

**IONIC EQUILIBRIA**

**ACID-BASE EQUILIBRIA**

**Arrhenius theory of acid and base**

**Acid**

Is a substance which on dissolving in water produces hydrogen ions.

**Base**

- Is a substance which on dissolving in water produces Hydroxyl ions
- Is a substance which combines with an acid to form a salt and water

**Brønsted – Lowry theorem**

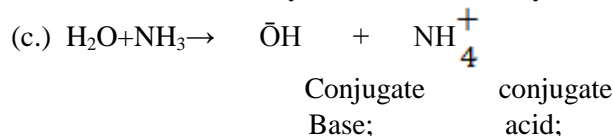
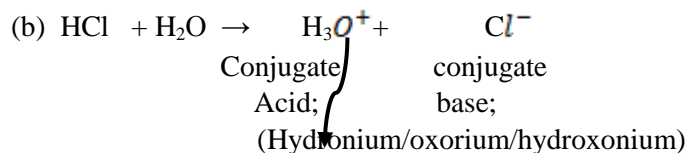
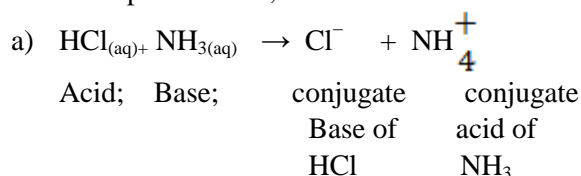
**Acid**

Is a substance which donates a proton (*proton donor*)

**Base**

Is a substance which accepts a proton (*proton acceptor*)

Examples include;



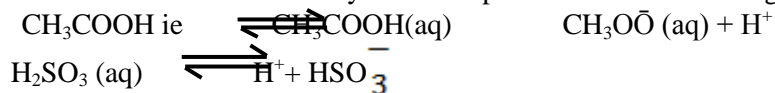
NB

i. **Strong acids**

Are acids which readily donate a proton to another molecule (base) eg H<sub>2</sub>SO<sub>4</sub>, etc ii.

**Weak acids**

Are acids which do not easily lose its proton with difficult eg



iii. **Strong base ;**

A base which has a high affinity for protons eg NaOH

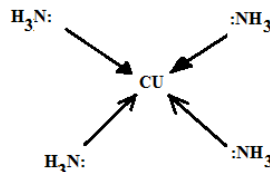
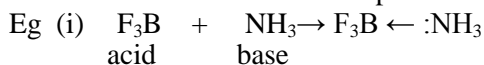
**Lewis acid theory**

**Acid;**

- Is a substance which can accept a pair of electrons.

**Base**

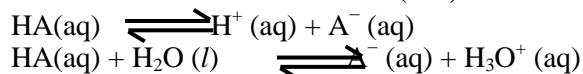
Is a substance which donates a pair of electrons in a dative covalent bond



**IONISATION CONSTANTS OF ACIDS AND BASES**

**a) Ionisation constants of weak acids (Ka)**

Consider a weak monobasic acid(HA) of concentration C which ionizes in solution as follows;

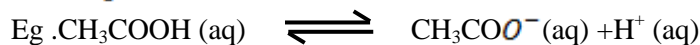


$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}, \text{ but } [\text{HA}] = C$$

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{C} \quad \text{At equilibrium; } [\text{H}^+] = [\text{A}^-]$$

$$K_a = \frac{[\text{H}^+][\text{H}^+]}{C}$$

$$K_a = \frac{[\text{H}^+]^2}{C}$$

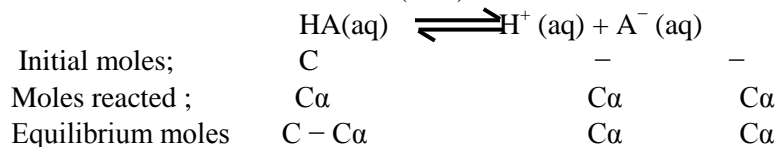


$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{At equilibrium } [\text{H}^+] = [\text{CH}_3\text{COO}^-], \text{ If } [\text{CH}_3\text{COOH}] = C \text{ moldm}^{-3}$$

$$K_a = \frac{[\text{H}^+]^2}{C}$$

**Relationship between Ka and degree of Dissociation, α**

Consider a weak monobasic acid( HA) of concentration C and degree of dissociation, α



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{C\alpha C\alpha}{C - C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

For weak acids, α is small,  $(1 - \alpha) \cong 1$

$$K_a = \frac{C\alpha^2}{(1)} = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

**Example**

1. The acid dissociation constant of a dibasic acid is  $4.39 \times 10^{-5} \text{mol}^2 \text{dm}^{-6}$  at  $25^\circ\text{C}$ , Calculate the degree of ionization of a 0.01M solution of the acid. **UNEB 2010**

**Solution**

For weak acids,  $K_a = \frac{C\alpha^2}{(1-\alpha)}$ , But also for weak acids;  $\alpha \lll 1$ ,

$$(1 - \alpha) \cong 1$$

$$K_a = C\alpha^2$$

$$4.39 \times 10^{-5} = 0.01 \alpha^2$$

$$\alpha = \sqrt{\frac{4.39 \times 10^{-5}}{0.01}}$$

$$\alpha = 0.066$$

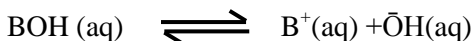
$$\alpha = 6.6\%$$

**Activity**

1. Calculate the degree of dissociation of a 0.01M ethanoic acid if K is  $1.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$  at 298K

**b) Ionisation constant for weak bases;  $K_b$**

Consider a weak base BOH of concentration C which ionizes in solution as follows.



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \quad \text{but } [\text{BOH}] = C \text{ moldm}^{-3}$$

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[C]} \quad \text{At equilibrium; } [\text{B}^+] = [\text{OH}^-];$$

$$K_b = \frac{[\text{OH}^-]^2}{c}$$

**Assumptions**

- ✓ At equilibrium;  $[\text{B}^+] = [\text{OH}^-]$ ;
- ✓ Concentration of unionized base is equal to the original concentration; because proportion of molecules ionized is small.

**Relationship between  $K_b$  and  $\alpha$**

Consider a weak base BOH of concentration C and degree of dissociation,  $\alpha$

	$\text{BOH (aq)} \rightleftharpoons \text{B}^+(\text{aq}) + \text{OH}^-(\text{aq})$		
Initial concentration	C		
Reacted moles	$C\alpha$	$C\alpha$	$C\alpha$
Equilibrium concn	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{C\alpha \cdot C\alpha}{[C - C\alpha]} = \frac{C^2 \alpha^2}{C(1-\alpha)} = \frac{C \alpha^2}{(1-\alpha)}$$

But for weak bases;  $\alpha \ll \ll \ll 1, (1 - \alpha) \cong 1$

$$K_b = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_b}{C}}$$

**Activity**

1. Write;
  - i. An equation for the ionization methylamine in water
  - ii. The expression for the base dissociation constant,  $K_b$  for Methylamine
2. At 25°C Ammonia has a base ionization constant,  $K_b$  of  $1.8 \times 10^{-5} \text{ moldm}^{-3}$ 
  - a) Write an expression for  $K_b$  of Ammonia
  - b) Calculate the concentration of  $\text{OH}^-$  in 0.1M Ammonia solution at 25°C

State any assumptions made (1997 No. 11 Paper 1, part of question)

**IONISATION OF WATER**

Pure water undergoes self-ionization as follows



By law of mass action;

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K_{\text{eq}} [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Since the degree of ionization of water is small;  $[\text{H}_2\text{O}] = \text{constant}$

$K_{eq} \cdot \text{constant} = [H^+][OH^-]$ , but  $K_{eq} \cdot \text{constant} = K_w$  (ionization product of water/ionic product of water)

$$K_w = [H^+][OH^-]$$

But pure water contains equal concentration of  $H^+$  and  $OH^-$  ions ( $1 \times 10^{-7} \text{ mol dm}^{-3}$ )

$$K_w = (1 \times 10^{-7} \text{ mol dm}^{-3})(1 \times 10^{-7} \text{ mol dm}^{-3})$$

$$K_w = (1 \times 10^{-14} \text{ mol dm}^{-6})$$

### pH

Is the negative logarithm to the base 10 of the hydrogen ion concentration of a solution.

$$pH = -\log_{10}[H^+]$$

OR;

is the logarithm to base 10 of the reciprocal of the hydrogen ion concentration of a solution. i.e.  $pH =$

$$\log_{10} \frac{1}{[H^+]}$$

a) **pH of water:**

pure water contains equal concentration of hydroxyl and hydrogen ions ( $1 \times 10^{-7} \text{ mol dm}^{-3}$ );  $pH$

$$= -\log_{10}[H^+] = -\log_{10}[1 \times 10^{-7}]$$

$$pH = 7$$

b) **pH of acids:**

i. **strong acids:**

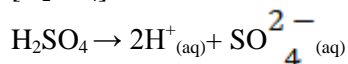
$pH$  of strong acids depends **only on its concentration** because strong acid is fully ionized;

