Acids and Bases

CHAPTER 7.0: IONIC EQUILIBRIA

7.1: Acids and bases

Learning outcomes:

At the end of this lesson , students should be able to:

- **Define acid and base according to Arrhenius, Bronsted- Lowry and Lewis theories.**
- **Define and identify conjugate acid and conjugate base according to Bronsted- Lowry theory.**

7.1.1 : Theory of Acids and Bases

Arrhenius Theory

Acid is a substance that dissociates in aqueous solution to produce hydrogen ion (H^+) or hydronium (H_3O^+) ion in aqueous solution.

e.g :

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

(acid)

or

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

(acid)

Base is a substance that dissociates in aqueous solution to produce hydroxide ion (OH^-).

e.g :

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

(base)

Bronsted-Lowry Theory

Acid is a substance that can donate a proton (H^+) to another substance.

Base is a substance that can accept a proton (H^+) from another substance.

e.g : $HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

(acid) (base)

Lewis Theory

Acid is a substance (atom, ion or molecules) that can accept a pair of electrons to form a coordinate covalent bond.

Base is a substance that can donate a pair of electrons to form a coordinate covalent bond.

example :

i. $NH_{3(aq)} + H^{+}_{(aq)} \longrightarrow NH_{4}^{+}{}_{(aq)}$

(base) (acid)

ii. $NH_{3(aq)} + BF_{3(aq)} \longrightarrow H_3N \rightarrow BF_3$

(base) (acid)

iii. $Cu^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+}_{(aq)}$

(acid) (base)

iv. $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$

(acid) (base)

Table 6.1 : Examples of Lewis acids and bases

Lewis acid	Lewis base
(a) Positive ions e.g : H^+ , Fe^{2+} , Al^{3+}	(a) Negative ions e.g : OH^- , CN^- , Cl^-
(b) Molecules with an incomplete octet of electrons. e.g : BF_3 , $BeCl_2$, BCl_3	(b) Molecules with lone pair of electrons. e.g : H_2O , NH_3 , ROH

7.1.2: Conjugate Acid-Base

Conjugate acid - a species formed when a base accepts proton.

Conjugate base – a species formed when an acid donates proton.

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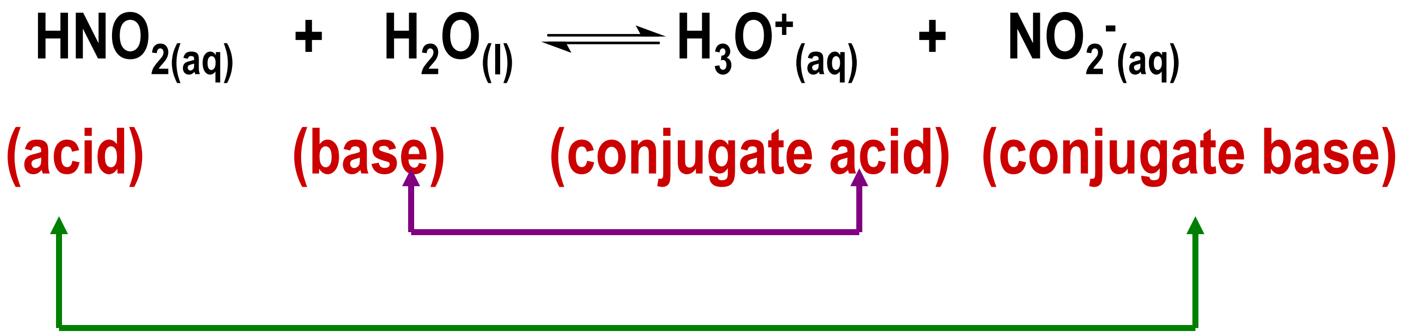
example :



$$HNO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NO_2^-{}_{(aq)}$$

(acid) (base) (conjugate acid) (conjugate base)

Conjugate acid-base pair :

HNO_2 / NO_2^- & H_2O / H_3O^+

Acid conjugate base base conjugate acid

Exercise :

1. Based on Arrhenius theory, identify whether these compounds are base, acid or salt.

   i. $HI_{(aq)}$ ii. $N_2H_{4(aq)}$ iii. $Ca(NO_3)_{2(aq)}$ iv. $Ba(OH)_{2(aq)}$

2. Write the conjugate base for the following acids :

   i. $H_2SO_{4(aq)}$ ii. $HS^-_{(aq)}$ iii. $NH_4^+{}_{(aq)}$ iv. $HClO_{4(aq)}$

3. Write the conjugate acid for the following bases :

i. $NH_{3(aq)}$ ii. $HCO_3^-{}_{(aq)}$ iii. $HPO_4^{2-}{}_{(aq)}$ iv. $CN^-{}_{(aq)}$

4. Identify the conjugate acid-base pairs for the following reaction:

i. $NH_2^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + OH^-{}_{(aq)}$

ii. $NH_4^+{}_{(aq)} + CN^-{}_{(aq)} \rightleftharpoons NH_{3(aq} + HCN_{(aq)}$

iii. $HClO_{4(aq)} + N_2H_{4(aq)} \rightleftharpoons N_2H_5^+{}_{(aq)} + ClO_4^-{}_{(aq)}$

5. **Identify the Lewis acid and Lewis base for the following compounds :**

   i. $AlCl_{3(aq)}$
   ii. $Br^{-}_{(aq)}$
   iii. $NH_{3(aq)}$
   iv. $Fe^{3+}_{(aq)}$
   v. $H_2S_{(aq)}$
   vi. $BCl_{3(aq)}$

Answers :

- Based on Arrhenius theory, these compounds

  i. acid ii. base iii. salt iv. base

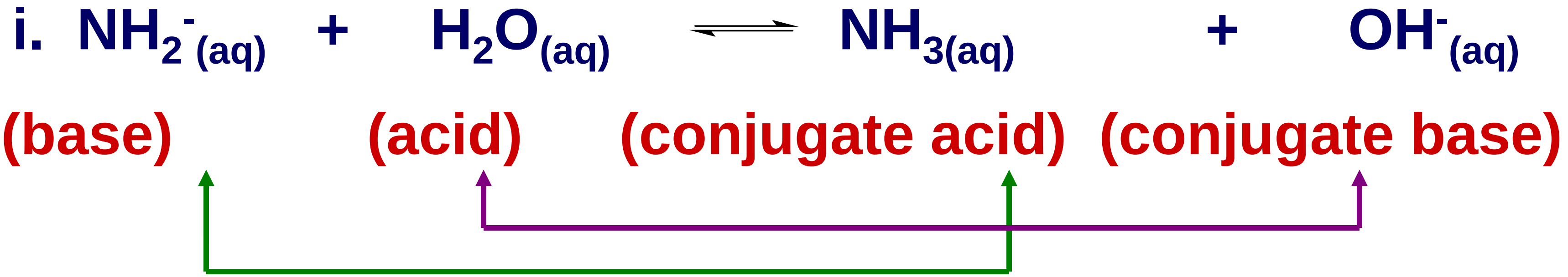
2. The conjugate base is:

   i. $HSO_4^-{}_{(aq)}$ ii. $S^{2-}{}_{(aq)}$ iii. NH_3 iv. ClO_4^-

3. The conjugate acid is:

   i. $NH_4^+{}_{(aq)}$ ii. $H_2CO_3^-{}_{(aq)}$ iii. $H_3PO_{4(aq)}$ iv. $HCN_{(aq)}$

4. The conjugate acid-base pairs for the following reaction:



i. $NH_2^-{}_{(aq)} + H_2O_{(aq)} \rightleftharpoons NH_{3(aq)} + OH^-_{(aq)}$

(base) (acid) (conjugate acid) (conjugate base)

ii. $NH_4^+{}_{(aq)} + CN^-{}_{(aq)} \rightleftharpoons NH_{3(aq} + HCN_{(aq)}$

Acid base c.base c.acid

iii. $HClO_{4(aq)} + N_2H_{4(aq)} \rightleftharpoons N_2H_5^+{}_{(aq)} + ClO_4^-{}_{(aq)}$

Acid base c. acid c. base

5. Identify the Lewis acid and Lewis base for the following compounds :

i. $AlCl_{3(aq)}$ -Lewis acid

ii. $Br^{-}{}_{(aq)}$ -Lewis base

iii. $NH_{3\ (aq)}$ -Lewis base

iv. $Fe^{3+}{}_{(aq)}$ -Lewis acid

v. $H_2S_{(aq)}$ -Lewis base

vi. $BCl_{3(aq)}$ -Lewis acid

At the end of this lesson, students should be able to:

- Define strong acid and base, weak acid and base.
- Define pH and pOH
- Relate pH and pOH to the ionic product of water, K_w at 25^0C

7.1.3: Strong Acid and Strong Base

- **Strong acid** – strong acids dissociate completely in an aqueous solution to produce high concentration of H_3O^+.

  - 100% ionisation or 100% dissociation

  - or α = 1

e.g: $HCl_{(aq)} + H_2O_{(l)} \xrightarrow{\text{100\% ionisation}} H_3O^+_{(aq)} + Cl^-_{(aq)}$

$HNO_{3(aq)} + H_2O_{(l)} \xrightarrow{\text{100\% ionisation}} H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$

- **Strong base** – strong bases dissociate completely in an aqueous solution to produce high concentration of OH^-.

  - 100% ionisation or 100% dissociated

  - or $\alpha=1$

e.g: $NaOH_{(aq)} \xrightarrow{\text{100\% ionisation}} Na^+_{(aq)} + OH^-_{(aq)}$

Weak Acid and Weak Base

- **Weak acid** –weak acids dissociate only slightly in an aqueous solution to produce a low concentration of H_3O^+.

  - % dissociation less than 100% or α<<1.

e.g: $CH_3COOH_{(ak)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

- **Weak base** – weak bases dissociate only slightly in an aqueous solution to produce a low concentration of OH^-.

