CHEMISTRY ENGINEERING
KEDAH TECHNICAL MATRICUATION COLLEGE
CHEMISTRY SYLLABUS

CHAPTER 7: IONIC EQUILIBRIUM (11 HOURS)

7.1 Acids and Bases
7.2 Acid – Base Titrations

CHAPTER 8.0 : THERMOCHEMISTRY (7 HOURS)

8.1 Concept of Enthalphy
8.2 Calorimetry
8.3 Hess's law
8.3 Born-Haber Cycle

CHAPTER 9.0: ELECTROCHEMISTRY (10 HOURS)

9.1 Galvanic Cell
9.2 Nernst Equation
9.3 Electrolytic Cell

CHAPTER 10.0 REACTION KINETICS (9 HOURS)

10.1 Reaction Rate
10.2 Collision Theory & Transition State Theory
10.3 Factors Affecting Reaction Rate

CHAPTER 11.0 ORGANIC CHEMISTRY (8 HOURS)

11.1 Introduction
11.2 Molecular & Structural Formulae
11.3 Functional Groups & Homologous Series
11.4 Reaction of Organic Compound
11.5 Isomerism

12.0 HYDROCARBON (10 HOURS)

12.1 Alkanes
12.2 Alkenes
12.3 Introduction to Aromatic Compounds

13.0 POLYMER (2 HOURS)

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CHEMISTRY ‘A’

S - Standard : Piawaian/peraturan

I - Inovasi : Kreativiti

K - Kesinambungan : Penambahbaikan

A - Amalan : Soalan tuto/workshop

P - Prosedur : Teknik belajar

CHAPTER 7:
IONIC EQUILIBRIA

7.1 ACIDS
&
BASES

Objective

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

a) Define acid and base according to the Arrhenius, Bronsted-Lowry and Lewis theories.

b) Define and identify conjugate acid and conjugate base according to Bronsted-Lowry theory.

IONIC EQUILIBRIA

Theory of acids and bases

- Arrhenius theory,
- Bronsted-Lowry theory (Conjugate acid-base pairs)
- Lewis Theory

ACIDS AND BASES

Properties of acids

- Turn **blue** litmus paper to **red**
- React with metal oxides : formed salts and H_2O
- React with reactive metals : formed salts and H_2
- React with carbonates and hydrogen carbonates : formed salt, H_2O and CO_2

Properties of bases

- Turn **red** litmus paper to **blue**
- React with acids : formed salts and H_2O

1. ARRHENIUS THEORY OF ACIDS & BASES

Arrhenius Theory of an acid

- Definition :

  -

- Examples :

  $HNO_{3\,(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$

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

Arrhenius Theory of a base

- Definition :

  -

- Examples :

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

$$Ba(OH)_2\ (aq) \longrightarrow Ba^{2+}\ (aq) + 2OH^{-}\ (aq)$$

- However, Arrhenius's Theory has it's limitations:
  - applicable to compounds **containing hydrogen and hydroxide**
  - restricted to **aqueous solution**
- ∴ **cannot** be used for reaction in **gaseous phase**
- Hence, to overcome the shortcoming, **J.N. BrØnsted & T.M. Lowry** put forward their theory

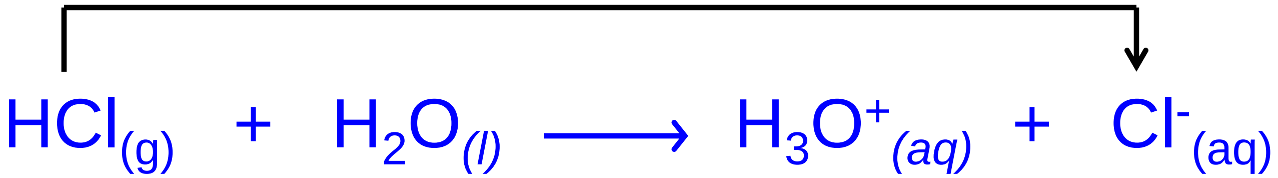
2. BRONSTED-LOWRY THEORY OF ACIDS AND BASES