### Examples

1. Calculate the  $pH$  of a  $0.02M H_2SO_4$

#### Solution

$$[H_2SO_4] = 0.02M$$



1 mole of  $H_2SO_4$  form 2 moles of  $H^+$

$0.02$  moles of  $H_2SO_4$  form  $(0.02)$  moles of  $H^+$

$$= 0.04 \text{ mol dm}^{-3}$$

$$\Rightarrow [H^+] = 0.04 \text{ mol dm}^{-3}$$

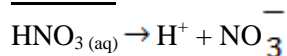
$$pH = -\log [H^+]$$

$$= -\log 0.04$$

$$= \underline{\underline{1.40}}$$

2. Calculate the  $pH$  value of  $2 \times 10^{-3} \text{ mol dm}^{-3}$  of  $HNO_3$

#### Solution



1 mole of  $HNO_{3(aq)}$  produces 1 mole  $H^+$

$$[HNO_3] = [H^+] = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

### ACTIVITY

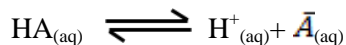
1. Calculate the  $pH$  of the following concentration of the following acids

(a)  $0.05 \text{ mol dm}^{-3} HCl$  (b)  $0.025 \text{ mol dm}^{-3}$  Sulphuric acid

NB: A **strong acid of concentration  $> 1.0 \text{ mol dm}^{-3}$ ;  $pH$  value  $< 0$  eg for  $2M HCl$ ;  $pH = -0.3$ ;**

### ii) pH of weak acids

Consider ionization of weak acid  $HA$  whose concentration is  $C \text{ mol dm}^{-3}$ , and the degree of ionization  $\alpha$



By law of mass action;

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

But at equilibrium;  $[\text{H}^+] = [\text{A}^-]$

$$K_a = \frac{[\text{H}^+]^2}{c}$$

$$[\text{H}^+]^2 = K_a c$$

$$[\text{H}^+] = \sqrt{K_a c} \text{ ----- (i)}$$

$$\text{Also; } \alpha = \sqrt{\frac{K_a}{c}} \text{ ----- (ii)}$$

**Examples**

1. Calculate the  $[\text{H}^+]$  and the pH of a 0.01M solution of ethanoic acid. ( $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ )

**Solution**

Concn of  $\text{CH}_3\text{COOH} = 0.01 \text{ mol dm}^{-3}$ ,  $K_a = 1.8 \times 10^{-5}$

From  $[\text{H}^+] = \sqrt{K_a c}$

$$[\text{H}^+] = \sqrt{1.8 \times 10^{-5} \times 0.01}$$

$$[\text{H}^+] = 4.24 \times 10^{-4} \text{ mol dm}^{-3}$$

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

$$= -\log(4.24 \times 10^{-4})$$

$$\equiv \underline{\underline{3.37}}$$

2. The pH of a 0.001M solution of ethanoic acid is 3.59. Calculate the;
- dissociation constant of the acid.
  - Degree of dissociation at the concentration given.

**Solution**

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

$$3.59 = -\log[\text{H}^+]$$

$$\log[\text{H}^+] = -3.59$$

$$[\text{H}^+] = \log^{-1}(-3.59)$$

$$= 2.57 \times 10^{-4} \text{ mol dm}^{-3}$$

From  $[\text{H}^+] = \sqrt{K_a c}$

$$[\text{H}^+]^2 = K_a c$$

$$K_a = \frac{[\text{H}^+]^2}{c} = \frac{(2.57 \times 10^{-4})^2}{0.001} = \underline{\underline{6.61 \times 10^{-5} \text{ mol dm}^{-3}}}$$

ii.  $\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{6.61 \times 10^{-5}}{0.001}} = \underline{\underline{0.26}}$

**ACTIVITY**

1. A solution of 0.05M propanoic acid had a pH of 4. Calculate its degree of dissociation and hence dissociation constant  $K_a$

c) **pH of bases**

pH of bases can be obtained from the ionization pH of water. ie ;

$$K_w = [H^+][\bar{O}H]$$

Taking  $-\log$  on both sides of the expression

$$-\log K_w = -\log([H^+][\bar{O}H])$$

$$-\log K_w = -\log [H^+] + -\log [\bar{O}H]$$

$$pK_w = pH + pOH$$

$$\text{from } K_w = 1 \times 10^{-14}$$

$$pK_w = -\log [K_w]$$

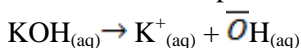
$$pK_w = -\log [1 \times 10^{-14}]$$

$$pK_w = 14$$

**i. pH of strong bases**

Examples

1. Calculate the pH of 0.001M Potassium hydroxide



1 mole of KOH produces 1 mole of  $\bar{O}H$  ions

$$[KOH] = [\bar{O}H] = 0.001 \text{ mol dm}^{-3}$$

$$pOH = -\log(0.001)$$

$$pOH = 3$$

But from  $pK_w = pH + pOH$

$$14 = pH + 3$$

$$pH = 14 - 3 = 11$$

OR:

$$K_w = [\bar{O}H][H^+]$$

$$1 \times 10^{-14} = [\bar{O}H][H^+]$$

$$[H^+] = \frac{1 \times 10^{-14}}{0.001} = \frac{1 \times 10^{-14}}{0.001} = 1 \times 10^{-11}$$

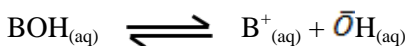
$$pH = -\log [H^+]$$

$$= -\log(1 \times 10^{-11})$$

$$pH = 11$$

**ii. pH of weak bases**

Consider a weak base BOH of concentration  $C \text{ mol dm}^{-3}$  and degree of dissociation,  $\alpha$



By law of mass action,

$$K_b = \frac{[B^+][\bar{O}H]}{[BOH]} = \frac{[B^+][\bar{O}H]}{[C]}$$

At equilibrium,  $[B^+] = [\bar{O}H]$

$$K_b = \frac{[\bar{O}H]^2}{c}$$

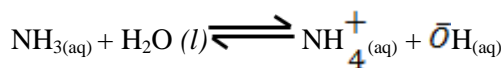
$$[\bar{O}H] = \sqrt{K_b C}$$

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

Example

1. Calculate the pH of 0.1M aqueous ammonia whose  $K_b$  is  $1.5 \times 10^{-6}$ .

Solution



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3(\text{aq})]}, \quad \text{At equilibrium } [\text{OH}^-] = [\text{NH}_4^+(\text{aq})]$$

$$K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3(\text{aq})]}$$

$$1.5 \times 10^{-6} = \frac{[\text{OH}^-]^2}{0.1}$$

$$[\text{OH}^-]^2 = 1.5 \times 10^{-6}$$

$$[\text{OH}^-] = \sqrt{1.5 \times 10^{-6}} = 3.87 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{pOH} &= -\log(3.87 \times 10^{-4}) \\ &= 3.41 \end{aligned}$$

$$\begin{aligned} \text{From pH} &= \text{pK}_w - \text{pOH} \\ &= 14 - 3.41 = \underline{\underline{10.587}} \end{aligned}$$

### ACTIVITY

1. 0.01M solution of phenylamine is 7.5% ionized
  - (a) Write the expression for dissociation of phenylamine
  - (b) Calculate;
    - (i)  $K_b$
    - (ii) pH of the solution

### BUFFER SOLUTION

Buffer solutions are *solutions which resist changes in their pH when small amounts of acid or base is added to them.*

#### Types of buffer solutions

##### (i) acidic buffer

- consists of solution of a weak acid and its salt from a strong base. eg *acetic acid and sodium acetate*, supplying a conjugate base of weak acid.
- Maintain nearly a constant pH value less than 7

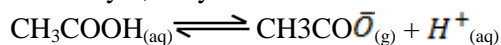
##### (ii) Basic buffer

- Consists of a solution of a weak base and its salt from a strong acid. Eg *ammonium hydroxide and ammonium chloride*, supplying a conjugate acid of weak base.
- Maintain nearly a constant pH value above 7

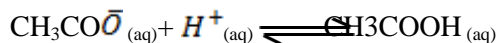
#### a) Action of acidic buffer:

Consider a solution of weak acid(acetic acid) and its highly ionisable salt ( sodium acetate)

- Acetic acid is a weak acid, is not fully ionized while sodium acetate is a strong electrolyte, fully ionized.

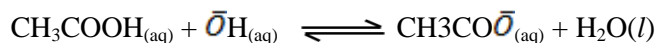


- Solution contains excess of acetate ions and a large amount of unionized acetic acid, and a small amount of hydrogen ions.
- Addition of  $\text{H}^+$  to this solution (inform of acid eg HCl) will combine with the acetate ions forming unionized acetic acid.



♣  $\text{H}^+$  are removed by excess ethanoate ions already present, solution retains its constant pH value.

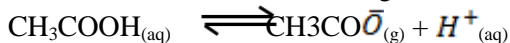
♣ **addition of  $\bar{\text{O}}\text{H}$**  ions to this solution from a base, it will be removed by reacting with the unionized acetic acid.



♣ the solution also maintains its pH value.

