COURSE CODE:    CHM 104

COURSE TITLE:  INTRODUCTORY INORGANIC CHEMISTRY

NO OF UNITS:           02

COURSE DURATION:    TWO HOURS PER WEEK

## COURSE DETAILS:

PART TITLE:                    ACID, BASE AND SALT

## COURSE CONTENT:

COURSE LECTURER:    DR. S.A. AHMED

## COURSE REQUIREMENTS:

- Concepts of acid and base

- Arrhenius concept
- Brönsted-Lowry concept
- Conjugate acid-base pairs
- Lewis concept

- Relative strength of acid and base

- The pH and pOH of solutions
  - Relationship between pH and pOH
  - Water auto ionization
  - Numerical problems on pH and pOH

- Salt Hydrolysis
  - Hydrolysis constant
  - Relationship between $K_h$, $K_w$ and $K_a$
  - Relationship between hydrolysis constants and degree of hydrolysis

- Buffer solution
  - Orientation of buffer
  - Henderson-Hasselbalch equation

**COURSE REQUIREMENTS:**

Students are expected to have a minimum of 75% attendance in this course before they could be allowed to write the examination.

## READING LIST:

1. Gross, J.M. and Wiseall, B. *Principle of physical chemistry*. MacDonald and Evans Handbook series, 1972

2. Atkins, P.W. *Physical chemistry*. Oxford University Press, sixth edition, 1999

3. Bahl, A and Bahl, B.S. *Essentials of physical chemistry*, S.Chand and Company Ltd. 2007

4. Brown, T.L., Lemay, H.E., Bursten, B.E and Murphy, C.J *Chemistry: The central science*. Pearson Education, 11th Edition 2009.

5. Sharma, K.K. and Sharma, L.K. *Physical chemistry*
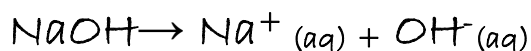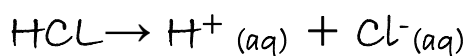
## LECTURE NOTES

# Concepts of acid and base

There are three concepts of acids and bases, they are:

(i)     Arrhenius concept

(ii)    Brönsted-Lowry concept

(iii)   Lewis concept

## Arrhenius concept

An acid is a compound that releases $H^+$ ions in water and a base is a compound that releases $OH^-$ ions in water.

e.g. HCl is an Arrhenius acid and NaOH is an Arrhenius base

$$HCL \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

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

## Limitations

(a) Definition limited to water only.

(b) Bases like Ammonia ($NH_3$) and basic oxide like MgO, CaO etc are left out in the definition of base.

(c) Free $H^+$ and $OH^-$ do not exist in water.

## Brönsted-Lowry concept

An acid is a molecule or ion that can donate a proton ($H^+$),
A base is a molecule or ion that can accept a proton.
e.g. when HCl gas dissolves in water. Each HCl molecule donates a proton to a water molecule to produce hydronium ion. HCl is a Bronsted acid and water is a Bronsted base.
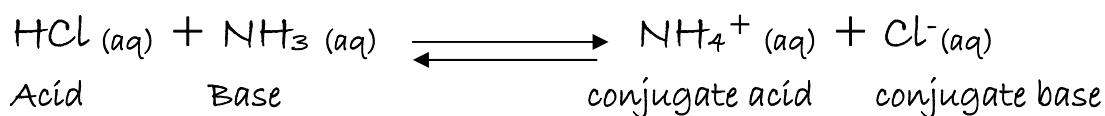
NB: More examples and illustrations on this concept shall be treated during the lecture hours.

<u>Conjugate Acid-Base pairs</u>

In an acid-base reaction, the acid (HA) gives up its proton ($H^+$) and produces a new base ($A^-$). The new base that is related to the original acid is a <u>conjugate base</u>. Similarly, the original base ($B^-$) after accepting a proton ($H^+$) gives a new acid (HB) and it is called a <u>conjugate acid</u>.