  - % dissociation less than 100% or α<<1.

e.g: $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

7.1.4: pH and pOH

- The hydrogen ion, H^+ concentration / $[H^+]$ in a solution is measured using pH scale method.

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

- The pH is defined as the negative logarithm (log) of the hydrogen ion, H+ or H_3O^+ concentration.
- If $[H^+]$ ↑ , pH ↓ .

- For base, concentration of OH- is measured using pOH.

$$pOH = -\log [OH^-]$$

- The pOH is defined as the negative logarithm (log) of the hydroxide ion.
- If $[OH^-]$ ↑ , pH ↑.

The Strengths of Acids and Bases

- **The strengths of acids and bases can be compared in terms of**

  i. the degree of dissociation (α)

  ii. the dissociation constant (*K*)

- **Degree of dissociation (α)**

  - ability of acids or bases to ionize or dissociate in aqueous solution.

$$\alpha = \frac{\text{concentration of acid or base dissociated}}{\text{initial concentration of acid or base}}$$

$$\%\ \text{dissociation} = \frac{\text{concentration of acid or base dissociated}}{\text{initial concentration of acid or base}} \times 100\%$$

Notes:

- Strong acid & strong base are strong electrolyte ($\alpha=1$).
- Weak acid & weak base are weak electrolyte ($\alpha<<1$).
- **Electrolyte** – substance that can conduct electricity in the liquid state or aqueous solution.

The Ionization of Water

- **Water ionization equation :**

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

- **Since the degree of dissociation of water is extremely small, $[H_2O]$ is assumed as constant.**

$$K_c\,[H_2O] = [H^+]\,[OH^-]$$

$$Kw = [H^+]\,[OH^-]$$

- **For pure water at 25°C,**

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$$

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$$

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

$$K_w = (1.0 \times 10^{-7}\ M)^2$$

$$= 1.0 \times 10^{-14}\ M^2$$

- Relationship between K_w, pH and pOH at 25°C,

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

$$-\log\,([H^+]\,[OH^-]) = -\log K_w$$

$$-\log\,[H^+] - \log\,[OH^-] = -\log\,(1.0 \times 10^{-14})$$

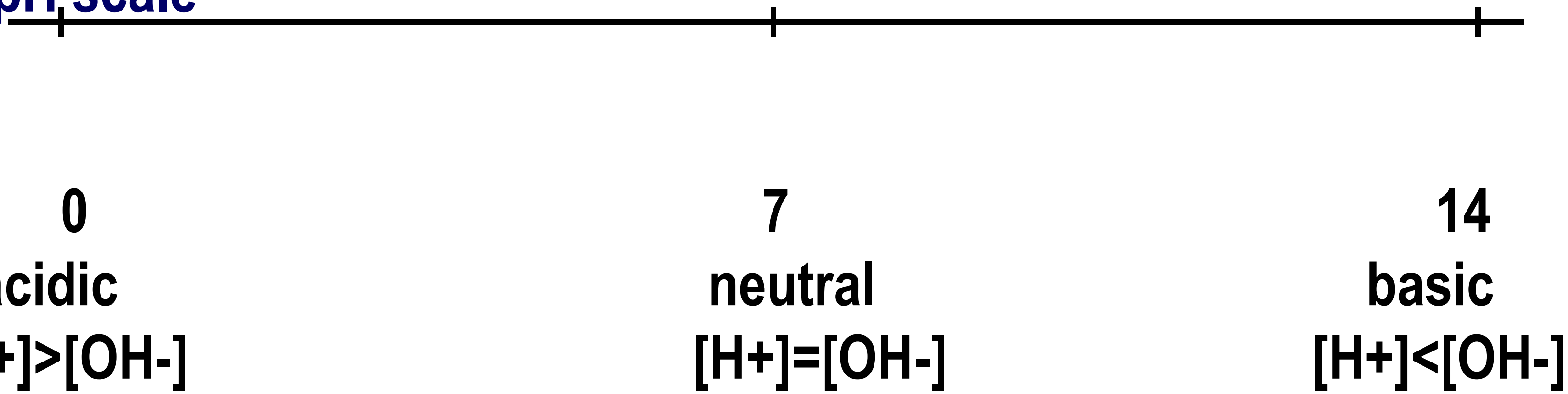
$$pH + pOH = pK_w$$

$$pH + pOH = 14$$

- **If,**

  pH < 7 – solution is acidic
  pH = 7 – solution is neutral
  pH > 7 – solution is basic

- **pH scale**



0	7	14
acidic	neutral	basic
[H+]>[OH-]	[H+]=[OH-]	[H+]<[OH-]

At the end of this lesson, students should be able to:

- Calculate the pH values of a strong acid and base.
- Relate the strength of a weak acid and weak base to the respective dissociation constant, K_a and $K_{b.}$
- Perform colculations involving pH, dissociation constant, initial concentration and the degree of dissociation, α

7.1.5: Calculation of pH values

The following examples illustrate calculations involving pH.

Calculate the concentration of H^+ and determine pH in

i. a solution in which $[OH^-]$ is 2.5×10^{-3} M

ii. a solution in which $[OH^-]$ is 1.8×10^{-9} M

Solution : (Method 1)

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

$= 1.0 \times 10^{-14}\ M^2$

$$[H+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-3}} = 4.0 \times 10^{-12}\ M$$

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

$= -\log (4.0 \times 10^{-12}\ M)$

$= 11.4$

Solution : (Method 2)

$[OH^-] = 2.5 \times 10^{-3}$ M

pOH = - log [OH-]

$= - \log (2.5 \times 10^{-3} \text{ M})$

= 2.6

From equation;

pH + pOH = 14

pH = 14 – pOH

= 14 – 2.6

= 11.4

From equation;

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

$11.4 = - \log [H^+]$

Thus, $[H^+]$ = antilog (-pH)

$= 4.0 \times 10^{-12}$ M

pH Calculation for Strong Acid and Strong Base

- Strong acid and strong base dissociate 100% in aqueous solution.
- Therefore the concentration of H^+ and OH^- ions can be obtained directly from their molarities.

Example 1 :

Calculate the pH of 0.15 mol dm^{-3} of HCl solution.

Solution :

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

$[\ ]_{initial}$	0.15 M	0	0
$[\ ]_{final}$	0	0.15 M	0.15 M

Thus,

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

$= - \log (0.15\ M)$

$= 0.82$

Exercise :

1. What is the pH of a 0.040 M solution of $HClO_4$ · ?
2. What is the pH of 0.05 M NaOH ?
3. An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid ?

(Ans : 1.40 , 12.7 , 0.0046)

Exercise:

1. What is the concentration of a solution of KOH for which the pH is 11.89?
2. What is the pH of a 0.028 M solution of NaOH?

Answers:

(7.8×10^{-3}, 12.45)

7.1.6: pH Calculation for Weak Acid and Weak Base

A. Weak Acid

General equation for dissociation of weak acid :

	HA +	$H_2O \rightleftharpoons$	H_3O^+ +	A^-
$[\ ]_{initial}$	c		0	0
$[\ ]_{change}$	$-x$		$+x$	$+x$
$[\ ]_{equilibrium}$	$c-x$		x	x
	@ $c(1-\alpha)$		$c\alpha$	$c\alpha$

acid-dissociation constant, Ka :

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

$\therefore$

$$= \frac{x^2}{c-x} \; @ \; \frac{c\alpha^2}{1-\alpha}$$

If x << c, c-x ≈ c, therefore pH of weak acid can be determined from $[H_3O^+]$ (that is the value of the x).

Degree of dissociation , $\alpha = \frac{x}{c}$

B. Weak Base

General equation for dissociation of weak base :

$$B \;+\; H_2O \;\rightleftharpoons\; BH^+ \;+\; OH^-$$

$[\;]_{initial}$	c	0	0
$[\;]_{change}$	$-x$	$+x$	$+x$
$[\;]_{equilibrium}$	$c-x$	x	x
	@ $c(1-\alpha)$	$c\alpha$	$c\alpha$

base-dissociation constant, K_b :

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

$$= \frac{x^2}{c-x} \;@\; \frac{c\alpha^2}{1-\alpha}$$

If $x << c$, $c - x \approx c$, therefore pH of weak base can be determined from $[OH^-]$ (that is the value of the x).

$$pOH = -\log [OH^-]$$

$$pH = 14 - pOH$$

Acid-dissociation constant (Ka) and base-dissociation constant (K_b)

- The value of K_a or K_b can be used to distinguish the relative acidity strength of weak acid and weak base.

- Ka ↑ (pK_a ↓) = $[H^+]$ ↑ , thus pH ↓ (more acidic)

- K_b ↑ (pK_b ↓) = $[OH^-]$ ↑ , thus pH ↑ (more basic)

Example :

Acid	pK_a
CH_3COOH	4.74
$HCOOH$	3.76

Relative acidity, $HCOOH > CH_3COOH$

Base	pK_b
$C_6H_5NH_2$	9.37
NH_3	4.74

Relative basicity, $NH_3 > C_6H_5NH_2$

7.1.7: a) Weak acid

Example 1 :

Calculate the pH of a 0.20 M solution of HCN. K_a for HCN is 4.9 x 10^{-10}.