### pH calculations of acidic buffers

- Consider a buffer solution consisting of acetic acid and sodium acetate



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

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

### Assumptions:

- $\text{CH}_3\text{COONa}$  is a strong electrolyte; fully ionizes;  $[\text{CH}_3\text{COO}^-] = [\text{salt}]$
- $\text{CH}_3\text{COOH}$  is a weak acid,  $[\text{CH}_3\text{COOH}] = [\text{acid}]$

$$\text{Therefore } [\text{H}^+] = \frac{K_a[\text{acid}]}{[\text{salt}]}$$

Taking  $-\log$  on both sides of the expression;

$$-\log [\text{H}^+] = -\log \frac{K_a[\text{acid}]}{[\text{salt}]}$$

$$-\log [\text{H}^+] = -\log K_a + -\log \frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

“The Henderson – Hassel balch equation”

### Examples

- (a) Calculate the pH of a buffer solution which consists of 4.1g of Sodium ethanoate per litre of solution and 0.01M ethanoic acid whose  $K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$

### solution

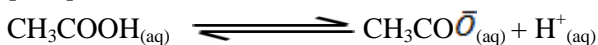
Relative molecular mass of  $\text{CH}_3\text{COONa} = (2 \times 14) + (2 \times 16) + (3 \times 1) + 23 = 82$

1 mole of  $\text{CH}_3\text{COONa}$  weighs 82g

X moles of  $\text{CH}_3\text{COONa}$  weighs 4.1g

$$X = \left(\frac{4.1}{82}\right) = 0.05 \text{ mol dm}^{-3}$$

$[\text{acid}] = 0.01$



From the *Henderson – Hassel balch equation*;

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$



$$\text{pH} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.7 \times 10^{-5}) + \log \frac{[0.05]}{[0.01]}$$

$$\text{pH} = 5.47$$

(b). Calculate the pH change of the solution above if;

(i) 1cm<sup>3</sup> of 1M NaOH is added

(ii) 1cm<sup>3</sup> of 1M HCl is added

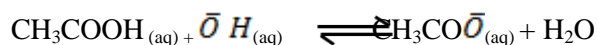
**Solution**

1000cm<sup>3</sup> of NaOH contain 1 mole

1cm<sup>3</sup> of solution contains  $\left(\frac{1}{1000}\right)$  moles of NaOH  
= 0.001 moles of NaOH

[NaOH] = [ $\bar{O}H$ ] = 0.001 moles

*$\bar{O}H$  ions reacts with unionized acetic acid, decreases the concentration of acid, increasing the concentration of salt ( $CH_3CO\bar{O}$ )*



New [salt] = 0.05 + 0.001 = 0.051 mol l<sup>-1</sup>

New [acid] = 0.01 - 0.001 = 0.009 mol l<sup>-1</sup>

$$\text{From pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.7 \times 10^{-5}) + \log \frac{[0.051]}{[0.009]}$$

$$\text{pH} = 4.7696 + 0.753 = \underline{5.523}$$

change in pH = 5.523 - 5.47

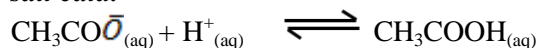
**change in pH = 0.053 units**

(b) 1000cm<sup>3</sup> of HCl contain 1 mole

1cm<sup>3</sup> of HCl contains  $\left(\frac{1}{1000}\right)$  moles

[HCl] = [ $H^+$ ] = 0.001 mol dm<sup>-3</sup>

*$H^+$  ions reacts with acetate ions, decreasing the concentration of salt, increasing the concentration of salt acid.*



New [salt] = 0.05 - 0.001 = 0.049 mol dm<sup>-3</sup>

New [acid] = 0.01 + 0.001 = 0.011 mol dm<sup>-3</sup>

$$\text{From pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.7 \times 10^{-5}) + \log \frac{[0.049]}{[0.011]}$$

$$\text{pH} = 5.418$$

change in pH = 5.418 - 5.47 = **-0.052 units**

2. Calculate the mass of Sodium ethanoate that should be added to 0.1M ethanoic acid at 25°C to give a solution of pH 5.5.

State any assumptions made ( $K_a$  of ethanoic acid =  $1.8 \times 10^{-5}$  mol dm<sup>-3</sup>)

**Solution**

$$\text{From pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$5.5 = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$5.5 = -\log (1.8 \times 10^{-5}) + \log \frac{[\text{salt}]}{[0.1]}$$

$$\log [\text{salt}] = -0.245$$

$$[\text{salt}] = 0.569 \text{ mol l}^{-1}$$

RMM of  $\text{CH}_3\text{COONa} = 82$ .

1 mole of  $\text{CH}_3\text{COONa}$  weighs 82g

0.569 moles of  $\text{CH}_3\text{COONa}$  weigh  $(82 \times 0.569) = 46.62\text{g}$

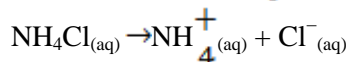
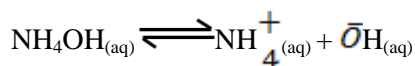
Mass of  $\text{CH}_3\text{COONa} = 46.62\text{g}$

**Activity UNEB 2001(paper 1 no.15, 1999(p1 No. 12), 2007 p1. 13a)**

**(b) Action of basic buffers**

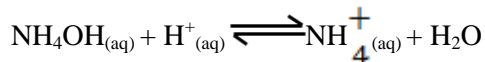
Consider a solution of weak base(ammonium hydroxide) and its highly ionisable salt( Ammonium chloride)

- $\text{NH}_4\text{OH}$  partially ionizes while  $\text{NH}_4\text{Cl}$  fully ionizes both producing  $\text{NH}_4^+$



-Solution contains excess of  $\text{NH}_4^+$ , a large amount of unionized ammonium hydroxide, and a small amount of hydroxyl ions.

-Addition of a small amount of strong acid,  $\text{HCl}$ , hydrogen ions added are removed by ammonium hydroxide;



-Solution suffers no change in pH

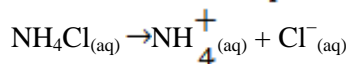
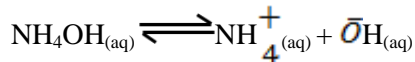
-Addition of a small amount of a base,  $\text{OH}^-$  added are removed by reacting with  $\text{NH}_4^+$  forming unionized ammonium hydroxide/ ammonia and water, thus

-pH remains constant;



**pH calculation of Basic buffers:**

❖ Consider a buffer solution consisting of ammonium hydroxide and ammonium chloride.



By law of mass action; 
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$K_b[\text{NH}_4\text{OH}] = [\text{NH}_4^+][\text{OH}^-]$$

$$[\text{OH}^-] = \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

---

### Assumptions

- i. Concentration unionized  $\text{NH}_4\text{OH}$  is equal to the concentration of base.
- ii.  $\text{NH}_4\text{Cl}$  fully ionizes,  $[\text{NH}_4^+] = [\text{salt}]$

$$\text{Therefore } [\bar{\text{O}}\text{H}] = K_b \frac{[\text{base}]}{[\text{salt}]}$$

$$-\log[\bar{\text{O}}\text{H}] = -\log K_b + -\log \frac{[\text{salt}]}{[\text{acid}]}$$

$$p\text{OH} = pK_b - \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$p\text{OH} = pK_b + \left( \log \frac{[\text{salt}]}{[\text{acid}]} \right)^{-1}$$

$p\text{OH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$

 But  $pK_w = p\text{H} + p\text{OH}$

$p\text{H} = pK_w - pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$

### Examples

1. A solution consists of 0.01M ammonia solution and 2.13g of ammonium chloride in a litre of solution ( $K_b$  for  $\text{NH}_4\text{OH} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ )
  - a) Calculate the pH of the solution
  - b) pH change of solution on addition of  $1\text{cm}^3$  of 1M HCl

#### Solution

Relative molecular mass of  $\text{NH}_4\text{Cl} = 53.5$

1 mole of  $\text{NH}_4\text{Cl}$  weighs 53.5g

X mole of  $\text{NH}_4\text{Cl}$  will weigh 2.13g

$$X = [\text{NH}_4\text{Cl}] = \frac{2.13}{53.5} = 0.0398 \text{ mol l}^{-1}$$

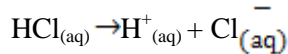
$$\text{From } p\text{OH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} = -\log(1.8 \times 10^{-5}) + \log \frac{0.0398}{0.01} = 5.345$$

$$pK_w = p\text{H} + p\text{OH} \quad , \quad p\text{H} = pK_w - p\text{OH} = 14 - 5.345 = \mathbf{8.655}$$

b) moles of HCl

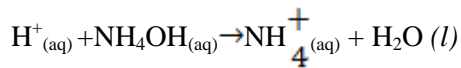
$1000\text{cm}^3$  of solution contains 1 mole of HCl

$1\text{cm}^3$  of solution contains  $\left(\frac{1}{1000}\right)$  moles



1 mole of acid produces 1 mole of  $\text{H}^+_{(\text{aq})}$

Concentration of  $\text{H}^+ = 0.001$  moles



$$\text{New } [\text{salt}] = 0.0398 + 0.001 = 0.0408 \text{ mol l}^{-1}$$

$$\text{New [Base]} = 0.01 - 0.001 = 0.009 \text{ mol l}^{-1}$$

$$\text{pOH} = -\log(1.8 \times 10^{-5}) + \log \frac{0.0408}{0.009}$$

$$\text{pOH} = 5.401$$

$$\text{pH} = 14 - 5.401 = \mathbf{8.59885}$$

$$\text{pH change} = 8.655 - 8.59855$$

**pH change = 0.056 units**

2. calculate the pH of the solution which was made by adding  $30\text{cm}^3$  of 0.1M HCl to  $80\text{cm}^3$  of 0.1M ammonia solution ( $K_b = 1.8 \times 10^{-5} \text{ mol l}^{-1}$ )