Conjugate pair

$$HA + B^- \rightleftharpoons HB + A^-$$
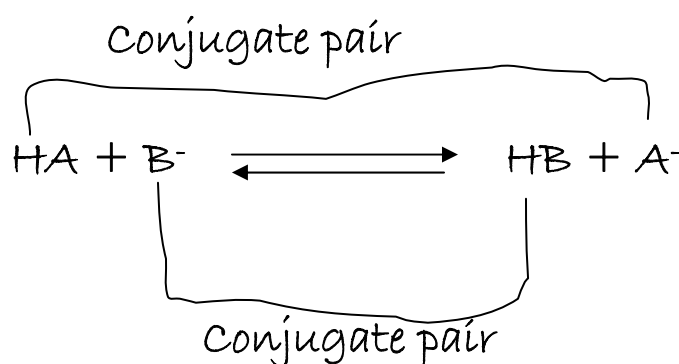
Conjugate pair

In every acid-base reaction involving H+ transfer, there are two acid-base conjugate pairs, e.g. reaction between HCl and $NH_3$.

$$HCl_{(aq)} + NH_{3\ (aq)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

Acid       Base       conjugate acid    conjugate base

In the example above, HCl (acid) and $CL^-$ (conjugate base) constitute one acid-base conjugate pair while $NH_3$ (base) and $NH_4^+$ (conjugate acid) make the second acid-base conjugate pair.

N.B: if the acid of a conjugate acid –base is strong, then the conjugate base will be weak. Therefore, a weak base has a strong conjugate acid and a weak acid has a strong conjugate base.

NB: More examples and illustrations on this concept shall be treated during the lecture hours.

Limitations

1. Neutralization reaction between $MgO_{(s)}$ and $SO_3$ to form $MgSO_4$ does not involve proton transfer.
2. Also, reaction between $BF_3$ and $NH_3$

Lewis Concept of acids and bases

An acid is an electron -pair acceptor and a base is an electron-pair donor.

Electron-pair donated by the base is used by the acid to form covalent (or coordinate) bond between the Lewis acid and Lewis base. The resulting combination is called a complex.

e.g.     A    +    : B ⟶ A—B

          Lewis acid        Lewis base        complex

NB: More examples and illustrations on this concept shall be treated during the lecture hours.

Relative Strength of Acids and Bases

1. For acid:

The strength of an acid is its tendency/ability to transfer its proton [H⁺] to a base to form its conjugate base.

OR

Is the concentration of [H⁺] in the aqueous solution of an acid.

When a monoprotic acid (HA) dissolves in water, it transfer its proton to water (a Bronsted base) to form hydronium ion (H₃O⁺) and a conjugate base.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (1)$$
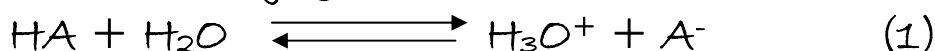
For simplification, let H₃O⁺ = H⁺, eqn. 1 becomes

$$\underset{c(1-\alpha)}{HA} + H_2O \rightleftharpoons \underset{c\alpha}{H^+} + \underset{c\alpha}{A^-} \qquad (2)$$
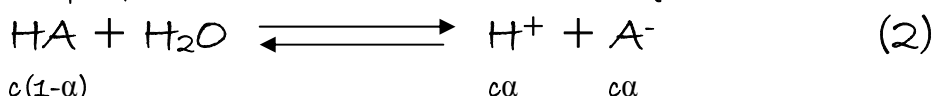
Applying the law of mass action to the acid dissociation equilibrium,

$$\therefore \qquad K_a = \frac{[H^+][A^-]}{[HA]} \qquad (3)$$

In dilute solution, the concentration of water [H₂O] is taken as constant, $K_a$ is the acid dissociation constant and it is a measure of acid strength.

$$K_a = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \qquad (4)$$

N.B: The value of $K_a$ is very large for strong acid because [HA] dissociate completely, vice-versa for the weak acid. Also, the concentration of the [H⁺] depends on the value of $K_a$.