Solution :

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$

$[\ ]_{initial}$	0.20 M	0	0
$[\ ]_{change}$	-x	+x	+x
$[\ ]_{equilibrium}$	0.20-x	x	x

at equilibrium, $K_a = \dfrac{[H_3O^+]\,[CN^-]}{[HCN]}$

$$K_a = \frac{(x)\,(x)}{(0.20 - x)} = 4.9 \times 10^{-10}\ M$$

Assume that the amount of acid dissociated, x is small compared with the initial concentration of acid, c; that is c-x ≈ c, therefore

$$\frac{x^2}{(0.20)} = 4.9 \times 10^{-10}\ M$$

$$x^2 = (4.9 \times 10^{-10}\ M)\ (0.20\ M$$

$$x = 9.9 \times 10^{-6}\ M$$

Therefore,

$$[H^+] = 9.9 \times 10^{-6}\ M$$

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

$$= 5.00$$

Exercise :

1. The K_a for formic acid is 1.8×10^{-4}. What is the pH of a 0.010 M solution of formic acid? (2.87)

2. Calculate the percentage of HF molecules ionized in

   (a) a 0.10 M HF solution and in (7.9 %)

   (b) a 0.010 M HF solution (23 %)

   the K_a of HF is 6.8×10^{-4}

Solution 1:

$$HCHO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+(_{aq}) + CHO_2^-{}_{(aq)}$$

[ ]initial	0.010 M	0	0
[ ]change	-x	+x	+x
[ ]equilibrium	0.010-x	x	x

at equilibrium, $$Ka = \frac{[H^+][CHO_2-]}{[HCHO_2]} = 1.8 \times 10^{-4}$$

$$= \frac{(x)(x)}{0.01-x} = 1.8 \times 10^{-4}$$

Assume that the amount of acid dissociated, x is small compared to the initial concentration of acid, c; that is c-x ≈ c, therefore

$$\frac{(x)(x)}{0.01-x} = 1.8 \times 10^{-4}$$

$$\frac{x^2}{0.01-x} = 1.8 \times 10^{-4}$$

$$x^2 = (1.8 \times 10^{-4})(0.01)$$

$$x = 1.34 \times 10^{-3} = [H^+]$$

Therefore,

$$[H+] = 1.34 \times 10^{-3}\ M$$

$$pH = -\log [H+] = -\log [1.34 \times 10^{-3}]$$

$$= 2.87$$

Solution 2:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

[ ]initial	0.10 M		0	0
[ ]change	-x		+x	+x
[ ]equilibrium	0.10-x		x	x

at equilibrium, $K_a = \frac{[H^+][F^-]}{[HF^-]} = 6.8 \times 10^{-4}$

$$= \frac{(x)(x)}{0.01-x} = 6.8 \times 10^{-4}$$

Use quadratic equation:

$$Ka = \frac{(x)(x)}{0.01-x} = 6.8 \times 10^{-4}$$

$$x^2 = (0.01-x)(6.8 \times 10^{-4})$$

$$x^2 = (6.8 \times 10^{-5}) - (6.8 \times 10^{-4})(x)$$

$$x^2 + (6.8 \times 10^{-4})(x) - (6.8 \times 10^{-5}) = 0$$

Use quadratic equation:

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

$$x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 - 4(6.8 \times 10^{-5})(1)}}{2}$$

$$x = \frac{-6.8 \times 10^{-4} \pm 1.6 \times 10^{-2}}{2}$$

$x = [H^+] = [F^-]$

$= 7.9 \times 10^{-3}$ M

$$\text{Percent ionization of HF} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$

$$= \frac{7.9 \times 10^{-3}\ \text{M}}{0.10\ \text{M}} \times 100\%$$

$= 7.9\%$

solving x by quadratic equation:

$$\frac{x^2}{0.010 - x} = 6.8 \times 10^{-4}$$

$x = [H^+] = [F^-]$

$x = 2.3 \times 10^{-3}$ M

$$= \frac{0.0023}{0.010} \times 100\%$$

$= 23\%$

B.Weak Base

Example 1 :

The base-dissociation constant for ammonia, $NH_{3(aq)}$ is 1.8 x 10^{-5} M. Calculate the concentration of OH^- ion, pH and % dissociation at equilibrium if the initial concentration of NH_3 is 0.15 M.

Solution :

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$[\ ]_{initial}$	0.15 M	0	0
$[\ ]_{change}$	-x	+x	+x
$[\ ]_{equilibrium}$	0.15-x	x	x

at equilibrium, $$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

$$K_b = \frac{(x)\,(x)}{(0.15 - x)} = 1.8 \times 10^{-5}\ \text{M}$$

Assume that x is too small compared to the initial concentration of base, c; that is $c - x \approx c$, therefore

$$\frac{x^2}{(0.15)} = 1.8 \times 10^{-5}\ \text{M}$$

$$x^2 = (1.8 \times 10^{-5}\ \text{M})\ (0.15\ \text{M})$$

$$x = 1.64 \times 10^{-3}\ \text{M}$$

Therefore,

i. $[OH^-] = 1.64 \times 10^{-3}$ M

$$pOH = -\log\,[OH^-]$$

$$= 2.79$$

pH + pOH = 14

pH = 14 – 2.79

= 11. 21

ii. % dissociation = $\frac{1.64 \times 10^{-3}}{0.15} \times 100$

= 1.09 %

≈ 1.1 %

Degree of dissociation (α) = 0.011

Exercise :

1. A 0.20 M solution of weak acid HX is 9.4% dissociated. Using this information, calculate H_3O^+ , X^- and HX concentrations at equilibrium. Determine also pH and Ka for HX acid.

(1.88 x 10-2 M, 0.1812 M, 0.742, 1.86 x 10-3)

2. Calculate the fprmate ion concentration and pH of a solution that is 0.050 M in formic acid.($HCHO_2$: $K_a = 1.8 \times 10^{-4}$).

($CHO_2 = 9.0 \times 10^{-5}$, pH = 1.00)

At the end of this lesson, students should be able to:

- Explain salt hydrolysis and write hydrolysis equation for the salt formed from the reaction between:

  i. Strong acid and strong base
  ii. Strong acid and weak base
  iii. Weak acid and strong base

- Classify the salts as neutral, acidic or basic.

7.1.8 : Salt Hydrolysis

Salt hydrolysis is the reaction of an anion (-ve ion) or a kation (+ve ion) of a salt (or both) with water.

General equation of neutralization :

$$\underset{\text{(acid)}}{HX} + \underset{\text{(base)}}{MOH} \rightleftharpoons \underset{\text{(salt)}}{MX} + \underset{\text{(water)}}{H_2O}$$

MX salt dissociation equation:

$$MX \rightleftharpoons M^+ + X^-$$

Cation Hydrolysis : $M^+_{(aq)} + H_2O_{(c)} \rightleftharpoons MOH_{(aq)} + H^+_{(aq)}$

Anion Hydrolysis : $X^-_{(aq)} + H_2O_{(c)} \rightleftharpoons HX_{(aq)} + OH^-_{(aq)}$

(i) Salt formed from a Strong Acid and Strong Base

1. An example is NaCl, which is formed from hydrochloric acid (a strong acid) and sodium hydroxide (a strong base). In water NaCl dissociates completely into Na^+ and Cl^-:

   $NaCl\ (aq) \longrightarrow Na+\ (aq) + Cl\text{-}(aq)$

2. Both the Na^+ and Cl^- ions are not hydrolysed by water. There is no production of extra H^+ ions or OH^- ions.Hence solution is neutral.

(ii) Salt formed from a Strong Acid and Weak Base

1. An example is NH4Cl ,which is formed from hydrochloric acid (a strong acid) and ammonia (a weak base)

$$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$$

2. Ammonium chloride dissociates completely into ammonium ions and chloride ions:

$$NH_4Cl_{(s)} + aq \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

3. The NH^+_4 , acts as Bronsted-Lowry acid and donates a proton to water.On the other hand Cl- ion does not react with water.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$$

$$Cl^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + OH^-$$ (this reaction does not take place)

4. The production of $H_3O^+{}_{(aq)}$ ions from the hydrolysis of the $NH_4^+{}_{(aq)}$ ions causes the solution to be acidic. This is also known as cationic hydrolysis.

(iii) Salt formed from a Weak Acid and Strong Base

1. An example is Na_2CO_3, which is formed from carbonic acid (a weak acid) and sodium hydroxide NaOH (a strong base).
2. Sodium carbonate dissociates completely into sodium ions and carbonate ions.

$$Na_2CO_3 \longrightarrow CO_3^{2-}{}_{(aq)} + 2Na^{+}{}_{(aq)}$$

3. Carbonate ion acts as Bronsted-Lowry base by accepting a proton from water:

$$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^{-}{}_{(aq})\ +\ OH^{-}{}_{(aq)}$$

$$Na^{+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NaOH_{(aq)} + H^{+}$$ (this reaction does not take place)

4. Na^+ ion does not react with water, because the NaOH formed, dissociate completely to Na^+ and OH^-. The production of OH^- from the hydrolysis of CO_3^{2-} ions causes the solution to be basic. This is also known as anionic hydrolysis.

7.1.9: Types of Salt

i. **Neutral salt** - salt from strong acid-strong base.

- cation of a strong base and anion strong acid do not hydrolyze.

- e.g: NaCl

ii. **Acidic salt** - salt from strong acid-weak base.

- cation hydrolyzes as an acid.

- e.g: NH_4Cl

iii. **Basic salt** - salt from weak acid-strong base

- anion hydrolyzes as a base.

- e.g: CH_3COONa

(i) Hydrolysis Salts of Strong Acid-Strong Base

Neutral salt : pH = 7

Example : NaCl

Salt dissociation equation :

$$NaCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$ (completely dissociated)

$$Na^+_{(aq)} + H_2O \longrightarrow \text{no reaction}$$

$$Cl^-_{(aq)} + H_2O \longrightarrow \text{no reaction}$$

Salt from the strong acid-strong base not undergo hydrolysis.

(ii) Hydrolysis Salts of Strong Acid-Weak Base

Acidic salt : pH < 7

Example : Ammonium chloride, NH_4Cl

Salt dissociation equation :

$$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$ (completely dissociated)

- only cation will undergo hydrolysis to form H_3O^+ ion, therefore, NH_4Cl undergoes partial hydrolysis.

Hydrolysis equation for cation :

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$$

(iii) Hydrolysis Salts of Weak Acid-Strong Base

Basic salt : pH > 7

Example : Sodium ethanoate, CH_3COONa

Salt dissociation equation :

$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ (completely dissociated)

- only anion will undergo hydrolysis to form OH^- ion, therefore, CH_3COONa undergoes partial hydrolysis.