**Solution**

**Moles of acid**

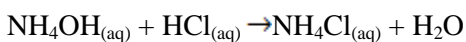
$1000\text{cm}^3$  of solution contains 0.1 moles of acid

$$30\text{cm}^3 \text{ of solution contains } \left( \frac{0.1}{1000} \times 30 \right) \\ = \mathbf{0.003 \text{ moles}}$$

**Moles of  $\text{NH}_4\text{OH}$**

$1000\text{cm}^3$  of solution contains 0.1 moles of base

$$80\text{cm}^3 \text{ of solution contains } \left( \frac{0.1}{1000} \times 80 \right) \\ = \mathbf{0.008 \text{ moles}}$$



Moles of acid that reacted = 0.003 = [salt]

Moles of base that reacted = 0.003

Moles of excess base =  $0.008 - 0.003$

$$= \mathbf{0.005 \text{ moles}}$$

**Excess  $\text{NH}_4\text{OH}$  and salt formed ( $\text{NH}_4\text{Cl}$ ) forms a basic buffer:**

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pOH} = -\log(1.8 \times 10^{-5}) + \log \left( \frac{0.003}{0.005} \right)$$

$$\text{pOH} = \mathbf{4.523}$$

$$\text{pK}_w = \text{pH} + \text{pOH}$$

$$\text{pH} = 14 - 4.523$$

$$\mathbf{\text{pH} = 9.477}$$

**Activity**

- 0.01M ammonia solution was 4.5% ionized when dissolved in water
  - Write the expression for the ionization of ammonia in water
  - Calculate the base dissociation constant,  $K_b$
  - Calculate the concentration of ammonium chloride in grams per litre that must be added to the solution in (a) to give a pH of 8.83.

2. **UNEB 2012 (2) NO. 3C**

**APPLICATIONS OF BUFFER SOLUTIONS:**

- ✓ Controlling the pH of the reactions in industrial processes eg in fermentation process.
- ✓ electroplating metals
- ✓ Maintaining the pH of blood plasma constant i.e. 7.4 eg carbonic acid and its conjugate base  $\text{HCO}_3^-$
- ✓ Used in preparations of standard solutions of definite pH
- ✓ Used in preservation of food.

- ✓ Control pH of shampoos.

### SALT HYDROLYSIS

Is a process whereby a salt dissolved in water produces cations and anions which interact with water producing more  $H^+$  and  $\bar{O}H$  ions so that pH of the resultant solution is either greater than or less than 7.

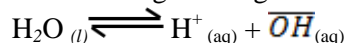
#### (a) Hydrolysis of salt of strong base and weak acid.

These salts include;

- Sodium acetate ( $CH_3COONa$ ), Sodium carbonate ( $Na_2CO_3$ ), Sodium cyanide ( $NaCN$ )

When Sodium acetate is dissolved in water;

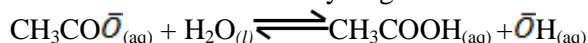
- ✓ Salt being a strong electrolyte; is highly dissociated and water is slightly dissociated.



Unionized  
water



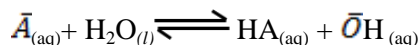
- ✓ Acetate ions react with hydrogen ions from water resulting in the excess of hydroxyl ions



- ✓ More water molecules ionize to restore water equilibrium producing more hydroxyl ions in excess; solution will have pH greater than 7;

#### a) Hydrolysis constant $K_h$ for a salt of a weak acid

Consider salt BA formed from combination of a weak acid HA and a strong base, BOH



By law of mass action;  $K_h = \frac{[HA][\bar{O}H]}{[\bar{A}]}$ ----- (i) (*Assumption  $H_2O$  is large in excess*)

At equilibrium  $[HA] = [\bar{O}H]$

$$K_h = \frac{[OH]^2}{[A^-]}$$

Since  $[A^-] = [\text{salt}]$

$$K_h = \frac{[OH]^2}{[\text{salt}]}$$

### Relationship between $K_h$ , $K_a$ , $K_w$

Multiplying the denominator and numerator of the expression (i) by the concentration of hydrogen ions;

$$K_h = \frac{[HA][\bar{O}H]}{[\bar{A}]} \times \frac{[H^+]}{[H^+]}$$

$$K_h = \frac{[HA]}{[\bar{A}][H^+]} \cdot [\bar{O}H][H^+]$$

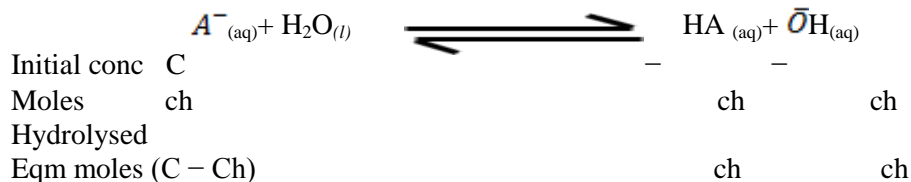
But  $[\bar{O}H][H^+] = K_w$  and  $K_a = \frac{[HA]}{[\bar{A}][H^+]}$

$$K_h = \frac{1}{K_a} K_w$$

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

### Degree of hydrolysis of a salt of weak acid and strong base:

-Is the fraction of the total salt that undergoes hydrolysis when equilibrium has been established;  
Consider a salt of initial concentration,  $C \text{ moldm}^{-3}$ , degree of hydrolysis, h



By law of mass action:  $K_h = \frac{[HA][\bar{O}H]}{[A]}$

At equilibrium  $[\bar{O}H] = [HA]$

$$K_h = \frac{[\bar{O}H]^2}{[A]} = \frac{ch \cdot ch}{C - ch} = \frac{C^2 c^2}{C(1-h)}$$

$$K_h = \frac{C h^2}{(1-h)}; \text{ For dilute solution, } h \text{ is very small, } 1 - h \cong 1$$

$$h = \sqrt{\frac{K_h}{C}} \text{ **Examples**}$$

1. Calculate the degree of hydrolysis of 0.1M solution of potassium cyanide. (dissociation constant of hydrogen cyanide at 25°C is  $7.2 \times 10^{-10} \text{ moldm}^{-3}$ )

**Solution**

$$\text{From } K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{7.2 \times 10^{-10}}$$

$$= \underline{\underline{1.388889 \times 10^{-5} \text{ moldm}^{-3}}}$$

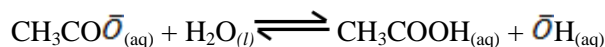
$$\text{But } h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{1.388889 \times 10^{-5}}{0.1}}$$

$$\underline{\underline{h = 0.012 = 1.2\%}}$$

2. Calculate the pH of solution of sodium ethanoate made by dissolving  $8.4 \text{ gdm}^{-3}$  in water ( $K_h = 5.5 \times 10^{-10} \text{ moldm}^{-3}$ )

**Solution**



$$K_h = \frac{[CH_3COOH][\bar{O}H]}{[CH_3CO\bar{O}]}$$

But at equilibrium  $[CH_3COOH] = [\bar{O}H]$

$$K_h = \frac{[\bar{O}H]^2}{[CH_3CO\bar{O}]} \text{-----(i)}$$

RFM of  $CH_3COONa = 82$

1 mole of  $CH_3COONa$  weighs 82g

X mole of  $CH_3COONa$  weighs 8.4g

$$X = \frac{8.4}{82} = 0.1024 \text{ moldm}^{-3}$$

From (i)  $[\bar{O}H]^2 = 0.1024 \times 5.5 \times 10^{-10}$

$$[\bar{O}H] = 7.5 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{pOH} &= -\log [\bar{O}H] \\ &= -\log(7.5 \times 10^{-6}) \\ \text{pOH} &= 5.125 \end{aligned}$$

$$\text{pH} = \text{pK}_w - \text{pOH}$$

$$\text{pH} = 14 - 5.125$$

$$\text{pH} = 8.875$$

### ACTIVITY

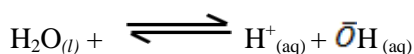
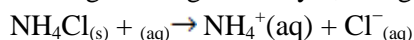
1. When a certain mass of sodium propanoate was dissolved in 1 litre of water, 10cm<sup>3</sup> of this solution required 7.0cm<sup>3</sup> of 6.0 × 10<sup>-3</sup> M for complete neutralization. Calculate the mass of sodium propanoate dissolved in 1 litre of water ( K<sub>h</sub> = 6.0 × 10<sup>-10</sup> )

2. The pH of a solution formed by dissolving 7.2g of sodium benzoate in 1litre of water is 8.6. Calculate the hydrolysis constant of sodium benzoate

### b) Hydrolysis of a salt from strong acid and weak base eg NH<sub>4</sub>Cl;

When NH<sub>4</sub>Cl is dissolved in water;

-Salt being a strong electrolyte; is highly dissociated; and water partially ionizes.