For weak acids, $1-\alpha \approx 1$

$$\therefore \quad K_a = c\alpha^2$$

For two different acids, say acid 1 and 2, the dissociation constant $K_1$ and $K_2$ are expressed as

Acid 1: $\qquad K_1 = c\alpha_1^2$ $\hspace{3cm}$ (i)

Acid 2: $\qquad K_2 = c\alpha_2^2$ $\hspace{3cm}$ (ii)

Divide equation (i) by (ii)

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}$$

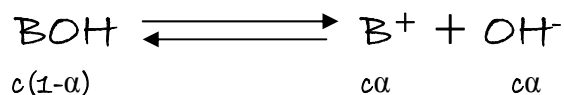Since $[H^+]$ is a measure of acid strength and it depends on the degree of dissociation.

$$\therefore \quad \frac{strength\,of\,acid_1}{strength\,of\,acid_2} = \sqrt{\frac{K_1}{K_2}}$$

NB: More examples and illustrations on this topic shall be treated during the lecture hours.

2. For bases:

According to Arrhenius model, a base is a substance which produces $OH^-$ in aqueous solution.

So,

$$BOH \rightleftharpoons B^+ + OH^-$$

$\hspace{2.5cm}$ $c(1-\alpha)$ $\hspace{3cm}$ $c\alpha$ $\hspace{1.5cm}$ $c\alpha$

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

$K_b$ is the base dissociation constant

The strength of a base is defined as the concentration of OH ion its aqueous solution at a given temperature.

For Bronsted bases which do not conform to the Arrhenius definition of a base e.g. $NH_3$ and amines

i.e.   B   +   $H_2O$   ⇌   $BH^+$   +   $OH^-$
       base        acid              conjugate acid    conjugate base
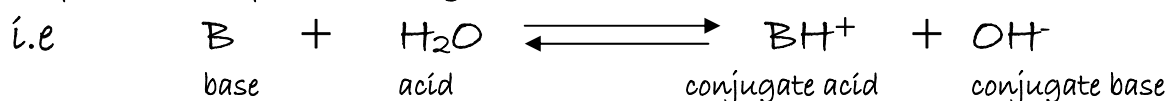
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$K_b = \frac{c\alpha^2}{1-\alpha}$$

## The pH and pOH of solutions

The pH of a solution is defined as the negative of the base-10 logarithm (log) of the $H^+$ ion concentration.

i.e.  pH= -log$[H^+]$  where $[H^+]$ is the concentration of the hydrogen ion in mol/L.

Mathematically,

$$pH = \log\frac{1}{[H^+]}$$   OR   $[H^+] = 10^{-pH}$

Similarly, pOH of a basic solution is the negative of the base-10 logarithm of the $OH^-$ concentration.

$$pOH = \log\frac{1}{[OH^-]}$$

i.e.

WATER AUTOIONIZATION

The Bronsted-Lowry theory designates water as an acid in its reactions with bases and as a base in its reactions with acids. This implies that water can react with itself acting both as an acid and a base.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$
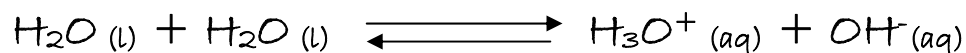
In the above reaction, water dissociates to $H_3O^+$ and $OH^-$ ions to a very small degree.

$$2 H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \qquad (i)$$

At equilibrium,

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad (ii)$$

Since water is so little dissociated, the concentration of the molecule, $[H_2O]$ is taken to be constant.

$\therefore [H_3O^+][OH^-] = K[H_2O] = K_w$

Experimentally, the value of $K_w$ at 25°C is $1.0 \times 10^{-14}$

$\Rightarrow \quad [H_3O^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}}$

$\therefore [H^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L

Thus, in pure water, the concentrations of $[H^+]$ and $[OH^-]$ are equal at 25°C i.e. neutral.

In acidic solution, $[H^+] > [OH^-]$

In basic solution, $[H^+] < [OH^-]$

pH scale is used in expressing the [H$^+$] or [OH$^-$] I term of pH for different solution.