BrØnsted-Lowry Theory of an acid

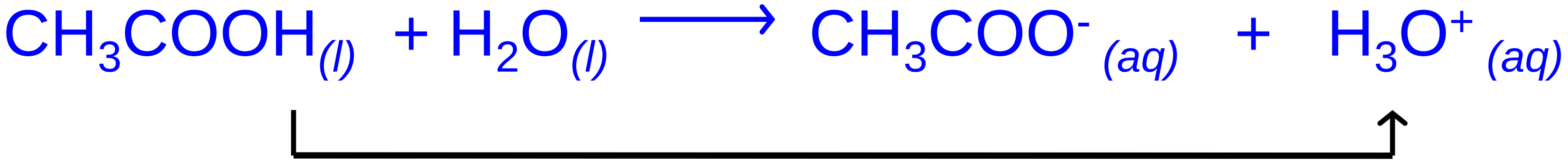
- Definition :

-

Examples :



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



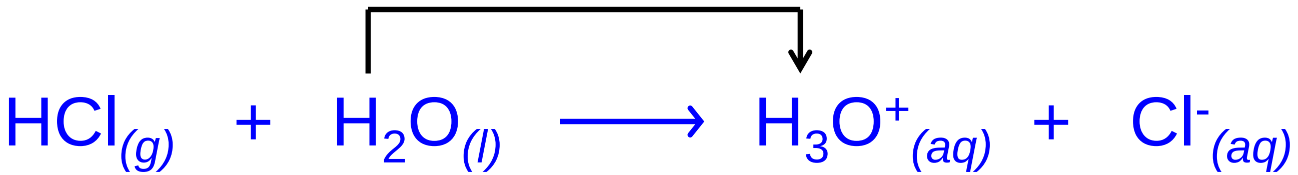
$$CH_3COOH_{(l)} + H_2O_{(l)} \longrightarrow CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

BrØnsted-Lowry Theory of a base

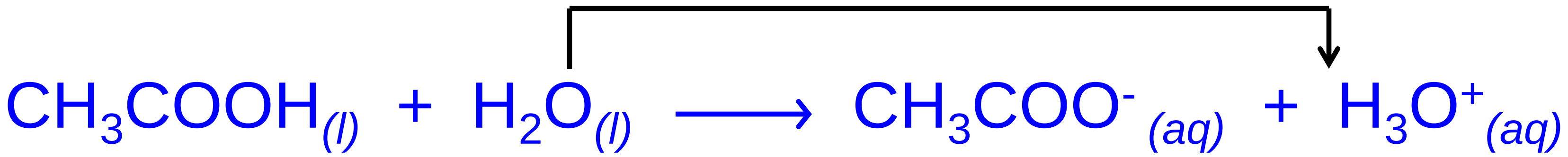
- Definition :

  -

Examples :



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



$$CH_3COOH_{(l)} + H_2O_{(l)} \longrightarrow CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

EXERCISE

$$\underset{\uparrow}{NH_3}\,(g) + \overset{\downarrow}{H_2O}\,(l) \longrightarrow NH_4^+\,(aq) + OH^-\,(aq)$$

$$\underset{\uparrow}{HSO_4^-}\,(aq) + \overset{\downarrow}{H_3O^+}\,(aq) \longrightarrow H_2SO_4\,(l) + H_2O\,(l)$$