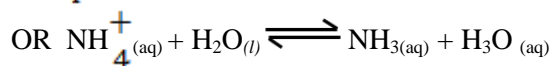
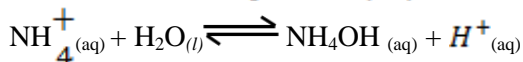
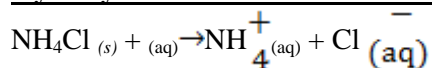


- NH<sub>4</sub><sup>+</sup> reacts with  $\bar{O}H$  ions from ionized water forming unionized NH<sub>4</sub>OH

-concentration of hydroxyl ions is decreased.

-More water molecules ionize producing more hydrogen ions; molar concentration of hydrogen ions exceed the hydroxyl ions , pH becomes less than 7.

### Hydrolysis constant of a salt from a weak base and strong acid



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

At equilibrium [ NH<sub>4</sub>OH ] = [ H<sup>+</sup> ]

$$K_h = \frac{[\text{H}^+]^2}{[\text{NH}_4^+]}$$

$$K_h = \frac{[\text{H}^+]^2}{[\text{salt}]}$$

$$[\text{H}^+] = \sqrt{K_n [\text{salt}]}$$

Degree of hydrolysis:

$$h = \sqrt{\frac{K_h}{c}}$$

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

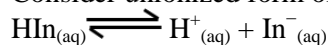
Activity.





**INDICATOR CONSTANT ( $K_{in}$ )**

Consider unionized form of indicator, HIn which is a weak acid



Colour x                      Colour y

By law of mass action;

$$K_{in} = \frac{[H^+][In^-]}{[HIn]}$$

**WORKING RANGES OF INDICATORS**

✓ Is the range of hydrogen ion concentration/pH ; over which different indicators change colour.

From  $K_{in} = \frac{[H^+][In^-]}{[HIn]}$ ,       $[H^+] = \frac{K_{in} [HIn]}{[In^-]}$

Taking negative logarithm on both sides

$$\log[H^+] = -\log K_{in} - \log \frac{HIn}{[In^-]}$$

$$\log[H^+] = -\log K_{in} + \log \frac{In^-}{HIn}$$

$$pH = p^{K_{in}} - \log \frac{HIn}{In^-}$$

$$pH = p^{K_{in}} + \log \frac{In^-}{HIn}$$

Henderson – Hasselbalch equation for Indicators

For colour Y;  $[In^-] = 10[HIn]$

$$\Rightarrow pH = p^{K_{in}} + \log \frac{In^-}{HIn},$$

$$pH = p^{K_{in}} + 1$$

For colour X;  $[HIn] = 10[In^-]$

$$\Rightarrow pH = p^{K_{in}} + \log \frac{In^-}{HIn}$$

$$pH = p^{K_{in}} \pm 1$$

Therefore range of pH over which indicator changes colour is  $pH = p^{K_{in}} \pm 1$ ,

e.g for phenolphthalein,  $P^{K_{in}}$  (9.4), for pink (colour y),  $9.4+1 = 10.4$ ; for colourless (colour x)  $9.4-1=8.4$ , range of **8.3-10.4**.

**Table showing some indicators, their colours and pH ranges**

Indicator	$P^{K_{in}}$	pH range	Colour	
			Acid	Base
Thymol blue	1.51	1.2-2.8	red	yellow
Methyl orange	3.70	3.0-4.5	red	yellow
Methyl red	5.10	4.2-6.3	red	yellow
Phenolphthalein	9.4	8.3-10.0	colourless	pink
Bromo thymol blue	7.0	6.0-7.3	yellow	blue

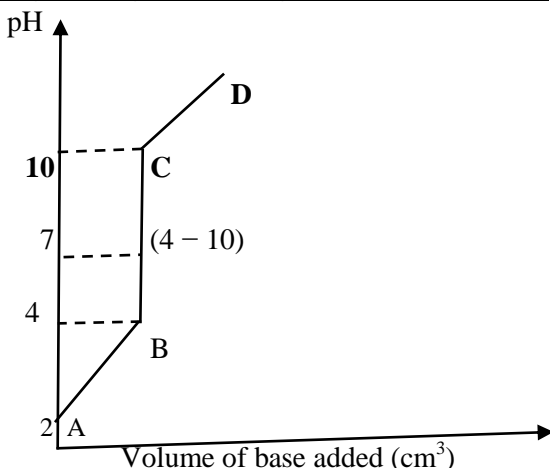
**NB:**

– Universal indicator is a *mixture of indicators which give a gradual change in colour over a wide range of pH.*

**pH CHANGES DURING ACID – BASE TITRATIONS**

❖ Depends on the nature of acid and base used eg;

**Strong base against strong acid (HCl Vs NaOH)**

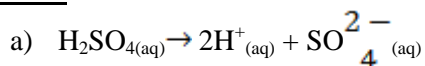


- At A, pH is low, HCl is a strong acid which completely ionizes producing many hydrogen ions.
- AB:
- Slow pH rise, hydrogen ion from acid is removed from hydroxyl ion added.
- BC:
- A sharp rise in pH, (4–10), is due to a small amount of Sodium hydroxide added at the end point; when equivalent amounts of acid and base are added
- pH at end point 7; neutral salt formed is not hydrolysed.
- *Methyl red, phenolphthalein, Bromothymol blue* are the most suitable indicators used.
- CD
- Rise in pH is due to excess NaOH added after the end point

**Example**

1. 20.0cm<sup>3</sup> of a 0.02M sodium hydroxide was added to 30cm<sup>3</sup> of 0.025M sulphuric acid. Calculate the;
  - a) Molar concentration of the hydrogen ions in the initial sulphuric acid.
  - b) Molar concentration of the hydrogen ions in the resultant solution
  - c) pH of the resultant solution (**Uneb 1999 (No 5)**)

**Solution**



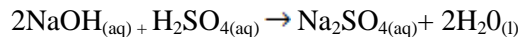
1 mole of H<sub>2</sub>SO<sub>4</sub> produces 2 moles of H<sup>+</sup>  
 0.025moles of H<sub>2</sub>SO<sub>4</sub> produces (2 × 0.025)  
**= 0.05M**

b) Moles of Sulphric acid

1000cm<sup>3</sup> of solution contains 0.025moles of H<sub>2</sub>SO<sub>4</sub>  
 30cm<sup>3</sup> of solution contains  $\left(\frac{0.025 \times 30}{1000}\right)$  moles  
 = 7.5 × 10<sup>-4</sup> moles

Moles of sodium hydroxide

1000cm<sup>3</sup> of solution contains 0.02 moles of NaOH.  
 20.0cm<sup>3</sup> of solution contains  $\left(\frac{0.02 \times 20}{1000}\right)$  moles  
 = 4 × 10<sup>-4</sup> moles



2 moles of NaOH reacts 1 mole of  $\text{H}_2\text{SO}_4$

Moles of  $\text{H}_2\text{SO}_4$  that reacted =  $\frac{1}{2} \times 4.0 \times 10^{-4}$  moles =  $2 \times 10^{-4}$  moles

Moles of unreacted/ excess  $\text{H}_2\text{SO}_4 = 7.5 \times 10^{-4} - 2 \times 10^{-4} = 5.5 \times 10^{-4}$  moles

Total volume of solution =  $(20 + 30) \text{ cm}^3$   
 $= 50.0 \text{ cm}^3$

50  $\text{cm}^3$  of solution that contains  $5.5 \times 10^{-4}$  moles of  $\text{H}_2\text{SO}_4$

1000  $\text{cm}^3$  of solution contains  $\left( \frac{5.5 \times 10^{-4} \times 1000}{50} \right)$  moles

Molar concentration = 0.011M

Molar concentration of  $\text{H}^+ = (2 \times 0.011)\text{M}$   
 $= 0.022\text{M}$

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

$$\text{pH} = -\log(0.022)$$

$$\text{pH} = 1.66$$

2. Calculate the pH obtained by addition of 20  $\text{cm}^3$  of 0.1M NaOH to 40  $\text{cm}^3$  of 0.1M HCl

**Solution**

Moles of Hydrochloric acid;

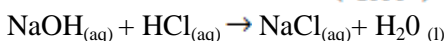
1000  $\text{cm}^3$  of solution contain 0.1 moles of HCl

40  $\text{cm}^3$  of solution contains  $\left( \frac{0.1 \times 40}{1000} \right)$  moles =  $4 \times 10^{-4}$  moles

Moles of sodium hydroxide;

1000  $\text{cm}^3$  of solution contain 0.1 moles of NaOH

20  $\text{cm}^3$  of solution contains  $\left( \frac{0.1 \times 20}{1000} \right)$  moles =  $2 \times 10^{-3}$  moles



From the reaction equation, 1 mole of NaOH reacts with 1 mole of HCl

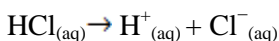
Moles of HCl that reacted = moles of sodium hydroxide,  $2 \times 10^{-3}$  moles