<u>Relationship between pH and pOH</u>

Recall that pH=-log [H$^+$] and pOH = -log [OH$^-$]

Similarly, pK$_w$ = -log K$_w$

So, K$_w$= [H$^+$] [OH$^-$]

Log K$_w$= log [H$^+$] + log [OH$^-$]

OR

-Log K$_w$= -log [H$^+$] - log [OH$^-$]

Thus, pK$_w$ = pH + pOH

Since K$_w$=$1.0 \times 10^{-14}$

pK$_w$=-log $(1.0 \times 10^{-14})$= 14.0

N.B: Numerical treatment of problems involving pH, pOH and pK$_w$ shall be extensively treated during the lecture hours.
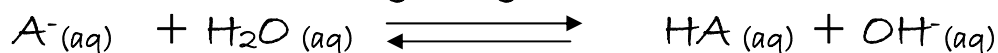
<u>SALT HYDROLYSIS</u>

Hydrolysis is defined as the reaction of water with the conjugate base of a weak molecular acid (anion) or with the conjugate acid of a weak molecular base (cation).

In anionic hydrolysis, the solution becomes slightly basic due to the generation of excess OH$^-$ ions; e.g. the reaction between acetate ion and water.

Also, cationic hydrolysis involves the generation of excess $H^+$ which makes the solution slightly acidic; e.g. reaction between ammonium ion and water.
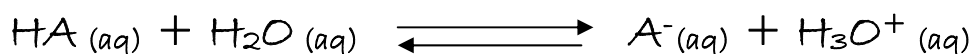
### Hydrolysis constant

Consider this anionic hydrolysis reaction:

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

The hydrolysis constant, $K_h$ can be expressed as

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

For the reverse reaction (i.e. ionization of HA),

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

The value of $K_h$ for this reaction is the reciprocal of that for ionization of HA because the equation is the reverse of the ionization reaction. (i.e. $\frac{1}{K_a}$)

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

The hydrolysis constant, $K_h$ is related to acid and water dissociation constant $K_a$ and $K_w$ respectively by the expression:

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

From the expression above, it can be seen that the weaker the acid, the greater the hydrolysis constant of the salt.

Similarly, for the hydrolysis of the conjugate acid of a weak base is expressed as

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

The hydrolysis constant for salts of weak acid and weak base

is given by $\quad\quad K_h = \dfrac{K_w}{K_a \times K_b}$

## Relationship between hydrolysis constant and degree of hydrolysis

The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is represented by α. The degree of hydrolysis for salt of weak base and strong acid is given by

$$\alpha = \sqrt{\frac{K_w}{K_h \times C}}$$

Similarly, the degree of hydrolysis of salt of weak acid and weak base is given by

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

N.B: Examples and problems related to this topic shall be treated during the lecture hours.

## BUFFER SOLUTION

A buffer solution is a solution which maintains its pH fairly constant even upon the addition of small amounts of acid or base.

Two common types of buffer solutions are:

(i)     Acid buffers- formed by a weak acid and its salt with a strong base. e.g. $CH_3COOH + CH_3COONa$

(ii)    Basic buffer- formed by a weak acid and its salt with a strong base. e.g. $NH_4OH + NH_4Cl$

### Operation/ action of Buffer

Consider this acid buffer:  $CH_3COOH/CH_3COONa$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad (i)$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+ \qquad (ii)$$
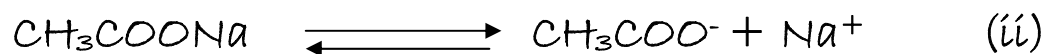
Since the salt is completely ionized, it provides the common ions $CH_3COO^-$ in excess. The common-ion effect suppresses the ionization of the acetic acid. This reduces the concentration of $H^+$ ion thereby raising the pH of the solution.

N.B: Diagrams and other illustrations on this topic shall be provided during the lecture hour.

### Henderson- Hasselbalch Equation

The pH of the buffer solutions can be calculated using the Henderson- Hasselbalch equation as expressed below

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$    For acid buffers

And

$$pH = pK_b + \log\frac{[salt]}{[base]}$$    For basic buffers

N.B: Numerical treatment of problems involving buffer solutions shall be treated during the lecture hours.