Hydrolysis equation for cation :

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

At the end of this lesson,students should be able to:

- **Define buffer solution**
- **Decribe qualitatively how a buffer solution controls its pH**

7.1.10: Buffer Solutions

- **Buffer solution** is a solution which has the ability to maintain its pH when a small amount of strong acid or strong base is added to the solution.

- Solution that contains a weak acid and its salt (its conjugate base) or a weak base and its salt (its conjugate acid).

- Two types of buffer solutions :
  i. Acidic buffer solution (pH<7)
  ii. Basic buffer solution (pH>7)

7.1.11. Acidic buffer solution

- An acidic buffer solution can be prepared by mixing a weak acid and its salt (its conjugate base).
- Example :

  Acetic acid, CH_3COOH and sodium ethanoate, CH_3COONa

- Reaction that occurs in the buffer solution :

  $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$ (partially dissociated)

  $CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ (completely dissociated)

- The amount of CH_3COO^- is mainly from the complete dissociation of CH_3COONa.

Actions of acidic buffer solution

- When a small amount of acid is added, the H^+ ions will be consumed by the ethanoate ion, CH_3COO^- to form CH_3COOH.

$$CH_3COO^-_{(aq)} + H^+_{(aq)(added)} \xrightarrow{} CH_3COOH_{(aq)}$$

As a result, there will be only a small change in pH and

$[CH_3COO^-]\downarrow$ and $[CH_3COOH]\uparrow$

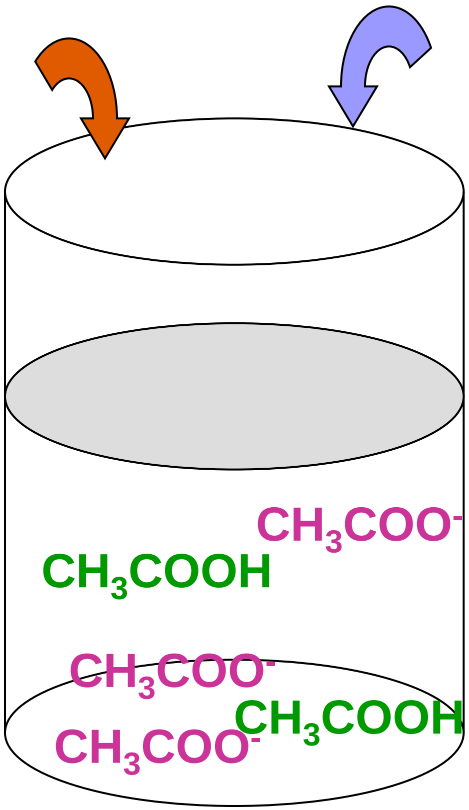
- When a small amount of base is added to the buffer system, the OH^- ions will be neutralized by the acid, CH_3COOH to form CH_3COO^- and H_2O.

$$CH_3COOH_{(aq)} + OH^-_{(aq)(added)} \xrightarrow{} CH_3COO^-_{(aq)} + H_2O_{(l)}$$

As a results, there will be a small change in pH and $[CH_3COO^-]\uparrow$ and $[CH_3COOH]\downarrow$

acid (H^+)

base (OH^-)



$$H^+_{(added)} + CH_3COO^- \rightleftharpoons CH_3COOH$$

$$OH^-_{(added)} + CH_3COOH \rightleftharpoons CH_3COO^- + H_2O$$

$$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

$$CH_3COONa\ (aq) \longrightarrow CH_3COO^-\ (aq) + Na^+\ (aq)$$

A buffer system contains ethanoic acid, CH_3COOH and ethanoat ion, CH_3COO^- from CH_3COONa

Basic buffer solution

- **A basic buffer solution** can be prepared by mixing a weak base and its salt (its conjugate acid).
- Example :

  Ammonia, NH_3 and ammonium chloride, NH_4Cl
- Reaction that occurs in the buffer solution :

  $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)}$ (partially dissociated)

  $NH_4Cl_{(aq)} \longrightarrow NH_4{}^+{}_{(aq)} + Cl^-{}_{(aq)}$ (completely dissociated)
- The amount of NH_4^+ is mainly from the complete dissociation of NH_4Cl.

Actions of basic buffer solution

- When a small amount of acid is added, the H^+ ions will be consumed by the ammonia, NH_3 to form NH_4^+.

  $$NH_{3(aq)} + H^+_{(aq)\ (added)} \longrightarrow NH_4^+{}_{(aq)}$$

  As a result, there will be only a small change in pH and $[NH_3]\downarrow$ and $[NH_4^+]\uparrow$

- If a small amount of base is added to the buffer system, the OH^- ions will be removed by the ammonium ions, NH_4^+ to form NH_3 and H_2O.

  $$NH_3^+{}_{(aq)} + OH^-_{(aq)\ (added)} \longrightarrow NH_{3(aq)} + H_2O_{(aq)}$$

  As a results, there will be a small change in pH and $[NH_4^+]\downarrow$ and $[NH_3]\uparrow$.

At the end of this lesson, students should be able to:

- Derive the Henderson-Hasselbalch equation.
- Calculate the pH of buffer solutions.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

$$pOH = pK_a + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

7.1.12. pH of buffer solution

pH of acidic buffer solution

- $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$

$$Ka = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{Ka\,[CH_3COOH]}{[CH_3COO^-]}$$

$$-\log[H^+] = -\log Ka - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pKa + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$ -OR- $$pH = pKa + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

(Henderson-Hasselbalch equation)

Example 1 :

1. 1.0 litre buffer solution is prepared by mixing 0.10 mole of CH_3COOH with 0.10 mole of CH_3COONa.
   i. Calculate the pH of a the buffer solution.
   ii. Calculate the pH of the buffer solution after the addition of (a) 0.02 mole HCl

      (b) 0.02 mol NaOH

   (Assume that the volume of the solution does not change when HCl and NaOH is added)

   Ka for $CH_3COOH = 1.8 \times 10^{-5}$ M

Solution:

- V = 1 L
  $[CH_3COOH] = 0.10$ M

  $[CH_3COONa] = 0.10$ M

  $$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

  $$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

  $$pH = -\log(1.8 \times 10^{-5}) + \log\frac{(0.10)}{(0.10)}$$

  pH = 4.74

ii. (a) pH when 0.02 mol HCl is added

Buffer action :	$CH_3COO^-_{(aq)}$	$+ \quad H^+_{(aq)}$	$\longrightarrow CH_3COOH_{(aq)}$
$[\ ]_{initial}$	0.10 M	0.02 M	0.10 M
$[\ ]_{change}$	-0.02 M	-0.02 M	+0.02 M
$[\ ]_{final}$	0.08 M	0	0.12 M

$[CH_3COO^-] = 0.08\ M$

$[CH_3COOH] = 0.12\ M$

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

$$pH = -\log(1.8 \times 10^{-5}) + \log \frac{(0.08)}{(0.12)}$$

$pH = 4.57$

ii.(b) pH when 0.02 mol NaOH is added

Buffer action : $CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$

$[\ ]_{initial}$	0.10 M	0.02 M	0.10 M
$[\ ]_{change}$	-0.02 M	-0.02 M	+0.02 M
$[\ ]_{final}$	0.08 M	0	0.12 M

$[CH_3COO^-] = 0.12\ M$

$[CH_3COOH] = 0.08\ M$

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

$$pH = -\log(1.8 \times 10^{-5}) + \log \frac{(0.12)}{(0.08)}$$

$pH = 4.92$

pH of basic buffer solution

- $NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

$$[OH^-] = \frac{K_b\ [NH_3]}{[NH_4^+]}$$

$$-\log [OH-] = -\log K_b - \log \frac{[NH_3]}{[NH_4^+]}$$

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$ **-OR-** $$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

(Henderson-Hasselbalch equation)

Example 2 :

A buffer solution is prepared by mixing 400 mL of 1.50 M NH_4Cl solution with 600 mL of 0.10 M NH_3.

i. Calculate the pH of a the buffer solution.

ii. Calculate the pH of the buffer solution after the addition of (a) 0.15 M NaOH

(b) 0.011 M H

(Assume that the volume of the solution does not change when HCl and NaOH is added)

K_b for NH_3 = 1.8×10^{-5} M

Solution :

i. V = 400 ml + 600 ml
= 1000 ml
= 1 L

$$\text{mol } NH_4Cl = \frac{MV}{1000} = \frac{1.50 \times 400}{1000} = 0.6 \text{ mol}$$

$$\text{mol } NH_3 = \frac{MV}{1000} = \frac{0.10 \times 600}{1000} = 0.06 \text{ mol}$$

$$[NH_4Cl] = \frac{0.6 \text{ mol}}{1 \text{ L}} = 0.6 \text{ M}$$

$$[NH_3] = \frac{0.06 \text{ mol}}{1 \text{ L}} = 0.06 \text{ M}$$

$$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

@ $$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{(0.6)}{(0.06)}$$

$$= 5.74$$

$$pH = 14 - 5.74 = 8.26$$

ii. (a) pH when 0.15 M NaOH is added

Buffer action : $NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow NH_{3(aq)} + H_2O_{(l)}$

	$NH_4^+{}_{(aq)}$	$OH^-{}_{(aq)}$	$NH_{3(aq)}$	$H_2O_{(l)}$
$[\ ]_{initial}$	0.60 M	0.15 M	0.06 M	
$[\ ]_{change}$	-0.15 M	-0.15 M	+0.15 M	
$[\ ]_{final}$	0.45 M	0	0.21 M	

$$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{(0.45)}{(0.21)}$$

$$= 5.08$$

$$pH = 14 - 5.08$$

$$= 8.92$$

ii.(b) pH when 0.011 M HCl is added

Buffer action :	$NH_{3(aq)}$	+ $H^+_{(aq)}$ $\longrightarrow$	$NH_4^+{}_{(aq)}$
$[\ ]_{initial}$	0.06 M	0.011 M	0.6 M
$[\ ]_{change}$	-0.011 M	-0.011 M	+0.011 M
$[\ ]_{final}$	0.049 M	0	0.611 M

$$pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{(0.611)}{(0.049)}$$

$$= 5.84$$

$$pH = 14 – 5.84$$

$$= 8.16$$

Exercise :