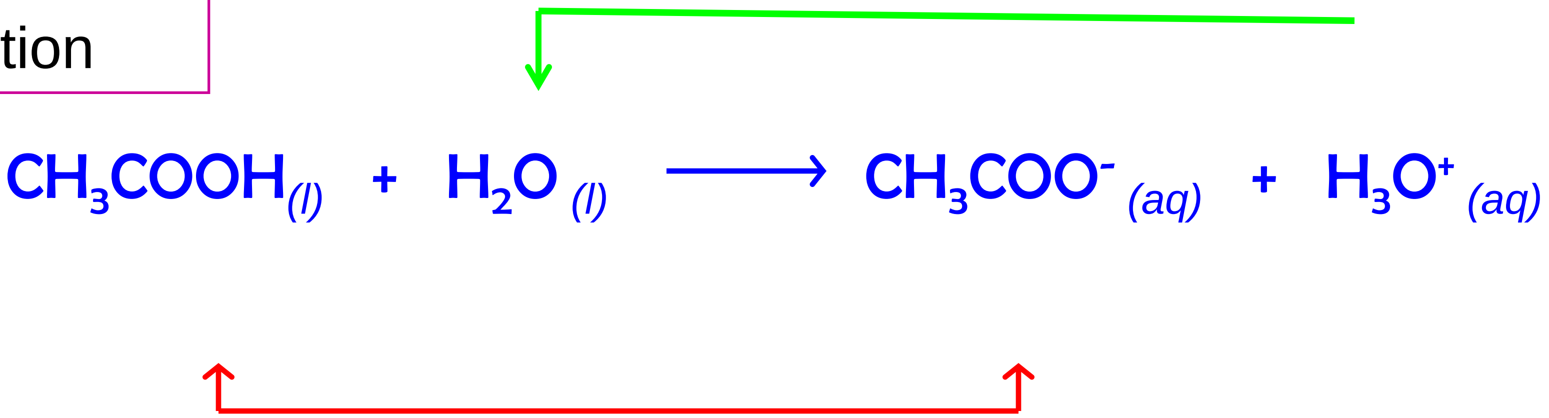
- Extension of BrØnsted-Lowry acids-bases definition:

  - **conjugate acid-base pair**
    - every BrØnsted-Lowry acid has a **conjugate base**
    - every BrØnsted-Lowry base has a **conjugate acid**
    - when an **acid loses a proton** : **conjugate base** is produced
    - when a **base accepts proton** : **conjugate acid** is produced

Example:

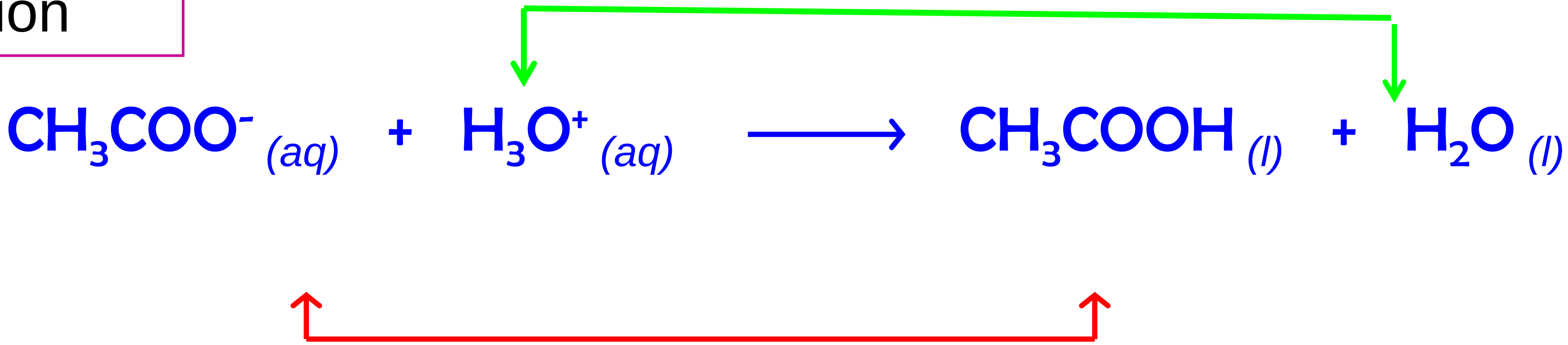
$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

For forward reaction



$$CH_3COOH_{(l)} + H_2O_{(l)} \longrightarrow CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

For reverse reaction



$$CH_3COO^-_{(aq)} + H_3O^+_{(aq)} \longrightarrow CH_3COOH_{(l)} + H_2O_{(l)}$$

EXERCISE

Identify acid, base, conjugate acid and conjugate base for the following reactions :

i. $NH_4^+{}_{(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{3\,(aq)} + H_3O^+{}_{(aq)}$

