IONIC EQUILIBRIUM

INTRODUCTION

1.Equilibrium is the state at which the concentration of reactants and products do not change with time .

2. Equilibrium may also be defined as state of process in which properties like temperature,colour,pressure,

Concentration of the system do not show any change with time.

TYPES OF EQUILIBRIUM

- **PHYSICAL EQUILIBRIUM**—If the opposing processes involves only physical changes(melting of ice water)the equilibrium is called physical equilibrium.
- **CHEMICAL EQUILIBRIUM**—If opposing processes involves chemical changes(the reaction between H_2 and I_2)the equilibrium is called chemical equilibrium

TERMS USED IN IONIC EQUILIBRIUM

ELECTROLYTE---

An electrolyte may be defined as substance which either in molten state or in aqueous solution can conduct electricity.Acids ,bases and salts are mostly electrolytes.There are two types of electrolytes.

TYPES OF ELECTROLYTES

- **STRONG ELECTROLYTES--**

  THE ELECTROLYTES WHICH ARE ALMOST COMPLETELY IONIZED IN Aq. SOLUTION.
  Eg.H_2SO_4 ,HCl
- **WEAK ELECTROLYTES**—THE ELECTROLYTES WHICH ARE IONIZED TO SMALL EXTENT IN Aq. SOLUTION .

  Eg.CH_3COOH,NH_4OH

Ionization of an Electrolyte in aqueous solution

The molecules of some compounds, when dissolved in water gets decomposed in two types of charged particles called ions.The ions which carry positive charge are called cations . The ions which carry negetive charge are called Anions.Initially, very few molecules get decomposed into ions. Gradually, the concentration of ions increases.When the concentration of ions becomes too high, the ions reunite to form molecules again. At certain stage, Equilibrium is set up.This state of process is called ionic equilibrium.

Arrhenius Theory of Ionization

The main points of theory are---

1. When an electrolyte is dissolved in water,it splits up into charged particles called ion. The process of splitting of an electrolyte into ions is called ionization.
2. The positively charged ions are called cations and negatively charged ions are called anions.
3. The total charge on cation is equal to that on the anions and solution as a whole is electrically neutral.

Arrhenius Theory of Ionization

(contd.)

4.The ions present in solution constantly reunite to form molecules and there exists a state dynamic equilibrium between the ions and unionized molecules eg.

$$AB_{(S)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)}$$

5.The properties of electrolyte are the properties of ions .The conductivit depend on number of ions .

Contd.

6.At moderate concentration, only a fraction of the total amount of electrolyte ionizes.The fraction of total number of molecules of an electrolyte which ionizes on dissolution is called degree of ionization.

FACTORS INFLUENCING THE DEGREE OF IONIZATION

1.DILUTION

2.TEMPERATURE

3.NATURE OF SOLUTE

4.NATURE OF SOLVENT

5.PRESENCE OF OTHER SUBSTANCES

OTHER RELATED TOPICS

1. Ionic equilibrium in Aq solution(derivation of ostwald dilution law)

$$K = C\alpha^2$$

2. Ionization of water

3. Concept of pH

IONIC EQUILIBRIUM IN Aq. SOLUTION

When weak acid AB(acetic acid)is dissolved in water it dissociates into $A^+$and B^- and following eq. is obtained

$$AB \leftrightarrow A^+ + B^-$$

Initially t =0	C	0	0
At equilibrium	C(1-α)	Cα	Cα

Contd.

dissociation constant may be given

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{(C\alpha * C\alpha)}{C(1-\alpha)}$$

$$= C\alpha^2/(1-\alpha) \ldots\ldots\ldots \text{(i)}$$

For very weak electrolytes,

$\alpha <<< 1$, $(1 - \alpha) = 1$.·. $K = C\alpha^2$

$\alpha = \sqrt{K/C}$ ..... (ii)

Contd.