1. How many moles of NH_4Cl must be added to 2.0 L of 0.10 M NH_4 to form a buffer whose pH is 9.00 ? (Assume that the addition of NH_4Cl does not change the volume of the solution) (0.36 mol)
2. Calculate the concentration of sodium benzoate that must be present in a 0.20 M solution of benzoic acid ($HC7H_5O_2$) to produce a pH of 4.00.(0.13 M)
3. Calculate the pH of a buffer composed of 0.12 M benzoic acid and 0.20 M sodium benzoate. $K_a = 6.3 \times 10^{-5}$. (4.43)
4. What is the pH of a buffer that is 0.12 M in lactic acid ($HC_3H_5O_3$) and 0.10 M in sodium lactate? $K_a = 1.4 \times 10^{-4}$

(3.77)

At the end of this lesson, students should be able to:

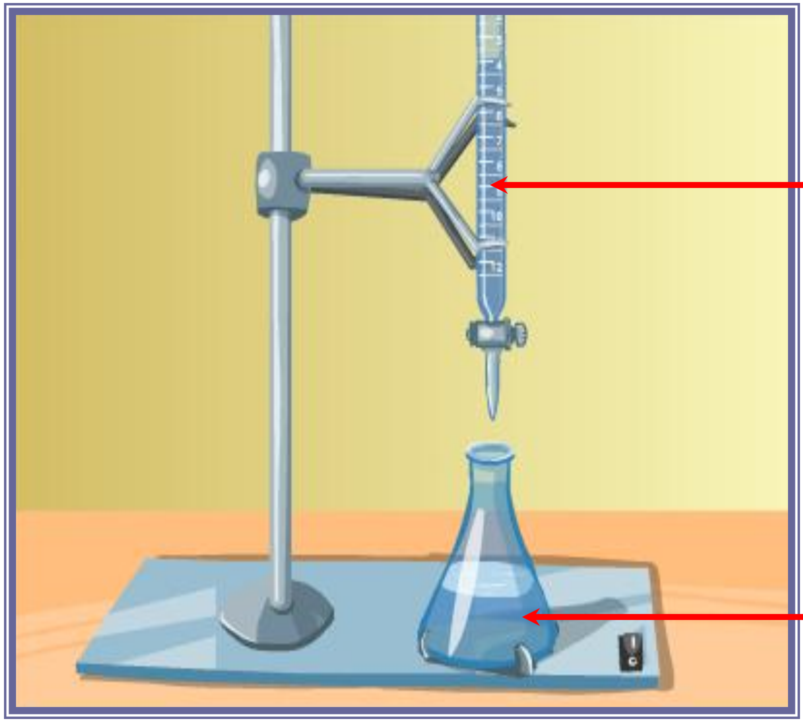
- Describe the titration process and distinguish the end point and equivalence point.
- Perform calculation involving titrations.

7.2.1 : Acid- Base Titration

- **Titration** is a procedure for determining the volume of two solution (acid & base) which will exactly neutralize one another.

  By using a solution known concentration, (standard solution) the concentration of another solution can be determined.

Titration apparatus



titrant

analyte

- **Titrant** is the solution added from the burette.
- The **equivalent point** is the point at which the amount of acid and base present exactly neutralizes one another. (number of moles of OH^- ions and number of moles of H^+ ions are equal)
- **Indicator** is a substance that is generally added to the solution in the receiving vessel an which undergoes some sort of colour change when reaction is over.

The **end point** of titration is the point when the indicator changes colour.

Types of Acid-Base Titrations

- 3 types of acid-base titration :

(A) Strong Acid-Strong Base Titration

(B) Strong Acid-Weak Base Titration

(C) Weak Acid-Strong Base Titration

7.2.2: pH Calculation for Acid-Base Titration

(A)Strong Acid-Strong Base Titration

Example :

A 25.00 mL sample of 0.10 M HCl is titrated with 0.1 M NaOH. Calculate the pH of the solution

i. before the addition of NaOH

ii. after the addition of 10.0 mL of NaOH

iii. after the addition of 24.9 mL of NaOH

iv. at the equivalence point

v. after the addition 25.1 mL of NaOH

vi. after the addition of 35.0 mL of NaOH

Sketch the titration curve and determine the appropriate indicator for this titration.

Solution :

i. pH before the addition of 0.10 M NaOH

Dissociation equation of HCl :

	$HCl_{(aq)}$	$\longrightarrow$	$H^+_{(aq)}$	$+$	$Cl^-_{(aq)}$
$[\ ]_{initial}$	0.10 M		0		0
$[\ ]_{final}$	0		0.10 M		0.10 M

$$\begin{aligned} pH &= -\log[H+] \\ &= -\log(0.1) \\ &= 1.0 \end{aligned}$$

ii. pH after the addition of 10.0 mL of 0.10 M NaOH

	$HCl_{(aq)}$	+	$NaOH_{(aq)}$	$\longrightarrow$	$NaCl_{(aq)}$	+	$H_2O_{(l)}$
$n_{initial}$	2.5×10^{-3}		1.0×10^{-3}		0		
n_{final}	1.5×10^{-3}		0		1.0×10^{-3}		

$[\ ]_{final}$ $\dfrac{1.5 \times 10^{-3}\ \text{mol}}{35.0 \times 10^{-3}\ \text{L}}$ $\dfrac{1.0 \times 10^{-3}\ \text{mol}}{35.0 \times 10^{-3}\ \text{L}}$

= 0.043 M = 0.029 M

The pH solution is calculated from the amount of HCl left after partial neutralization.

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

$= -\log (0.043)$

$= 1.37$

iii. pH after the addition of 24.9 mL of 0.10 M NaOH

	$HCl_{(aq)}$	+	$NaOH_{(aq)}$	$\longrightarrow$	$NaCl_{(aq)}$	+	$H_2O_{(l)}$
$n_{initial}$	2.5×10^{-3}		2.49×10^{-3}		0		
n_{final}	0.01×10^{-3}		0		2.49×10^{-3}		
$[\ ]_{final}$	$\frac{0.01 \times 10^{-3}\ mol}{49.9 \times 10^{-3}\ L}$				$\frac{2.49 \times 10^{-3}\ mol}{49.9 \times 10^{-3}\ L}$		
	$= 2.0 \times 10^{-4}\ M$				$= 0.0499\ M$		

The pH solution is calculated from the amount of HCl left after partial neutralization.

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log (2.0 \times 10^{-4}) \\ &= 3.7 \end{aligned}$$

iv. at the equivalence point

At the equivalence point, moles of H^+ = moles of OH^-

$$\frac{M_{NaOH}\ V_{NaOH}}{M_{HCl}\ V_{HCl}} = \frac{n_{NaOH}}{n_{HCl}} = \frac{1}{1}$$

$$M_{NaOH}.V_{NaOH} = M_{HCl}.V_{HCl}$$

$$= 25.0\ \text{mL}$$

	$HCl_{(aq)}$	+	$NaOH_{(aq)}$	$\longrightarrow$	$NaCl_{(aq)}$	+	$H_2O_{(l)}$
$n_{initial}$	2.5×10^{-3}		2.5×10^{-3}		0		
n_{final}	0		0		2.5×10^{-3}		
$[\ ]_{final}$	0				$\frac{2.5 \times 10^{-3}\ \text{mol}}{50.0 \times 10^{-3}\ \text{L}}$ $= 0.05$ M		

The calculation involves a complete neutralization reaction.

$$\mathrm{NaCl} \longrightarrow \underbrace{\mathrm{Na}^+_{(aq)} + \mathrm{Cl}^-_{(aq)}}_{\text{(does not undergo hydrolysis)}}$$

The pH solution is calculated from the dissociation of water.

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

where : $[H^+] = [OH^-]$

$[H^+] = \sqrt{1.0 \times 10^{-14}\ M^2}$

= 1.0 x 10-7 M

$pH = -\log(1.0 \times 10^{-7})$

= 7

v. pH after the addition of 25.1 mL of 0.10 M NaOH

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

	$HCl_{(aq)}$	$NaOH_{(aq)}$	$NaCl_{(aq)}$	$H_2O_{(l)}$
$n_{initial}$	2.5×10^{-3}	2.51×10^{-3}	0	
n_{final}	0	0.01×10^{-3}	2.51×10^{-3}	
$[\ ]_{final}$		$\frac{0.01 \times 10^{-3}\ mol}{50.1 \times 10^{-3}\ L}$ $= 1.996 \times 10^{-4}\ M$	used limiting reagent $\frac{2.5 \times 10^{-3}\ mol}{50.1 \times 10^{-3}\ L}$ $= 0.05\ M$	

The pH solution is determined from the amount of NaOH left.

$pOH = -\log [OH^-]$

$= -\log (1.996 \times 10^{-4})$

$= 3.70$

$pH = 14 - 3.70$

$= 10.3$

vi. pH after the addition of 35.0 mL of 0.10 M NaOH

	$HCl_{(aq)}$	+	$NaOH_{(aq)}$	$\longrightarrow$	$NaCl_{(aq)}$	+	$H_2O_{(l)}$
$n_{initial}$	2.5×10^{-3}		3.5×10^{-3}		0		
n_{final}	0		1.0×10^{-3}		2.5×10^{-3}		
$[\;]_{final}$			$\frac{1.0 \times 10^{-3}\text{ mol}}{60.0 \times 10^{-3}\text{ L}}$		$\frac{2.5 \times 10^{-3}\text{ mol}}{60.0 \times 10^{-3}\text{ L}}$		
			= 0.0167 M		= 0.0417 M		

The pH solution is determined from the amount of NaOH left.