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

iii. $C_2H_5O^-{}_{(aq)} + H_2O_{(\ell)} \rightleftharpoons C_2H_5OH_{(aq)} + OH^-{}_{(aq)}$

answers

Acid	Base	Conjugate acid	Conjugate base

3. LEWIS THEORY OF ACIDS & BASES

- The Arrhenius and BrØnsted-Lowry theories are further extended by G.N. Lewis

Lewis Theory of an **acid**

-

Lewis Theory of a **base**

-

Example of **Lewis acids**

- **Cations** of metals from Groups 1 & 2 *(eg:* Li^+, Ca^{2+}*)*
- **Cations** of transition metals *(eg:* Cu^{2+}, Fe^{3+}*)*
- Molecules whose central atom with **incomplete octet** *(eg: Al in* $AlCl_3$*, B in* BF_3*)*
- Molecules whose central atom has **1/more multiple covalent bonds** *(eg: C in* CO_2 *;* $O=C=O$*)*

Example of **Lewis bases**

- **All anions** which have a **lone pair to be donated** *(eg: OH^-, Br^-, CN^-)*
- Molecules whose **central atom has a lone pair** to be donated *(eg: N in NH_3 & O in H_2O)*
- Molecules with **multiple covalent bonds between 2 carbon atoms** *(eg: C=C)*

EXERCISE

Identify the **Lewis acid and Lewis base** in the following reactions :

i. $Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$

ii. $SO_3 + CaO \longrightarrow CaSO_4$

iii. $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$

answers

Acid	Base

Objective

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

c) Define pH and pOH.
d) Relate pH and pOH to the ionic product of water, K_w at 25°C.
e) Define strong acid and base, weak acid and base.
f) Relate the strength of a weak acid and and a weak base to the respective dissociation constants, K_a and K_b.
g) Perform calculation involving pH, dissociation constant, initial concentration, equilibrium concentration and the degree of dissociation, α.

pH SCALE

- pH is defined as :

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

- used to measure the $[H^+]$ or $[H_3O^+]$

- pOH is defined as :

$$\boxed{pOH = -\log [OH^-]}$$

- used to measure the $[OH^-]$

DISSOCIATION CONSTANT OF WATER

- H_2O molecules **can both act as an acid and** act as a **base**
- **Auto-ionisation process** of H_2O molecules

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

At equilibrium : $K_c = \frac{[OH^-][H_3O^+]}{[H_2O]^2}$

H_2O is a pure liquid $\therefore$ **$[H_2O]$ is a constant**

$K_c \times [H_2O]^2 = [OH^-][H_3O^+]$

The **dissociation constant for water;** Symbol : K_w

$$\boxed{\therefore \; K_w = [OH^-][H_3O^+]}$$

At 25°C:

$[OH^-] = [H_3O^+] = 1 \times 10^{-7}$ mol dm^{-3}

$\therefore$ At 25°C $\quad K_w = (1 \times 10^{-7}) \times (1 \times 10^{-7})$

$$= \boxed{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}$$

- At 25°C,

$$K_w = [OH^-]\,[H_3O^+] = 1 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

$$-\log K_w = -\log([OH^-]\,[H_3O^+]) = -\log 1 \times 10^{-14}$$

$$-\log K_w = -\log [OH^-] - \log [H_3O^+] = -\log 1 \times 10^{-14}$$

$$\boxed{pK_w = pOH + pH = 14}$$

THE STRENGTH OF ACIDS AND BASES

- The relative **strength of acids and bases** can be compared based on :
  - **degree of dissociation (α)** in water
    - \- the fraction of the total amount of the molecules @ ions that has split into smaller molecules @ ions in a reaction
  - **dissociation constant**