Moles of unreacted/excess HCl =  $(4 \times 10^{-3} - 2 \times 10^{-3}) = 2 \times 10^{-3}$  moles

Total volume of solution =  $(20 + 40) \text{ cm}^3 = 60.0 \text{ cm}^3$

60  $\text{cm}^3$  of solution that contains  $2 \times 10^{-3}$  moles of HCl

1000  $\text{cm}^3$  of solution contains  $\left( \frac{2 \times 10^{-3} \times 1000}{60} \right)$  moles = 0.033M



1 mole of HCl ionizes to produce 1 mole of  $\text{H}^+$

$[\text{H}^+] = 0.033\text{M}$

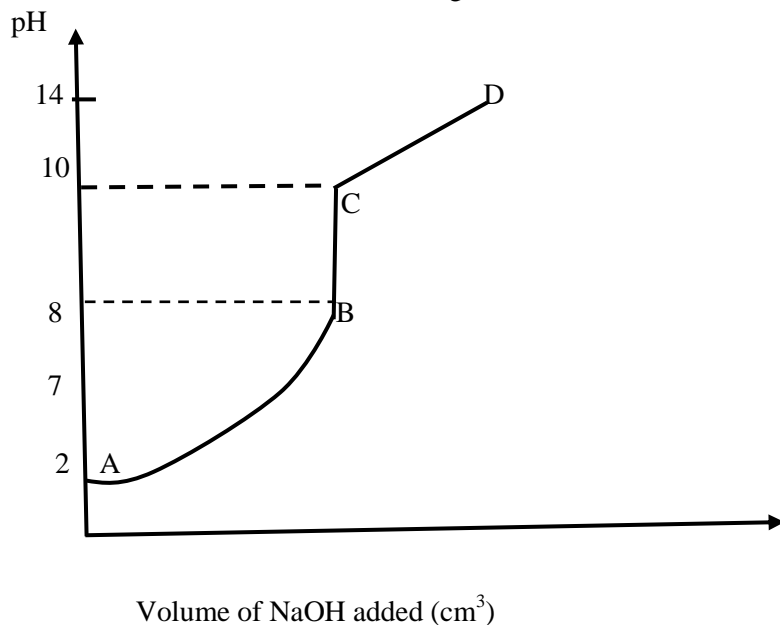
$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(0.033)$$

$$\text{pH} = 1.48$$

**STRONG ALKALI VS WEAK ACID (CH<sub>3</sub>COOH VS NaOH)**

Titration curve of weak acid Vs strong base



- pH of the ethanoic acid is slightly higher compared to that of HCl. Ethanoic acid is a weak acid, only partly ionized in solution producing few hydrogen ions.
- Addition of NaOH,  $\bar{O}H$  from the NaOH reacts with  $H^+$  of the solution, leading to an increase in pH along AB
- pH at endpoint, when equivalent amounts of NaOH and CH<sub>3</sub>COOH are present is greater than 7 ie 9  
**reason**
- NaOH reacts with ethanoic acid to produce sodium ethanoate  
 $CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa(s) + H_2O$
- Salt formed undergoes hydrolysis producing excess  $\bar{O}H$  ions;  
 $CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$   
 $CH_3CO\bar{O}_{(aq)} + H_2O \rightleftharpoons CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$
- Excess  $\bar{O}H$  produced rises the pH along BC from 8 – 10.
- Between CD rise in pH is due to the excess NaOH added
- **Phenolphthalein** is the most suitable indicator.

**Example**

1. Calculate the pH of the solution obtained when 20cm<sup>3</sup> of 0.1M NaOH is added to 10.0cm<sup>3</sup> of 0.1M CH<sub>3</sub>COOH (K<sub>a</sub> = 1.8 × 10<sup>-5</sup>mol dm<sup>-3</sup>)

**Solution**

Moles of ethanoic acid

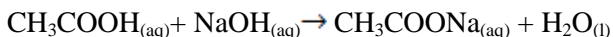
1000cm<sup>3</sup> of solution contains 0.1 mole of CH<sub>3</sub>COOH

100cm<sup>3</sup> of solution will contain  $\left(\frac{0.1 \times 100}{1000}\right)$  moles = 0.01 moles

Moles of NaOH

1000cm<sup>3</sup> of solution contains 0.1 mole of NaOH

20cm<sup>3</sup> of solution will contain **0.002** moles



1 mole of acid reacts 1 mole of NaOH to produce 1 mole of salt

0.002 moles of acid reacts 0.002 moles of NaOH to produce 0.002 moles of salt

Moles of unreacted / excess acid = 0.01 – 0.002 = 0.008moles

Total volume of solution = 100 + 20 = 120cm<sup>3</sup>

120cm<sup>3</sup> of solution contains 0.008 moles

1000cm<sup>3</sup> of solution contains  $\left(\frac{0.008 \times 1000}{120}\right)$  moles

$$= 0.067 \text{ moles l}^{-1}$$

***Salt formed and unreacted acid form a buffer solution;***

$$\text{pH} = \text{pKa} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

[salt] = ?

120cm<sup>3</sup> of CH<sub>3</sub>COONa contains 0.002moles

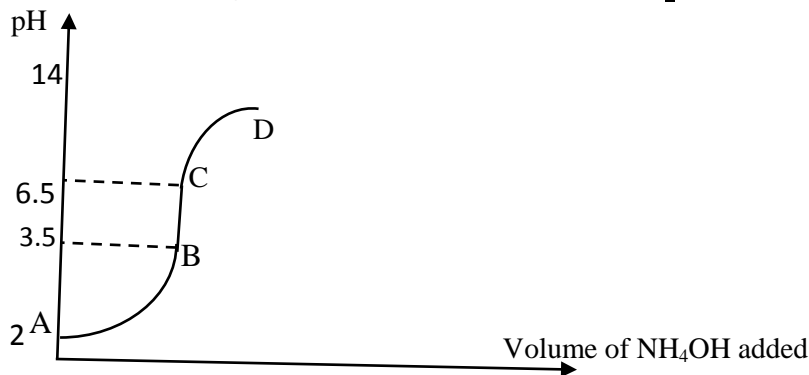
1000cm<sup>3</sup> of CH<sub>3</sub>COONa contains  $\left(\frac{0.002 \times 1000}{120}\right)$  moles = 0.01667M

$$\Rightarrow \text{pH} = -\log(1.8 \times 10^{-5}) + \log \left[ \frac{0.01667}{0.067} \right]$$

$$= 4.14$$

**activity UNEB: 2001 paper 2 (4b)**

**Titration of strong acids and weak base (HCl Vs NH<sub>4</sub>OH)**



A:

Low pH , HCl is a strong acid which fully ionizes in solution; giving a high concentration of hydrogen ions

AB:

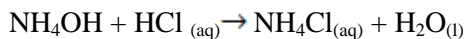
As the NH<sub>4</sub>OH is added;- OH ions from the base reacts with hydrogen ions in solution, pH rises

BC:

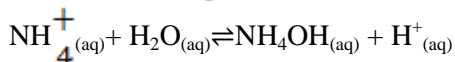
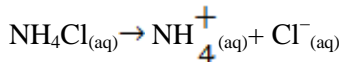
-pH rises from 3.5 to 6.5, ammonium solution reacts with HCl producing ammonium chloride.

-pH at end point is below 7;

**Reason:-**



-Salt formed undergoes hydrolysis in water



-Hydrolysis leaves excess of  $\text{H}^+$  ions; hence pH less than 7

-Further rise in pH along CD is due to excess of  $\text{NH}_4\text{OH}$  is added.

-**Methyl orange** is a suitable indicator.

**Example**

Calculate the pH of a solution when  $100\text{cm}^3$  of  $0.1\text{M}$   $\text{NH}_4\text{OH}$  is added to  $20\text{cm}^3$  of  $0.1\text{M}$   $\text{HCl}$  ( $K_b$  for  $\text{NH}_3 = 2.12 \times 10^{-5}$ )

**Solution**

Moles of  $\text{NH}_4\text{OH}$

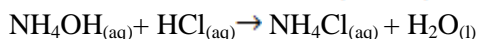
$1000\text{cm}^3$  of solution contains 0.1 moles of  $\text{NaOH}$

$100\text{cm}^3$  of solution contains  $\left(\frac{0.1 \times 100}{1000}\right)$  moles = 0.01 moles

Moles of  $\text{HCl}$

$1000\text{cm}^3$  of solution contains 0.1 moles of  $\text{HCl}$

$20\text{cm}^3$  of solution contains  $\left(\frac{0.1 \times 20}{1000}\right)$  moles =  $2 \times 10^{-3}$



From the equation of reaction above,

Excess moles of base =  $(0.01 - 0.002) = 0.008$  moles

Total volume =  $(100 + 20) = 120\text{cm}^3$

$120\text{cm}^3$  of solution contains **0.008** moles of  $\text{NH}_4\text{OH}$