$pOH = -\log [OH^-]$

$= -\log (0.0167)$

$= 1.78$

$pH = 14 – 1.78$

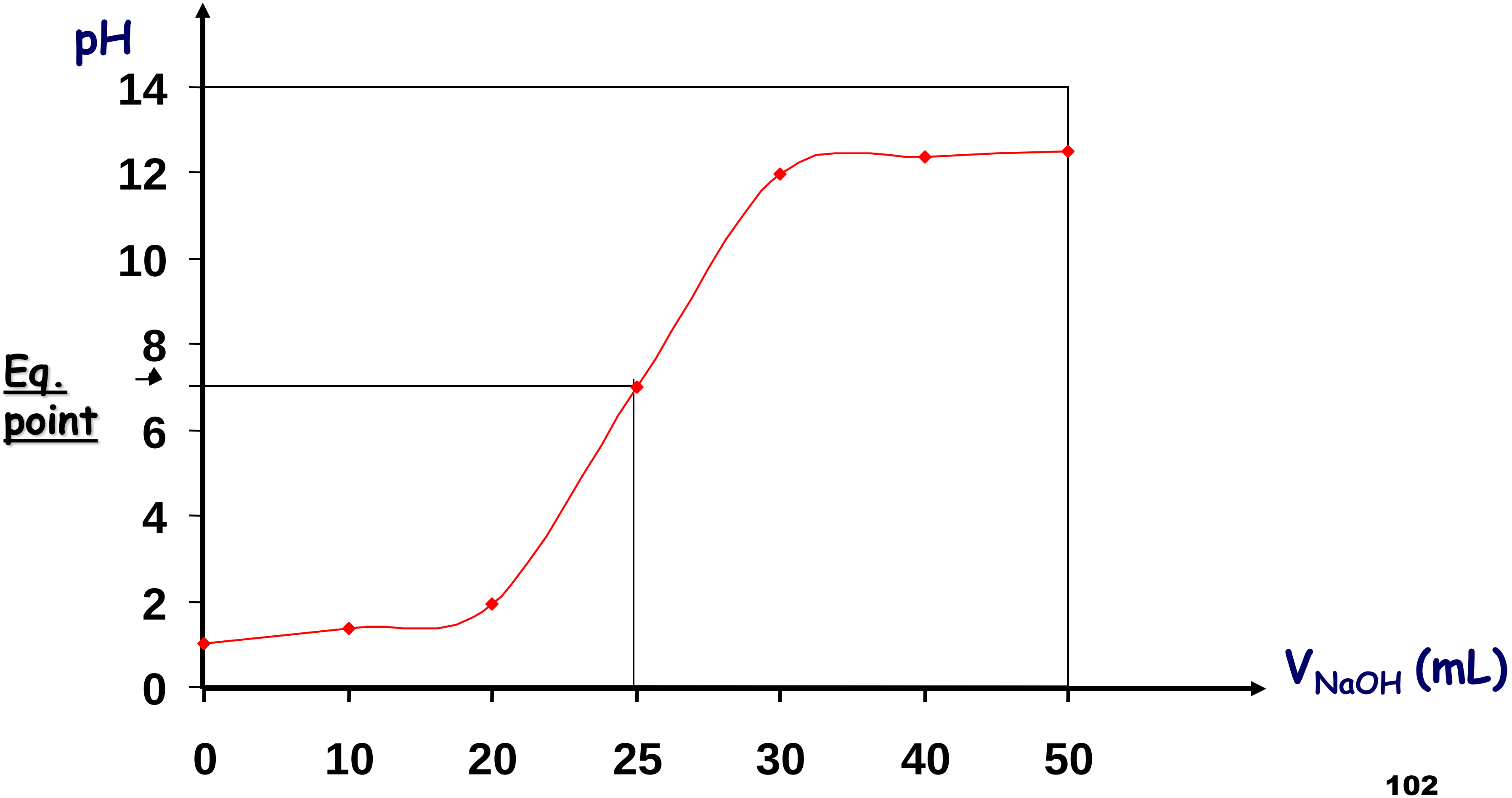
$= 12.2$

The titration curve for strong acid-strong base titration

NaOH (mL)	0	10	24.9	25	25.1	35
pH	1.0	1.37	3.7	7	10.3	12.2

7.2.3: i)The titration curve for strong acid-strong base titration

NaOH (mL)	0	10	24.9	25	25.1	35
pH	1.0	1.37	3.7	7	10.3	12.2



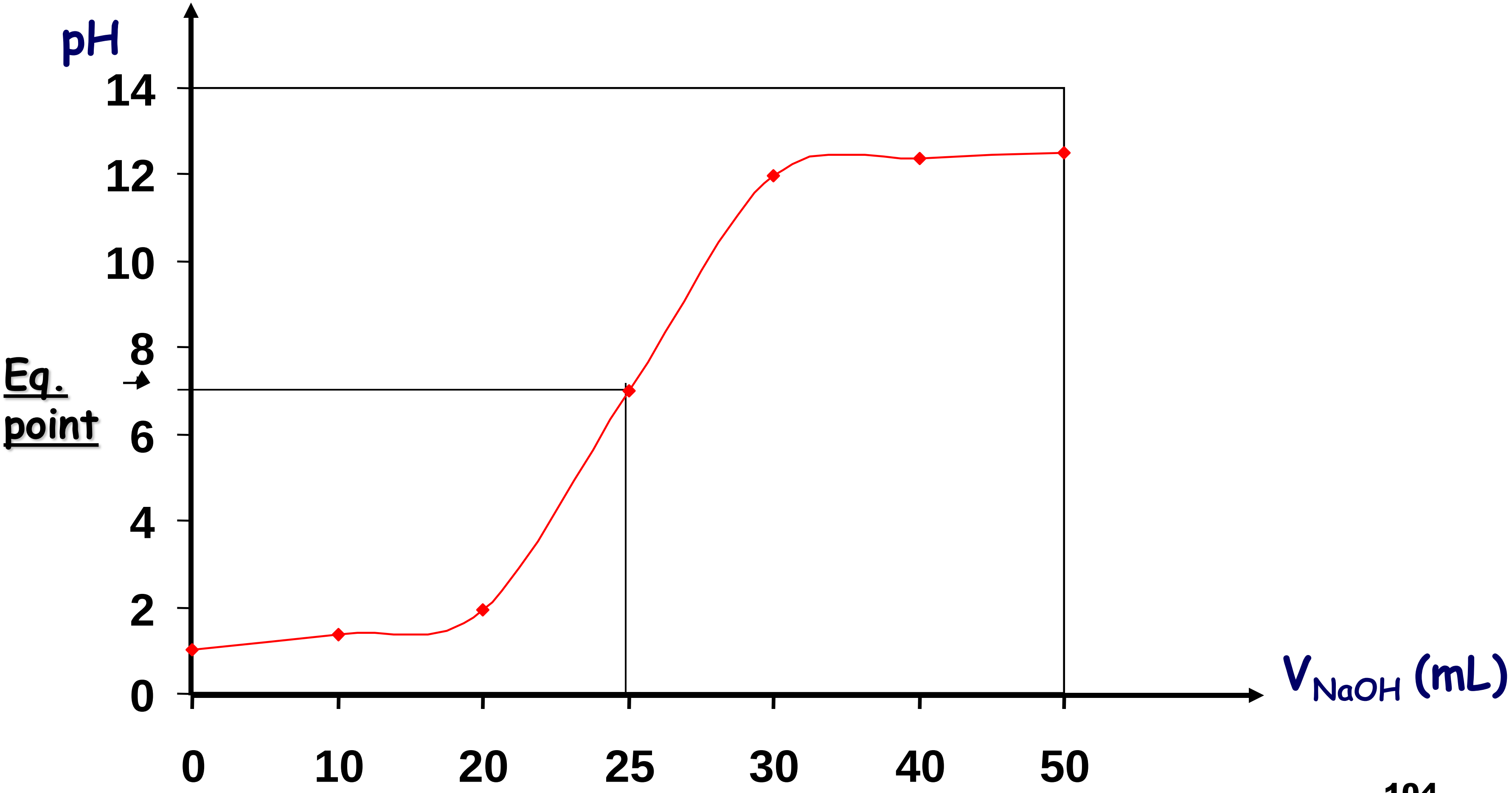
At the end of this lesson students should be able to:

- Sketch and interpret the variation pH against titre value for titration between :
  i. strong acid- strong base
  ii. strong acid-weak base
  iii. weak acid-strong base

- Identify suitable indicators for acid-base titrations.