STRONG *ACIDS*

- **dissociate completely** in water

$$HNO_{3\,(aq)} \longrightarrow H^{+}_{(aq)} + NO_{3\,(aq)}^{-}$$

0.5M **0.5M**

- $\alpha = 1$ @ 100%
- $[H^+]$ or $[H_3O^+]$ can be obtained from the **original concentration of the acid**
- examples :

i. HNO_3 iii. HCl v. HI

ii. H_2SO_4 iv. HBr

STRONG ***BASES***

- **dissociate completely** in water

$$\underset{0.1M}{NaOH_{(aq)}} \longrightarrow Na^{+}_{(aq)} + \underset{0.1M}{OH^{-}_{(aq)}}$$

- α = 1 @ 100%
- $[OH^-]$ can be obtained from the **original concentration of the base**
- examples :

i. NaOH iii. $Mg(OH)_2$
ii. KOH iv. $Ca(OH)_2$

EXAMPLE

Calculate the pH of the following solution :

1. An aqueous solution contains 0.700g NaOH in 485 mL H_2O, where NaOH is a strong base.
2. A solution of 5.0×10^{-3} M H_2SO_4.

SOLUTION :

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

$$\boxed{pOH = -\log [\, OH^{-} \,]}$$

$$\boxed{pOH + pH = 14}$$

SOLUTION :

2. $H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO_4^-{}_{(aq)}$

WEAK ACIDS AND WEAK BASES

- **dissociate partially** in water
- **α = < 1** @ < 100%
- **α value** can be determined by :

DISSOCIATION CONSTANT FOR WEAK ACIDS

- Consider the following general equation :

$$HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

At equilibrium :

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

[H_2O] is constant

$$K_c \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_c \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

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

$$\therefore\ pK_a = -\log K_a$$

For weak acids :

- α value is **less than 1** @ less than 100%
- [H_3O^+] is **less than** [acid]
- [H_3O^+] can be calculated as follows :

Given, the $[HA]_o$ =

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

$[\ ]_o$				
Δ				
[ ] at equilibrium				

The ionisation expression is;

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

$$= \frac{(x) \times (x)}{a - x}$$

If K_a and a were given, value of x can be found.
Since $x = [H_3O^+]$

Thus, pH = $-\log [H_3O^+]$

For weak acid,

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

$$= \frac{(x) \times (x)}{a - x}$$

Assume HA is a weak acid , x **is too small;** $x \ll 1$;

$\therefore$ $[HA] = a - x \approx a$

Thus the expression can be simplified:

K_a =

EQULIBRIUM CALCULATIONS WHEN K_a IS VERY SMALL

- ☞ The concentration change (*x*) can often be neglected.

$$[A]_{initial} - x = [A]_{equilibrium} \approx [A]_{initial}$$

Note: You must check that the assumption is justified or not.

CHECK: 5% rule

$$\frac{x}{[A]_{initial}} \times 100 < 5\%$$

- ☞ Assumption is OK

$$\frac{x}{[A]_{initial}} \times 100 > 5\%$$

- ☞ Assumption is NOT OK
- ☞ Use quadratic formula

EXAMPLE

Calculate

i. pK_a

ii. pH

iii. Degree of association

of 0.01 mol dm^{-3} nitrous acid, HNO_2

($K_a = 5.1 \times 10^{-6}$ mol dm^{-3})

SOLUTION

ii)

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

$[\ ]_o$				
Δ				
[ ] at equilibrium				

OR

**CHECK:
5% rule**

SOLUTION

iii) Degree of dissociation, α

$$\boxed{\alpha_{\text{weak acid}} = \frac{[H_3O^+]\ \text{dissociated}}{[\text{acid}]\ \text{before dissociation}}\ \text{x}\ 100\%}$$

SUMMARY OF K_a

- When **K_a is small**, **α is low**, ∴ the **strength of the acid is**
- When **K_a is small**, **pK_a value is**
- The **bigger the K_a**, the
- The **smaller the pK_a**, the
- K_a is **affected by**

DISSOCIATION CONSTANT FOR WEAK BASES

- Consider the following general equation :

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

At equilibrium :

