub> = 4.0 x 10<sup>-4</sup>); CH<sub>3</sub>COOH (K<sub>a</sub> = 1.8 x 10<sup>-5</sup>), and C<sub>6</sub>H<sub>5</sub>COOH (K<sub>a</sub> = 6.3 x 10<sup>-5</sup>).

- (a) Rank (or list) these acids in order of decreasing strength (strongest first).

**HCl (K<sub>a</sub> is very large); HF (K<sub>a</sub> = 7.2 x 10<sup>-4</sup>); HNO<sub>2</sub> (K<sub>a</sub> = 4.0 x 10<sup>-4</sup>); C<sub>6</sub>H<sub>5</sub>COOH (K<sub>a</sub> = 6.3 x 10<sup>-5</sup>); CH<sub>3</sub>COOH (K<sub>a</sub> = 1.8 x 10<sup>-5</sup>) and HCN (K<sub>a</sub> = 6.2 x 10<sup>-10</sup>);**

- (b) List their conjugate bases in order of increasing strength (weakest base first) and write the K<sub>b</sub> value for each conjugate bases. (K<sub>w</sub> = 1.0 x 10<sup>-14</sup>)

**Cl<sup>-</sup> (K<sub>b</sub> is very small); F<sup>-</sup> (K<sub>b</sub> = 1.39 x 10<sup>-11</sup>); HNO<sub>2</sub> (K<sub>b</sub> = 2.50 x 10<sup>-11</sup>); C<sub>6</sub>H<sub>5</sub>COOH (K<sub>b</sub> = 1.59 x 10<sup>-10</sup>); CH<sub>3</sub>COOH (K<sub>b</sub> = 5.56 x 10<sup>-10</sup>) and HCN (K<sub>b</sub> = 1.6 x 10<sup>-5</sup>);**

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<sub>a</sub> 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<sub>2</sub>SO<sub>4</sub> is larger than the ionization constant for H<sub>2</sub>SO<sub>3</sub>.

The oxidation state for sulfur (+6) in H<sub>2</sub>SO<sub>4</sub> is greater the oxidation state for sulfur (+4) in H<sub>2</sub>SO<sub>3</sub>. 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<sup>+</sup> release easier.

13. Explain why the ionization constant, K<sub>a</sub>, 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<sub>3</sub>NH<sub>3</sub><sup>+</sup>, the conjugate acid of the weak base CH<sub>3</sub>NH<sub>2</sub>, K<sub>b</sub> = 4.4 x 10<sup>-4</sup>.

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

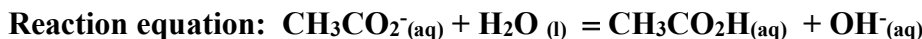
15. The ionization constant for water (K<sub>w</sub>) is 2.9 x 10<sup>-14</sup> at 40 °C. Calculate [H<sub>3</sub>O<sup>+</sup>], [OH<sup>-</sup>], pH and pOH for pure water at 40 °C.

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

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

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

16. Determine K<sub>b</sub> for acetate ion, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> in a 0.10 M solution, the base is 0.0075 % ionized.



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

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

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

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

17. Formic acid, HCO<sub>2</sub>H, 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<sub>a</sub> Formic acid = 1.8 x 10<sup>-4</sup>)



|                    |                  |           |           |
|--------------------|------------------|-----------|-----------|
| <b>Initial mol</b> | <b>0.534</b>     | <b>0</b>  | <b>0</b>  |
| <b>Change</b>      | <b>-x</b>        | <b>+x</b> | <b>+x</b> |
| <b>Equilibrium</b> | <b>0.534 - x</b> | <b>x</b>  | <b>x</b>  |

$$K_a = [\text{H}^+][\text{HCO}_2^-] / [\text{HCO}_2\text{H}]$$

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

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

18. Calculate the concentration of all species and the pH of a solution of a 0.05 M  $\text{CH}_3\text{COONa}$ . ( $K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}$ )

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



|              |            |      |    |    |
|--------------|------------|------|----|----|
| Initial mols | 0.05       | ---- | 0  | 0  |
| Change       | -x         | ---- | +x | +x |
| Equilibrium  | $0.05 - x$ | ---- | x  | x  |

$$K_b = [\text{OH}^-][\text{CH}_3\text{COOH}] / [\text{CH}_3\text{COO}^-]$$

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

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

Solve for  $x = [\text{OH}^-] = 5.27 \times 10^{-6} \text{ M}$  and  $\text{pOH} = 5.28$

$$\text{pH} = 14.00 - 5.28 = 8.72$$

$$[\text{Na}^+] = 0.05 \text{ M}$$

$$[\text{OH}^-] = [\text{CH}_3\text{COO}^-] = 5.27 \times 10^{-6} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.05 - 5.27 \times 10^{-6} \sim 0.05 \text{ M}$$

19. For  $\text{H}_3\text{PO}_4$ ,  $K_{a1} = 7.5 \times 10^{-3}$ ,  $K_{a2} = 6.3 \times 10^{-8}$  and  $K_{a3} = 3.6 \times 10^{-13}$ , calculate the  $[\text{H}^+]$ ,  $[\text{H}_3\text{PO}_4]$ ,  $[\text{H}_2\text{PO}_4^-]$ ,  $[\text{HPO}_4^{2-}]$  and  $[\text{PO}_4^{3-}]$  in a 0.100 M solution of  $\text{H}_3\text{PO}_4$ .