$1000\text{cm}^3$  of solution contains  $\left(\frac{0.008 \times 1000}{120}\right)$  moles of  $\text{NH}_4\text{OH}$   
= 0.0167M

$$\text{From } p^{\text{OH}} = p^{\text{Kb}} + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\Rightarrow p^{\text{OH}} = -\log(2.12 \times 10^{-5}) + \log \frac{(0.0167)}{(0.0667)}$$

$$p^{\text{OH}} = 4.07$$

$$\Rightarrow \text{from } p^{\text{Kw}} = p^{\text{H}} + p^{\text{OH}}$$

$$p^{\text{H}} = p^{\text{Kw}} - p^{\text{OH}}$$

$$= 14 - 4.07$$

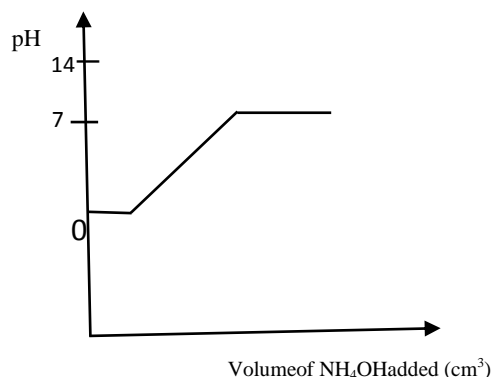
$$p^{\text{H}} = 9.93$$

**Activity . Uneb 2012 (paper 2 , 3b)**

**Titration of weak acids and weak bases eg CH<sub>3</sub>COOH and NH<sub>4</sub>OH**

-p<sup>H</sup> range between 6.5 – 7.5

-no suitable indicator can be used; there is no sharp change in pH at any point

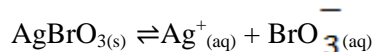


**SOLUBILITY PRODUCT**

Consider a sparingly soluble salt silver bromate, AgBrO<sub>3</sub>

-AgBrO<sub>3</sub> added to water, a saturated solution( containing both the ions & undissolved solute ) is formed

-Equilibrium is established between ions and excess undissolved solute, AgBrO<sub>3</sub>



Excess

undissolved

Solute

By law of mass action, 
$$K_c = \frac{[\text{Ag}^+(aq)][\text{BrO}_3^-(aq)]}{[\text{AgBrO}_3(s)]}$$

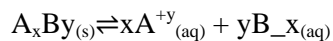
$$K_c [\text{AgBrO}_3] = [\text{Ag}^+][\text{BrO}_3^-]$$

But;  $[\text{AgBrO}_3] = \text{constant}$

$$K_c \times [\text{AgBrO}_3] = K_{sp} \text{ (solubility product)}$$

$$\text{Therefore, } K_{sp} = [\text{Ag}^+(aq)][\text{BrO}_3^-(aq)]$$

Generally for a saturated solution of a sparingly soluble salt



$$K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

**Definition**

-Solubility product (K<sub>sp</sub>) is the *product of the molar concentration of ions raised to their powers of stoichiometric coefficients in a saturated solution of a sparingly soluble salt of an ionic compound of a given temperature;*

**ACTIVITY.**

Write an expression for the solubility product of;

- (i). Bi<sub>2</sub>S<sub>3</sub>    (ii). AgCl    (iii). PbI<sub>2</sub>    (iv). Ca(OH)<sub>2</sub>

**Limitations of solubility product/conditions of solubility product**

- Valid for only saturated solutions
- Only valid at constant temperature
- Only applied for sparingly soluble salts

**Example**

1. The solubility of Calcium hydroxide in water at 20°C is 2.78gdm<sup>-3</sup>. What is the solubility product (Ca = 40, O = 16, H = 1)

**Solution:**

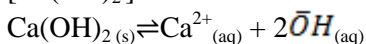
Relative formula mass of Ca(OH)<sub>2</sub> = 40 + (16 × 2) + (1 × 2) = 74

1 mole of Ca(OH)<sub>2</sub> weighs 74g

X mole of Ca(OH)<sub>2</sub> will weigh 2.78

$$\therefore \text{Molarity} = \frac{2.78}{74} = 0.038 \text{dm}^{-3}$$

$$[\text{Ca}(\text{OH})_2] = 0.038 \text{dm}^{-3}$$



$$[\text{Ca}^{2+}] = 0.038 \text{dm}^{-3}$$

$$[\text{OH}^{-}] = 2 \times 0.038 = 0.076 \text{mol dm}^{-3}$$

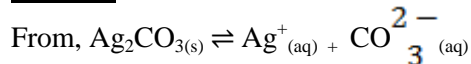
$$K_{sp} = [\text{Ca}^{2+}] [\text{OH}^{-}]^2$$

$$= 0.038 \times (0.076)^2$$

$$K_{sp} = 2.19 \times 10^{-4} \text{mol}^3 \text{dm}^{-9}$$

2. The solubility product of silver Carbonate at 20°C is  $8 \times 10^{-2} \text{mol}^3 \text{dm}^{-9}$ . What is the solubility at this temperature?

**Solution**



If the solubility of Ag<sub>2</sub>CO<sub>3(s)</sub> is S mol dm<sup>-3</sup>

$$[\text{Ag}^{+}] = 2S \text{ mol dm}^{-3}$$

$$[\text{CO}_3^{2-}] = S \text{ mol dm}^{-3}$$

$$K_{sp} = [\text{Ag}^{+}] [\text{CO}_3^{2-}]$$

$$8 \times 10^{-2} = (2S)^2 S$$

$$8 \times 10^{-2} = 4S^3$$

$$\text{Solubility} = 0.27 \text{mol dm}^{-3}$$

**Activity:**

1. Calculate the solubility of silver ethanedioate (Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) in water. (K<sub>sp</sub> of Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> =  $5 \times 10^{-12} \text{mol}^3 \text{dm}^{-9}$ )
2. The solubility of AgCl at 18°C is  $1.46 \times 10^{-3} \text{g dm}^{-3}$ . What is the solubility product (Ag = 108, Cl = 35.5)
3. The solubility product of calcium Phosphate at 25°C is  $6 \times 10^{-29} \text{mol}^5 \text{dm}^{-15}$ . Calculate the solubility of Calcium phosphate in g dm<sup>-3</sup> at 25°C.

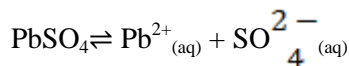
**FACTORS AFFECTING THE SOLUBILITY OF SPARINGLY SOLUBLE SALT.**

**(i) Common ion effect:**

-Is the *precipitation of a sparingly soluble ionic compound from a saturated solution by addition of another soluble compound containing a similar ion*

Consider a saturated solution of PbSO<sub>4</sub>;





Addition of  $\text{Pb}(\text{NO}_3)_2$  solution;

-More  $\text{Pb}^{2+}$  ions, a common ion is produced; increasing the concentration of  $\text{Pb}^{2+}$  in the equilibrium.

-To restore the equilibrium, excess  $\text{Pb}^{2+}$  from  $\text{Pb}(\text{NO}_3)_2$  reacts with  $\text{SO}_4^{2-}$  to precipitate  $\text{PbSO}_4$

-This decreases solubility of  $\text{PbSO}_4$

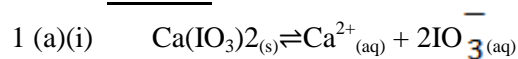
**Example:**

1. Calcium iodate,  $\text{Ca}(\text{IO}_3)_2$  is sparingly soluble in water. Write an,

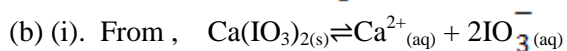
- (a) (i) equation for the solubility of  $\text{Ca}(\text{IO}_3)_2$
- (ii) expression for the solubility product  $K_{\text{sp}}$  of  $\text{Ca}(\text{IO}_3)_2$
- (b) If the  $K_{\text{sp}}$  of  $\text{Ca}(\text{IO}_3)_2$  at  $25^\circ\text{C}$  is  $1.95 \times 10^{-4} \text{ moldm}^{-3}$ . Calculate the solubility in  $\text{moldm}^{-3}$ .  
Calculate the solubility in  $\text{moldm}^{-3}$  at  $25^\circ\text{C}$ .
  - i. In water
  - ii. 0.1M solution of  $\text{NaIO}_3$ .
- (c) Comment on your answer in (b) above

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**Solution**



(ii)  $K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2$



Let the solubility of  $\text{Ca}(\text{IO}_3)_2$  be  $m \text{ moldm}^{-3}$

$$\Rightarrow [\text{Ca}^{2+}] = m \quad [\text{IO}_3^{-}] = 2m$$

From  $K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2$

$$\Rightarrow 1.9 \times 10^{-4} = (m)(2m)^2$$

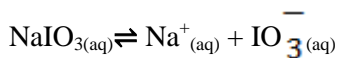
$$4m^3 = 1.9 \times 10^{-4}$$

$$m = \sqrt[3]{\frac{1.9 \times 10^{-4}}{4}}$$

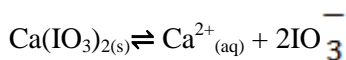
$$= 0.036 \text{ moldm}^{-3}$$

**Solubility of  $\text{Ca}(\text{IO}_3)_2$  is  $0.036 \text{ moldm}^{-3}$  in water**

(ii) 0.1M of  $\text{NaIO}_3$



Let the new solubility of  $\text{Ca}(\text{IO}_3)_2$  in iodate solution be  $S' \text{ moldm}^{-3}$



Solubility of  $\text{Ca}^{2+} = S' \text{ moldm}^{-3}$

Solubility of  $\text{IO}_3^{-} = (2S' + 0.1)$

But  $S' \lllll 0.1$ ,  $(2S' + 0.1) \cong 0.1$

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

$$1.95 \times 10^{-4} = S' (0.1)^2$$

**Solubility of  $\text{Ca}(\text{IO}_3)_2$  in iodate solution  $S' = 0.0195 \text{ mol dm}^{-3}$**

(c.) Comment

– Solubility of  $\text{Ca}(\text{IO}_3)_2$  in  $\text{NaIO}_3$  is lower than that in water; because in  $\text{NaIO}_3$  concentration of  $\text{IO}_3^-$  is higher; therefore  $\text{IO}_3^-$  react with  $\text{Ca}^{2+}$  to precipitate out  $\text{Ca}(\text{IO}_3)_2$ .