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

$[H_2O]$ is constant

$$\boxed{K_c \times [H_2O]} = \frac{[BH^+][OH^-]}{[B]}$$

$$K_c \times [H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

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

$$pK_b = -\log K_b$$

- For **weak bases** :
  - α value is **less than 1** @ less than 100%
  - [OH^-] is **less than** [bases]
  - [OH^-] can be calculated as follows :

Given, the $[B]_o = a$ mol dm^{-3}

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

$[\ ]_o$				
Δ				
[ ] at equilibrium				

The ionisation expression is;

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

$$= \frac{(x) \times (x)}{a - x}$$

If K_b and a were given, value of x can be found.
Since x = $[OH^-]$

Thus, pH = 14 – pOH; where pOH = - log $[OH^-]$

For weak base,

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

$$= \frac{(x) \times (x)}{a - x}$$

Assume B is a weak base , **x is too small;** x <<1;

$\therefore$ [B] = $a - x \approx a$

Thus the expression can be simplified:

K_b =

EXAMPLE

Calculate the pH value of 0.1 mol dm^{-3} NH_2OH

(K_b = 9.1 x 10^{-9} mol dm^{-3})

SOLUTION

$$NH_2OH_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_3OH^+_{(aq)} + OH^-_{(aq)}$$

[ ]o				
Δ				
[ ] at equilibrium				

OR

GUIDELINE IN PROBLEM SOLVING RELATED TO WEAK ACIDS @ BASES

- **Write** the dissociation equation of the weak acid/base
  - **Dissociate partially**
- Tabulate the data
  - Enter the **[ ]$_o$** of all species
  - Determine the **Δ in [ ]**
  - Write the **[ ] at equilibrium**
- Enter the [ ] at equilibrium into **K_a @ K_b expression**
- **Solve for *x*** by assuming ***a* – *x* = *a***
- Determine **[H^+] @ [OH^-] & pH** value

EXERCISE

For ethanoic acid, CH_3COOH of 0.5M, determine :

i. $[H^+]$

ii. α

iii. pH

(K_a $CH_3COOH = 1.8 \times 10^{-5}M$)

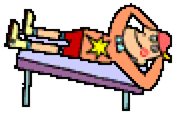
Given, at 25°C, 0.15M $C_4H_9NH_2$ solution, pH = 12. Determine

i. K_b

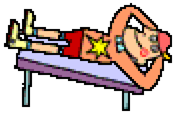
ii. α

$$C_4H_9NH_2 + H_2O \rightleftharpoons C_4H_9NH_3^+ + OH^-$$

EXERCISE



At 25°C, 0.1 M formic acid, HCOOH was dissociated at 4.2% in aqueous solution. Determine the K_a and pK_a of the formic acid



Determine the pH of 0.1 M CH_3COOH solution with $K_a = 1.85 \times 10^{-5}$ M at 25°C

RELATIONSHIP BETWEEN K_a AND K_b

- consider the following conjugate acid-base pair

$$NH_4^+\,_{(aq)} + H_2O\,_{(l)} \rightleftharpoons NH_{3\,(aq)} + H_3O^+\,_{(aq)}$$

- **For forward reaction :**

$$\underset{\text{acid}}{NH_4^+\,_{(aq)}} + H_2O\,_{(l)} \longrightarrow \underset{\text{conjugate base}}{NH_{3\,(aq)}} + H_3O^+\,_{(aq)}$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- **For reverse reaction :**