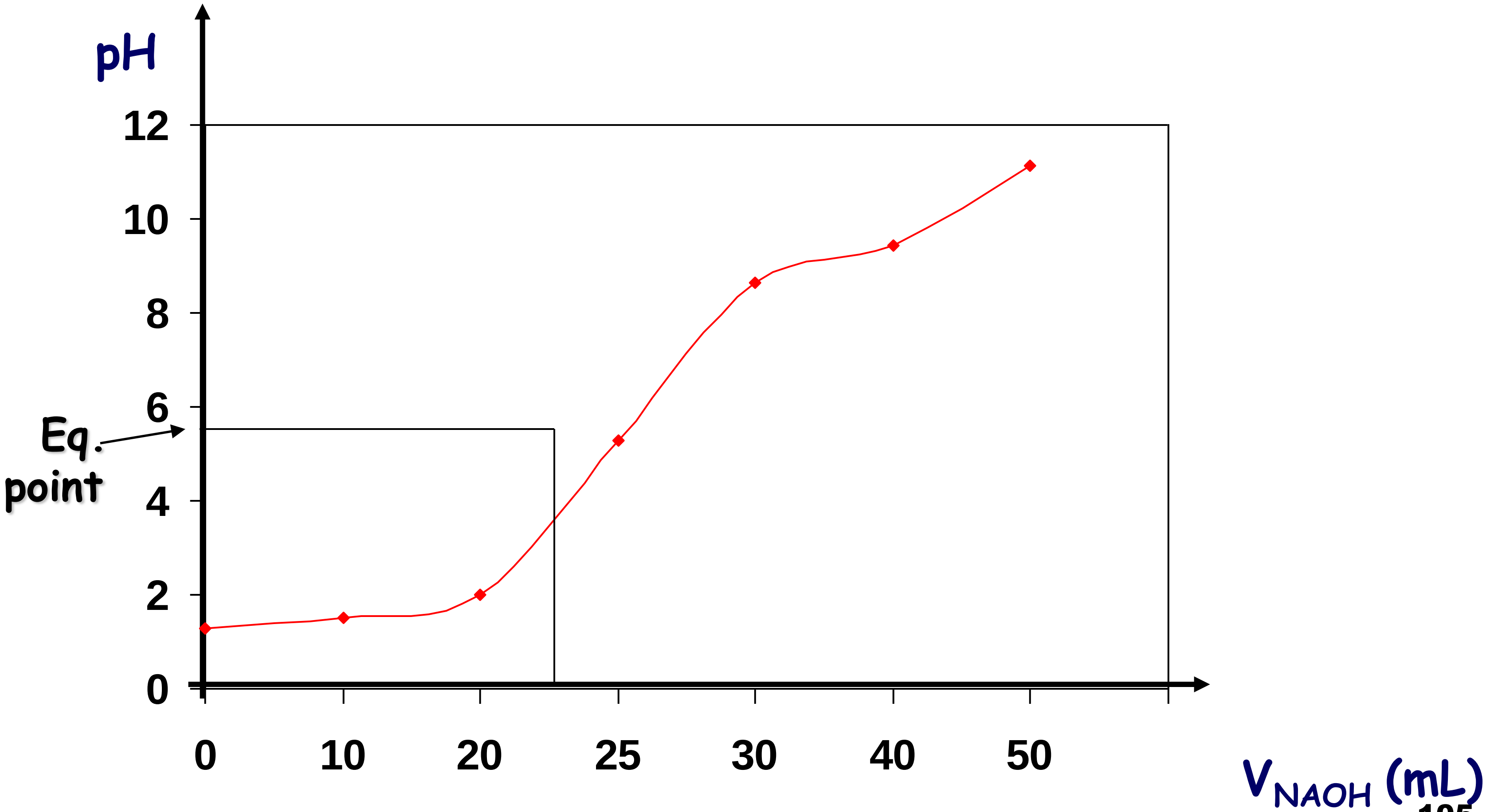
7.2.3: i)The titration curve for strong acid-strong base titration

NaOH (mL)	0	10	24.9	25	25.1	35
pH	1.0	1.37	3.7	7	10.3	12.2



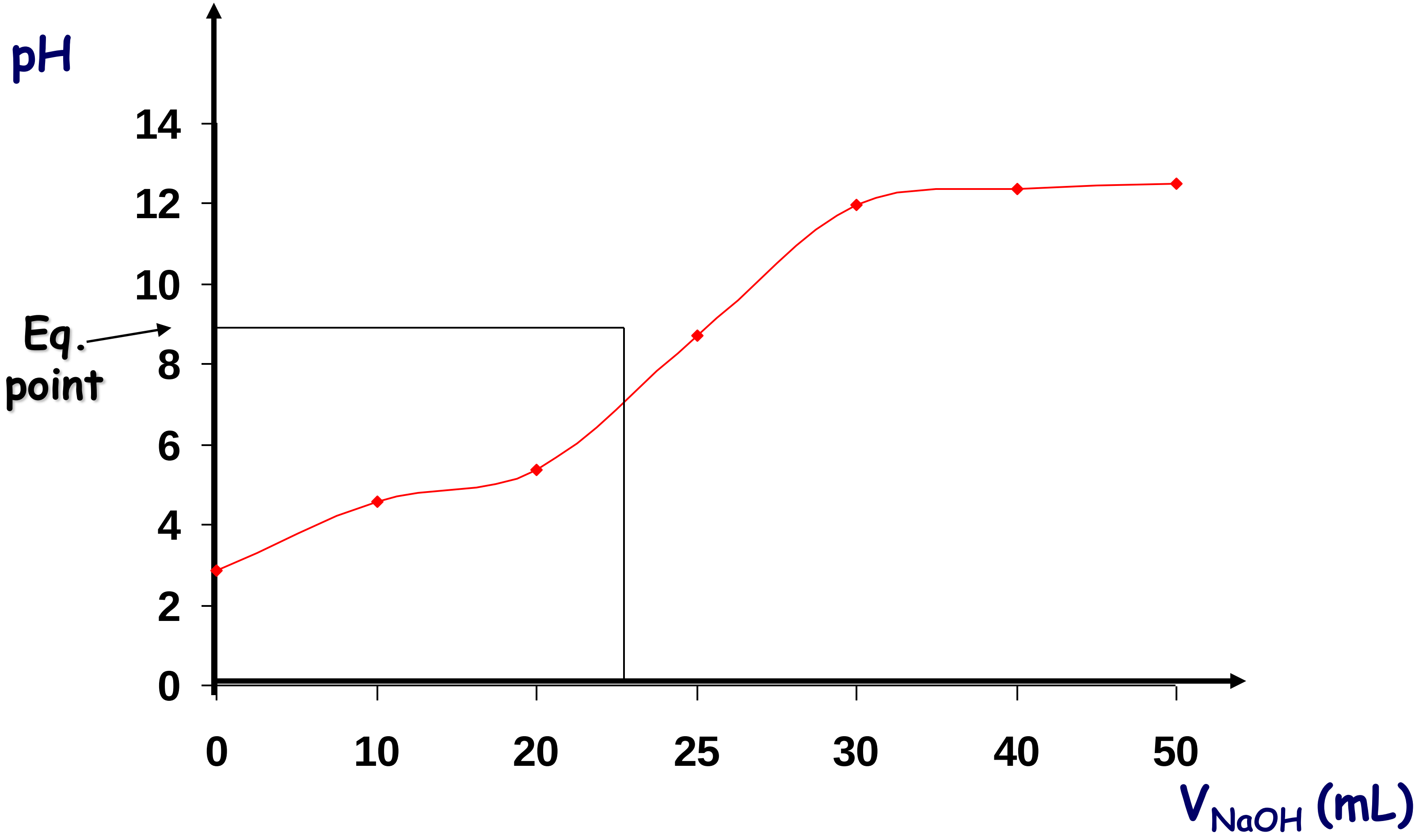
ii). The titration curve for strong acid-weak base titration

NAOH (mL)	0	10	24.9	25.0	25.1	35
pH	1.0	1.37	3.7	5.28	6.86	8.86



iii.) The titration curve for weak acid-strong base titration

NaOH (mL)	0	10	26.5	26.65	27.0	36.0
pH	2.76	4.69	7.37	8.83	11.13	12.39



7.2.4: Choosing The Suitable Indicator

- Choose an indicator which the end point pH range lies on the steep part of the titration curve.
- This choice ensures that the pH at the equivalent point will fall within the range over which indicator changes colour (Table 6.2)

Table 6.2 : pH Ranges for Indicator

Types of Titrations	End Point pH Range	Suitable Indicators
Strong Acid-Strong Base	3 – 10	Any Indicator
Weak Acid-Strong Base	7 – 11	Phenolphthalein, thymol blue
Strong Acid-weak Base	3 – 7	Methyl orange, methyl red
Weak Acid-Weak Base	-	-

Exercise :

1. What is the colour of the solution when 3 drops of the below indicators are added separately to water (pH = 7) ?

Indicator	pH range	colour change
Phenolphthalein	8.2 – 10.0	Colourless → reddish pink
Methyl orange	3.2 – 4.2	Red → Yellow
Bromothymol blue	6.0 – 7.6	Yellow → Blue
phenol red	6.8 – 8.4	Yellow → red

Exercise :

2. The pH range and the colour change for 3 indicator X, Y and Z is shown in the table below :

Indicator	pH range	colour change
X	1.2 - 2.8	Red → Yellow
Y	6.0 - 7.6	Yellow Blue
Z	8.3 - 10.5	Colourless Yellow

What is the colour of the solution when a few drops of the above indicators are added separately to a buffer solution whose pH is 6.52 ?

	X	Y	Z
A	Orange	Green	Blue
B	Orange	Yellow	Light blue
C	Yellow	Green	Colourless
D	Yellow	Orange	Colourless
E	Yellow	Yellow	Colourless

At the end of this lesson, students should be able to:

- Define solubility, molar solubility and solubility product, K_{sp}.
- Calculate K_{sp} from concentration of ion and vice versa
- Predict the possibility of precipitation of slightly soluble ionic compounds the values of ion-product, Q to K_{sp}.
- Define and explain the common ion effect.
- Perform calculations related to common ion effect.

7.3.1 : Solubility Equilibrium

- **Solubility Equilibrium** is the equilibrium exists between the undissolved solid solute and the aqueous ions formed.

Example : $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

- Other example of a slightly soluble salt :

i. $BaCO_{3\,(s)} \rightleftharpoons Ba^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

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

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

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

v. $Ag_2CrO_{4\,(s)} \rightleftharpoons 2Ag^{+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)}$

- **Each of salt/ionic compound which is slightly soluble have their own K_{sp} (the equilibrium constant for the equilibrium between an ionic solid and its saturated solution).**

- **Solubility – the mass of solute that dissolves in a given quantity of solvent to form a saturated solution (g L^{-1} or kg cm^{-3} or g cm^{-3}).**

- **Molar Solubility – the number of moles of a solute in 1 L of a saturated solution (mol L^{-1}).**

7.3.2: Solubility Product Constant, K_{sp}

- In a saturated solution of a slightly soluble ionic compound (salt), an equilibrium exist between the undissolved solid salt and its dissolved ions.