**Activities:**

UACE 2000(1) no 12, 2005(1) no 17, 2004(1) no 17, 2003(1) no 17, 2001(1) no 16(a, b(i).

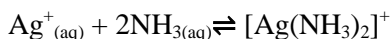
ii) **Complex ion formation:**

**-Increases solubility of a sparingly soluble salt** i.e.

Consider solubility of  $\text{AgCl}$  in water,



– Addition of ammonia solution, ammonia reacts with silver ions, forming diamine silver ion complex .



– Concentration of  $\text{Ag}^+$  decreases;

– to restore equilibrium,  $\text{AgCl}$  solid ionizes to produce more  $\text{Ag}^+$  ions, increasing the solubility.

**Example.**

a) State how the solubility of  $\text{Ag}_2\text{SO}_4$  is affected if the following substances were added;

i)  $\text{Na}_2\text{SO}_4$

ii)  $\text{NH}_4\text{OH}$

b) Explain your answer in (a) (**UACE, 2001(1) no.16 (b)**)

**Solution**

a) (i). solubility would decrease

(ii) Solubility would increase

b) a(i)

–  $\text{Na}_2\text{SO}_4$  is a strong electrolyte; therefore strongly ionizes in aqueous solution to form a higher concentration of  $\text{SO}_4^{2-}$  ions

–  $\text{Ag}^+$  react with excess  $\text{SO}_4^{2-}$  ions ; forming solid silver sulphate,  $\text{Ag}_2\text{SO}_4$ ; hence decreasing solubility.

(ii) Ammonia react with  $\text{Ag}^+$  to form a complex; decreasing the concentration of  $\text{Ag}^+$  in solution; therefore more silver sulphate dissolves to restore the equilibrium, hence increasing solubility of the salt.

**APPLICATION OF COMMON ION EFFECT**

**i. Purification of common salt: (NaCl)**

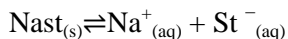
-NaCl contains small quantities of  $MgCl_2$  and  $CaCl_2$  as impurities.

-This causes it to be deliquescent (absorb water from the atmosphere and appear damp)

-Pure NaCl is obtained by *passing HCl gas into a saturated solution of impure NaCl (Addition of HCl gas provides  $Cl^-$  which precipitate only pure NaCl)*

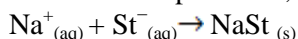
**ii. Salting out of soap:**

Saturated solution of soap, sodium stearate ( $NaSt$ ) contains the following ions;



During saponification (soap making), concentrated solution of NaCl is added

More  $Na^+$  are produced, excess  $Na^+$  react with  $St^-$  to precipitate soap



**APPLICATIONS OF SOLUBILITY PRODUCT ON QUALITATIVE ANALYSIS**

-Used in predicting precipitation of salts eg sulphides, hydroxides, chlorides, etc

**NB: For saturated solution, ionic product is equal to solubility Product; therefore can be used to predict whether or not precipitation occurs.**

Therefore if,

i. Ionic product is greater than the solubility product, solution is **supersaturated**, precipitation will occur

ii. If ionic product is less than the solubility product, solution is **unsaturated**, precipitation will occur not occur.

**Example:**

1. Predict whether or not precipitation occurs when  $0.001 \text{ mol dm}^{-3}$  solution of  $Ca^{2+}$  is mixed with an equal volume of a  $0.001 \text{ mol dm}^{-3}$  solution of  $SO_4^{2-}$  at  $25^\circ\text{C}$ . ( $K_{sp}$  of  $CaSO_4 = 2 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$  at  $25^\circ\text{C}$ ). Show your working.

**Solution**

-Mixing equal volumes of the two ions, molar concentration of the ions are halved, because each solution is diluted by mixing with the other.

$$\text{new}[SO_4^{2-}] = \frac{0.001}{2} = 0.0005 \text{ mol dm}^{-3}$$

$$\text{new}[Ca^{2+}] = \frac{0.001}{2} = 0.0005 \text{ mol dm}^{-3}$$

Ionic product immediately after mixing

$$\text{Ionic product} = [Ca^{2+}][SO_4^{2-}]$$

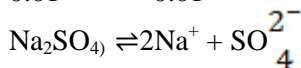
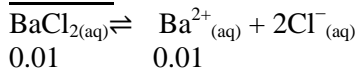
$$= 0.0005 \times 0.0005$$

$$= 2.5 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

Ionic product,  $2.5 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$  is less than the solubility product; no precipitation occurs.

2.  $20 \text{ cm}^3$  of  $0.01 \text{ M}$  Barium chloride solution and  $20 \text{ cm}^3$  of  $0.005 \text{ M}$  solution of Sodium Sulphate are mixed at  $25^\circ\text{C}$ . Determine whether or not precipitation occurs ( $K_{sp}$  of Barium sulphate is  $1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ ).

**Solution**



Mixing 2 equal volumes, the concentration of the ions are halved,

$$[\text{Ba}^{2+}] = \frac{0.01}{2} = 5 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{SO}_4^{2-}] = \frac{0.005}{2} = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Ionic product} &= [\text{Ba}^{2+}] [\text{SO}_4^{2-}] \\ &= (2.5 \times 10^{-3}) (5 \times 10^{-3}) = 1.25 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

Ionic product,  $1.25 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$  is greater than the solubility constant value, there precipitation will occur.

### ACTIVITY

1. A solution containing  $\text{Ag}^+$  was added to a solution containing 0.005M Chromate ions and 0.005M  $\text{Cl}^-$ . State which of the salts,  $\text{AgCl}$  or  $\text{Ag}_2\text{CrO}_4$  was precipitated first. Give a reason for your answer.
2. A solution is 0.01M in cuprous ion, ( $\text{Cu}^+$ ) and 0.001M in lead (II) ion.  $\text{Cl}^-$  is slowly added, will lead (II) Chloride ( $K_{\text{sp}} = 1.6 \times 10^{-5} \text{ mol}^3/\text{l}^3$ ) or  $\text{CuCl}$  ( $K_{\text{sp}} = 3.2 \times 10^{-7} \text{ mol}^3/\text{l}^3$ ) precipitate first? Show your working.

### Experimental determination of solubility product

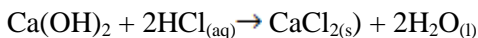
Solubility product can be determined directly by;

- Direct titration or Titrimetric method
- Ion exchange
- Conductivity measurements

#### a) Direct titration

##### i. Ca(OH)<sub>2</sub>

- A Known volume of water is placed in a bottle and a known mass of  $\text{Ca(OH)}_2$  is added to it.
- The bottle is corked, shaken for about 35 minutes, at fixed temperature; allowed to settle for equilibrium to be attained.
- Known volumes of clear solution are then pipetted into a conical flask, titrated with a standard solution of HCl using methyl orange indicator.
- Knowing the number of molecules of HCl, number of moles and concentration of  $\text{OH}^-$  can be calculated.



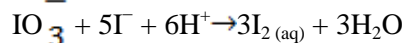
- Concentration of  $\text{Ca}^{2+}$  can be determined from

$$[[\text{Ca}^{2+}] = \frac{1}{2}[\text{OH}^-]] \text{ from mole ratio}$$

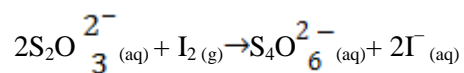
$$\Rightarrow K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

##### ii. Potassium Iodate in water

- A known volume of distilled water is placed in a bottle and a known mass of Potassium iodate is added.
- The bottle is stoppered, shaken for a period of time, at fixed temperature, allowed to settle to reach equilibrium.
- After equilibrium has been attained, known volumes of the clear saturated solution are pipetted into a conical flask containing potassium iodide with dilute  $\text{H}_2\text{SO}_4$



- Iodine liberated is then titrated with standard thiosulphate solution using starch as an indicator



- Titrate until when the solution turns blue, repeat and note the average volume of the thiosulphate solution used.
- Knowing the concentration of the thiosulphate, mole of Iodine liberated can be determined, from which concentration of iodate ions can be obtained.

$$[\text{IO}_3^-] = [\text{K}^+]$$

$$K_{sp} = [\text{IO}_3^-][\text{K}^+]$$