$$NH_3\,(aq) + H_2O\,(l) \longrightarrow NH_4^+\,(aq) + OH^-\,(aq)$$

base

conjugate
acid

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

- **net reaction =** forward reaction x reverse reaction

$$= K_a \times K_b$$

$K_a \times K_b =$

Objective

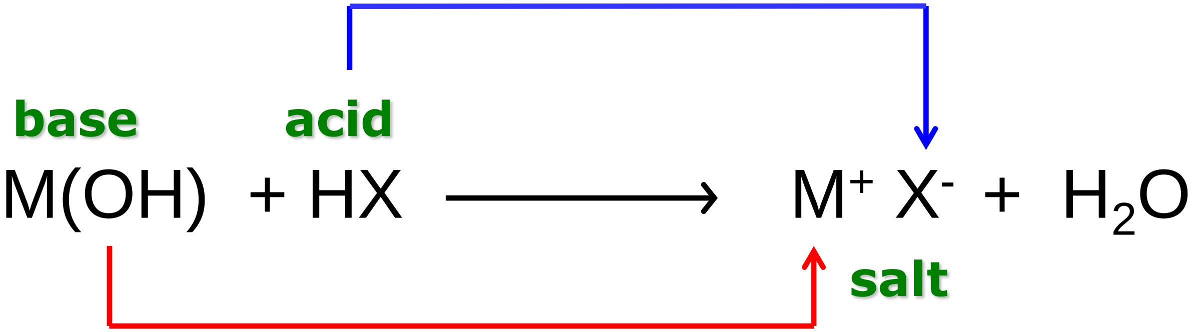
At the end of this topic, students should be able to:

h) Explain salt hydrolysis equation for the salt formed from the reaction between:
  - strong acid and strong base
  - strong acid and weak base
  - weak acid and strong base

i) Classify the slats as neutral, acidic or basic.

PROPERTIES OF SALT

- an **ionic compound**
- formed when an **acid neutralises a base**
- are strong electrolytes; i.e. **completely dissociate** to form ions in H_2O



- general eq^n: $\overset{\textbf{base}}{M(OH)} + \overset{\textbf{acid}}{HX} \longrightarrow \underset{\textbf{salt}}{M^+ X^-} + H_2O$
- classified as **neutral, acidic or basic salt** through **hydrolysis process**

- Hydrolysis : a chemical reaction between anion and/or cation of a salt, with H_2O
- Occurs when weak acid reacts with strong base @ strong acid with weak base
- either cations @ anions are hydrolyse

- **pH of solution** : depends on whether the **cation or anion** of the salt **is hydrolysed**

$$\underset{\textit{salt}}{MX} \longrightarrow M^+ + X^-$$

If **cation, M⁺** is hydrolysed :

$$M^+ + H_2O \rightleftharpoons MOH + H^+$$

∴ H^+ presence ; **acidic solution** is obtained

If **anion, X⁻** is hydrolysed :

$$X^- + H_2O \rightleftharpoons HX + OH^-$$

∴ OH^- presence ; **basic solution** is obtained

SALT OBTAINED FROM STRONG ACID + STRONG BASE

- formed neutral salt
- pH of salt solution = 7
- neutral salt : NaCl, Na_2SO_4, KNO_3
- eg : $HCl + NaOH \longrightarrow NaCl + H_2O$
- completely dissociate; i.e. $NaCl \longrightarrow Na^+ + Cl^-$
- cation & anion : do not hydrolyse

SALT OBTAINED FROM STRONG ACID + WEAK BASE

- formed **acidic salt**
- acidic salt : NH_4Cl, $CuSO_4$
- eg : $HCl + NH_3 \longrightarrow NH_4Cl$

- dissociation : $NH_4Cl \longrightarrow NH_4^+ + Cl^-$
- **cation** : hydrolyse in H_2O

  $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

- **pH < 7**

SALT OBTAINED FROM WEAK ACID + STRONG BASE

- formed **basic salt**
- basic salt : CH_3COONa, Na_2CO_3, KCN, Na_2SO_3
- eg : $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

- dissociation : $CH_3COONa \longrightarrow CH_3COO^- + Na^+$
- **anion** : hydrolyse in H_2O

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

- **pH > 7**

SUMMARY

Type of acid/base	Type of salt	Species which hydrolyse	pH solution	Examples
strong acid + strong base	neutral	none	7	NaCl, KI, KNO_3, $NaSO_4$
strong acid + weak base	acidic	cation	< 7	NH_4Cl, $(NH_4)_2CO_3$, $CuSO_4$
weak acid + strong base	basic	anion	> 7	CH_3COONa, KCN, NaCN, Na_2S