Example : $A_xB_{y(s)} \rightleftharpoons x\,A^{y+}_{(aq)} + yB^{x-}_{(aq)}$

$$K_c = \frac{[A^{y+}]^x\,[B^{x-}]^y}{[A_xB_y]}$$

$* \; [A_xB_y]_{(solid)}$ – constant

$$K_c\,[A_xB_y] = [A^{y+}]^x\,[B^{x-}]^y$$

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

Unit for K_{sp} = mol L^{-1} @ mol dm^{-3} @ M

- **Solubility Product, K_{sp}**

  - is the product of the molar concentrations of the ions involved in the equilibrium, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

Exercise :

Write the expression for solubility product, K_{sp} and state its unit for the following salt :

1. $Mg_3(PO_4)_{2\,(s)} \rightleftharpoons 3Mg^{2+}{}_{(aq)} + 2PO_4{}^{3-}{}_{(aq)}$
2. $Ag_2S_{(s)} \rightleftharpoons 2Ag^{+}{}_{(aq)} + S^{2-}{}_{(aq)}$
3. $ZnCl_{2\,(s)} \rightleftharpoons Zn^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$
4. $Ag_2SO_{4\,(s)} \rightleftharpoons 2Ag^{+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$
5. $Fe(OH)_{3\,(s)} \rightleftharpoons Fe^{3+}{}_{(aq)} + 3OH^{-}{}_{(aq)}$

7.3. 2: Calculating Solubility Product, K_{sp}

Example 1 :

The solubility of PbI_2 is 1.2 x 10^{-3} mol dm^{-3}. Calculate its solubility product.

Solution :

assume that solubility = x

$$PbI_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^-_{(aq)}$$

$$\qquad\qquad\quad x \qquad\qquad 2x$$

$K_{sp} = [Pb^{2+}]\,[I^-]^2$

given $x = 1.2 \times 10^{-3}$ M

$K_{sp} = (x)\,(2x)^2$

$= (1.2 \times 10^{-3})\,(2 \times 1.2 \times 10^{-3})^2$

$= 6.91 \times 10^{-9}\ M^3$

Example 2 :

The solubility product, K_{sp} of $CaCO_3$ at 25°C is 2.8×10^{-9} M^2. Calculate the solubility of $CaCO_3$ in g dm^{-3} at this temperature.

Solution :

Equilibrium equation :

$$CaCO_{3\,(s)} \rightleftharpoons \underset{x}{Ca^{2+}}{}_{(aq)} + \underset{x}{CO_3^{2-}}{}_{(aq)}$$

Assume the solubility = x

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$$

$$= (x)\,(x)$$

$$1.8 \times 10^{-9} = x^2$$

$x = \sqrt{2.8 \times 10^{-9}}$

$= 5.29 \times 10^{-5}$

Molar solubility = 5.29×10^{-5} mol dm^{-3}

Molar mass of $CaCO_3$ = 100 g mol^{-1}

Solubility in g dm^{-3} = (5.29×10^{-5})(100 g mol^{-1})

$= 5.29 \times 10^{-3}$ g dm^{-3}

Exercise :

1. The solubility of magnesium hydroxide, $Mg(OH)_2$ is 1.7×10^{-4} mol dm^{-3}. Calculate the solubility product of this compound.

2. The solubility of calcium sulfate, $CaSO_4$ is found experimentally to be 0.67 g L^{-1}. Calculate the K_{sp} value for $CaSO_4$. (Molar mass of $CaSO_4$ = 136.2 g mol^{-1})

3. 1.00 liter of a saturated solution of silver chromate, Ag_2CrO_4 at 25°C contains 0.0435 gram of dissolved Ag_2CrO_4. Calculate its molar solubility and its solubility product constant.

7.3.3: Predicting Precipitation

- A mixture of two solutions will produce a precipitation or not depending on the ion product, Q present.
- The solubility equilibrium equation for a slightly soluble salt, MA :

$$MA_{(s)} \rightleftharpoons M^+_{(aq)} + A^-_{(aq)}$$

$$K_{sp} = [M^+]\,[A^-]$$

- If we mix a solution containing M^+ ions with one containing A^- ions, the ion product, Q is given by :

$$Q = [M^+]\,[A^-]$$

- Q has the same form as K_{sp} but the concentrations of ions are not equilibrium concentrations.

i. $Q = K_{sp}$

- the solution is saturated
- equilibrium exist between undissolved solid salt and its dissolved ions

ii. $Q < K_{sp}$

- the solution is unsaturated
- no precipitation of MA
- more salt should be dissolved to increase the ion concentrations until $Q = K_{sp}$

iii. $Q > K_{sp}$

- the solution is supresaturated
- $MA_{(s)}$ will precipitate out until the product of the ionic concentrations is equal to K_{sp}.

Example 1 :

If 500 mL of 0.014 M $CaCl_2$ is added to 250 mL of 0.25 M Na_2SO_4, will a $CaSO_4$ precipitate form ? (K_{sp} for $CaSO_4 = 2.0 \times 10^{-4}\ M^2$)

Solution :

$$[Ca^{2+}] = 0.014 \ \text{x}\ \frac{500 \times 10^{-3}}{750 \times 10^{-3}} = 0.0093\ M$$

$$[SO_4^{2-}] = 0.25 \ \text{x}\ \frac{250 \times 10^{-3}}{750 \times 10^{-3}} = 0.083\ M$$

Solubility equilibrium for $CaSO_4$:

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

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]$$
$$= 2.0 \times 10^{-14}\ M^2$$

the ion product, $Q = [Ca^{2+}] [SO_4^{2-}]$

$= (0.0093) (0.083)$

$= 7.72 \times 10^{-4}$ mol^2 dm^{-6}

$Q > K_{sp}$

Thus, the solution is supersaturated, some $CaSO_4$ will precipitate.

Exercise :

1. Will a $PbSO_4$ precipitate form when 100 cm^3 of 0.003 M $Pb(NO_3)_2$ is added to 400 cm^3 of 0.04 M Na_2SO_4 ? (K_{sp} for $PbSO_4$ = 1.5×10^{-8} mol^2 dm^{-6})

2. Determine whether a precipitate will formed when 100 mL of 1.00×10^{-3} M $MgCl_2$ is added to 400 mL of 1.50×10^{-3} M NaOH ? (K_{sp} for $Mg(OH)_2$ = 1.2×10^{-11} mol^3 dm^{-9})

3. (a) The solubility of Ag_2SO_4 in water at $25^{O}C$ is 0.506 g for each 100 mL solution. Calculate the solubility product at this temperature.

(b) If a solution of Na_2SO_4 is added dropwise to a 0.01 M Ag_2SO_4 solution, what is the minimum concentration of SO_4^{2-} is necessary to begin precepitate ?

7.3.4 : Common Ion Effect

- **Common ion** – an ion that is common to two or more components in a mixture of a solution of ions.

- **Common ion effect** – the reduction in the solubility of salt in the presence of a common ion.

Example :

Consider a saturated solution of silver chloride in water.

The solubility equilibrium is :

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

When NaCl is added to the saturated AgCl solution ; -
the concentration of $Cl^{-}_{(aq)}$ ions increases. Cl^{-} ion is the common ion.

- According to Le Chatelier's principle, the increase in [Cl$^-$] will cause the position of equilibrium shift to the left, thereby causing some AgCl to precipitate.

- So, the solubility of AgCl will decrease until the product once again equal to K_{sp}.

- Conclusion :

  Addition of common ions will reduce the solubility of a slightly soluble salt in its saturated solution.

Example 1 :

K_{sp} for AgCl is 1.7 x 10^{-10} mol^2 dm^{-6}. Calculate the molar solubility of AgCl in

i. Water

ii. In a solution of 0.1 mol dm^{-3} KCl.

Solution :

i. Let x be the molar solubility of AgCl in water.

$$\mathrm{AgCl}_{(s)} \rightleftharpoons \mathrm{Ag}^{+}_{(aq)} + \mathrm{Cl}^{-}_{(aq)}$$

$$\quad\quad\quad\quad\quad x \quad\quad\quad\quad x$$

$$K_{sp} = [\mathrm{Ag}^{+}]\,[\mathrm{Cl}^{-}]$$

$$1.7 \times 10^{-10} = x^{2}$$

$$x = 1.30 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$$

Thus, the solubility of AgCl in water is 1.30×10^{-5} M

ii. Let the solubility of AgCl in 0.10 mol dm^{-3} KCl = y mol dm^{-3}.

$$\begin{array}{ccccc} AgCl_{(s)} & \rightleftharpoons & Ag^+_{(aq)} & + & Cl^-_{(aq)} \\ & & y & & (y + 0.1) \end{array}$$

$$K_{sp} = [Ag^+]\,[Cl^-]$$

$$= (y)\,(y+0.1)$$

Assume $y \ll 0.1$, so, $(y+0.1) \approx 0.1$

$$1.7 \times 10^{-10} = 0.1y$$

$$y = 1.7 \times 10^{-9} \text{ mol dm}^{-3}$$

Thus, the solubility of AgCl in 0.1 mol dm^{-3} KCl is 1.7×10^{-9} M.

➡ the solubility of AgCl decrease in the presence of Cl^- ions (common ion)

Exercise :

1. It was found experimentally that the solubility of calcium sulphate is 0.67 g L^{-1}. Calculate the K_{sp} for calcium sulphate.

(2.4×10^{-4})

2. The solubility of silver sulphate is 1.5×10^{-2} mol L^{-1}. Calculate the solubility product of the salt. (1.4 x 10-5)

3. Will precipitate form if 200 mL of 0.0040 M $BaCl_2$ are added to 600 mL of 0.0080 M K_2SO_4 ? K_{sp} $BaSO_4 = 1.1 \times 10^{-10}$)

(Q> *K*sp therefore $BaSO_4$ will precipitate)