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



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

From the second dissociation



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

From the third ionization



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

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

20. A buffer solution is prepared from equal volumes of 0.200 M acetic acid and 0.600 M sodium acetate.  $K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}$ .

- (a) What is the pH of the solution?



$$\text{pH} = \text{p}K_a + \log [\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] \quad \text{p}K_a = 4.74$$

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

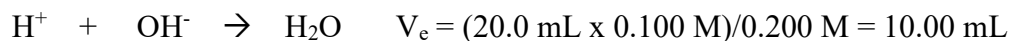
$$4.74 + 0.48 = \mathbf{5.22}$$

- (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?

|                       |                           |     |              |               |                          |
|-----------------------|---------------------------|-----|--------------|---------------|--------------------------|
|                       | $\text{CH}_3\text{COO}^-$ | $+$ | $\text{H}^+$ | $\rightarrow$ | $\text{CH}_3\text{COOH}$ |
| <b>Initial mmol</b>   | <b>20</b>                 |     | <b>0.102</b> |               | <b>60</b>                |
| <b>After reaction</b> | <b>19.898</b>             |     | <b>0</b>     |               | <b>60.102</b>            |

$$\text{pH} = 4.74 + \log (60.102)/(19.898) = 4.74 + 0.48 = \mathbf{5.22}$$

21. Determine the pH at the following points in the titration of 20.0 mL of 0.100 M  $\text{HClO}_4$ , a strong acid with 0.200 M KOH a strong base: 0.00, 5.00, 10.00 and 15.00 mL of base added.



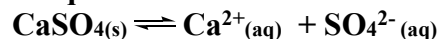
- (i) Before addition of base i.e. 0 mL KOH pH of a strong acid  

$$\text{pH} = -\log[\text{H}^+] = -\log(0.1) = \mathbf{1.00}$$
- (ii) After 5.00 mL acid is in excess by 1 mmole and  $[\text{H}^+] = 1.00\text{mmol}/25.00 \text{ mL} = 0.04 \text{ M}$  and  $\text{pH} = -\log 0.04 = \mathbf{1.40}$
- (iii) At  $V_e = 10.00 \text{ mL}$  all  $\text{H}^+$  and  $\text{OH}^-$  ions are consumed but will be in equal concentration from self ionization of water  $x^2 = K_w$  and  $x = [\text{H}^+] = \text{SQR}(1.00 \times 10^{-14}) = 1.00 \times 10^{-7} \text{ M}$  **pH = 7.00**
- (iv) After adding 15.00 mL of KOH, base is in excess by 1.00 mmol and  $[\text{OH}^-] = 1.00 \text{ mmol}/35.00 \text{ mL} = 0.0286 \text{ M}$  and  $\text{pOH} = 1.54$  i.e.  $\text{pH} = 14.00 - 1.54 = \mathbf{12.46}$

### SOLUBILITY EQUILIBRIUM

1. Given the solubility product of calcium sulphate,  $\text{CaSO}_4$  at  $25^\circ\text{C}$  is  $2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ , calculate the solubility at this temperature.

**Reaction equation for dissociation is**



$$x \qquad \qquad x$$

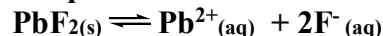
$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = x^2$$

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

$$x = 0.004899 = \mathbf{0.049 \text{ mol dm}^{-3}}$$

2. If the solubility of lead fluoride,  $\text{PbF}_2$ , is  $0.64 \text{ g dm}^{-3}$ , what is the value of solubility product?

**Reaction equation for dissociation is**



$$x \qquad \qquad 2x$$

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

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

$$K_{sp} = [\text{Pb}^{2+}][\text{F}^-]^2 = 4x^3 = 4(0.0026)^3 = \mathbf{7.0 \times 10^{-8} (\text{mol dm}^{-3})^3}$$

3. Calculate the solubility of  $\text{MnS}$  in

- (a) water

**Reaction equation for dissociation is**



$$x \qquad x$$

$$K_{sp} = [\text{Mn}^{2+}][\text{S}^{2-}] = x^2$$

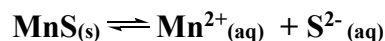
$$2.5 \times 10^{-13} = x^2$$

$$x = 5.0 \times 10^{-7} \text{ mol dm}^{-3}$$

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

$$K_{sp} (\text{MnS}) = 2.5 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}.$$

**Reaction equation for dissociation is**



$$x \qquad (0.01 + x)$$

**But x is very small as compared to 0.01, therefore  $(0.01 + x) \approx 0.01$**

$$K_{sp} = [\text{Mn}^{2+}][\text{S}^{2-}] = x(0.01)$$

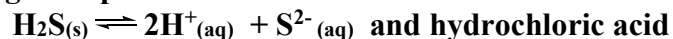
$$2.5 \times 10^{-13} = x(0.01)$$

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

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

$$K_{sp} (\text{CuS}) = 6 \times 10^{-36} \text{ mol}^2 \text{ dm}^{-6}. K_{sp} (\text{FeS}) = 6 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}.$$

**Hydrogen sulphide ionises as follows**



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

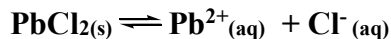
**Hence lower sulphide ion concentration.**

**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  $\text{PbCl}_2$  in water decreases on the addition of dilute hydrochloric acid and increases on the addition of concentrated hydrochloric acid.

**$\text{PbCl}_2$  and  $\text{HCl}$  dissociates in water as follows:**



**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  $[\text{PbCl}_4]^{2-}$ . 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:**



**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.**