- **$\alpha = \sqrt{K/C}$ .....** (ii)
- For a weak electrolyte degree of ionization is inversely proportional to molar conc.
-

From equation (ii) **it is a clear that degree of ionization increases on dilution.**

SELF IONIZATION OF WATER: Pure water is poor conductor of electricity.This shows that water is weak electrolyte and dissociates to a small extent

$$H_2O \leftrightarrow H^+ + OH^-$$

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

This equilibrium applies to pure water and any aqueous solution. The chemical equilibrium constant, K_{eq}, for this reaction is given by

Contd.

***Keq* for this reaction is given by**

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

$$k = \frac{[H_3O^+]\ [OH^-]}{[H_2O]^2} \quad (2)$$

$$[\ H_2O]^2 = \text{constant}$$

Eq (2) may be written as

Contd.

Eq.2 may be written as

$[H_3O^+]\ \ [OH^-] = K\,[H_2O]^2$

=constant x constant

=**Kw ,** called **ionic product of water**

It must be noted that ionic product of water is constant only at constant temperature . Its value at 298 K is found to be 1.008×10^{-14}

$K_W = 1.008 \times 10^{-14}$

Effect of temperature:

The ionic product increases with increase in temperature.

This is because with increase in temperature degree of

Ionization of water increases increases

$[H_3O^+]$and $[OH^-]$ ion concentration in pure water at 298 K

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

For any degree of ionization we will have

$$[H_3O]^+ = [OH^-]$$

But at 298 K

$$Kw = [H_3O^+]\ [OH^-] = 1.0 \times 10^{-14}$$

$$[H_3O^+]^2 = 1.0 \times 10^{-14}$$

$$[H_3O^+] = 1.0 \times 10^{-7}\ mol/l$$

Thus in pure water at 298 K

$$[H_3O]^+ = [OH^-] = 1.0 \times 10^{-7}\ mol/l$$

Contd

If some acid is added to pure water then

$[H_3O^+] > 1.0 \times 10^{-7}$ mol/l

Since Kw is constant, thus $[OH^-]$ decreases and may be calculated as

$$[OH^-] = \frac{Kw}{[H_3O^+]}$$

If some base is added to pure water then

$[OH^-] > 1.0 \times 10^{-7}$ mol/l

Since Kw is constant, thus $[H_3O^+]$ decreases and may be calculated as

$$[H_3O^+] = \frac{Kw}{[OH^-]}$$

In general,

- **For acidic solution:** $[H_3O^+] > [OH^-]$
- **For basic solution:** $[H_3O^+] < [OH^-]$
- **For neutral solution:** $[H_3O^+] = [OH^-]$

Concept of pH

The symbol pH has been taken from danish word ‘potenz the hydrogen ion’which means power of hydrogen ion.

The pH of solution may be defined as negetive logarithm of hydrogen ion concentration.

$$\mathbf{pH = -\log [H_3O^+]} \qquad (1)$$

$$= \log \frac{\mathbf{1}}{[H_3O^+]} \qquad (2)$$

Contd.

From eq.(1)

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

Taking antilog both sides

$[H_3O^+] = 10^{-pH}$

Thus pH may be defined as negative power to which 10 must be raised to equal the hydrogen ion concentration.

For neutral solutions, $[H_3O^+] = 1 \times 10^{-7}$ mol/l at 298K

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

$$= -\log [1 \times 10^{-7}]$$

$$= -(-7) \log 10$$

$$= +7$$

Acidic or basic solutions can be distinguished on basis of pH

- For neutral solutions $[H_3O^+] = 10^{-7}$ or pH=7
- For acidic solutions $[H_3O^+] > 10^{-7}$ or pH < 7
- For basic solutions $[H_3O^+] < 10^{-7}$ or pH > 7

pH of Solution

- For an acidic solution ---- pH < 7
- For an basic solution -----pH > 7
- For an neutral solution-----pH = 7

Relationship between pH and pOH

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

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

$$[H_3O^+][OH^-] = 10^{-14}$$

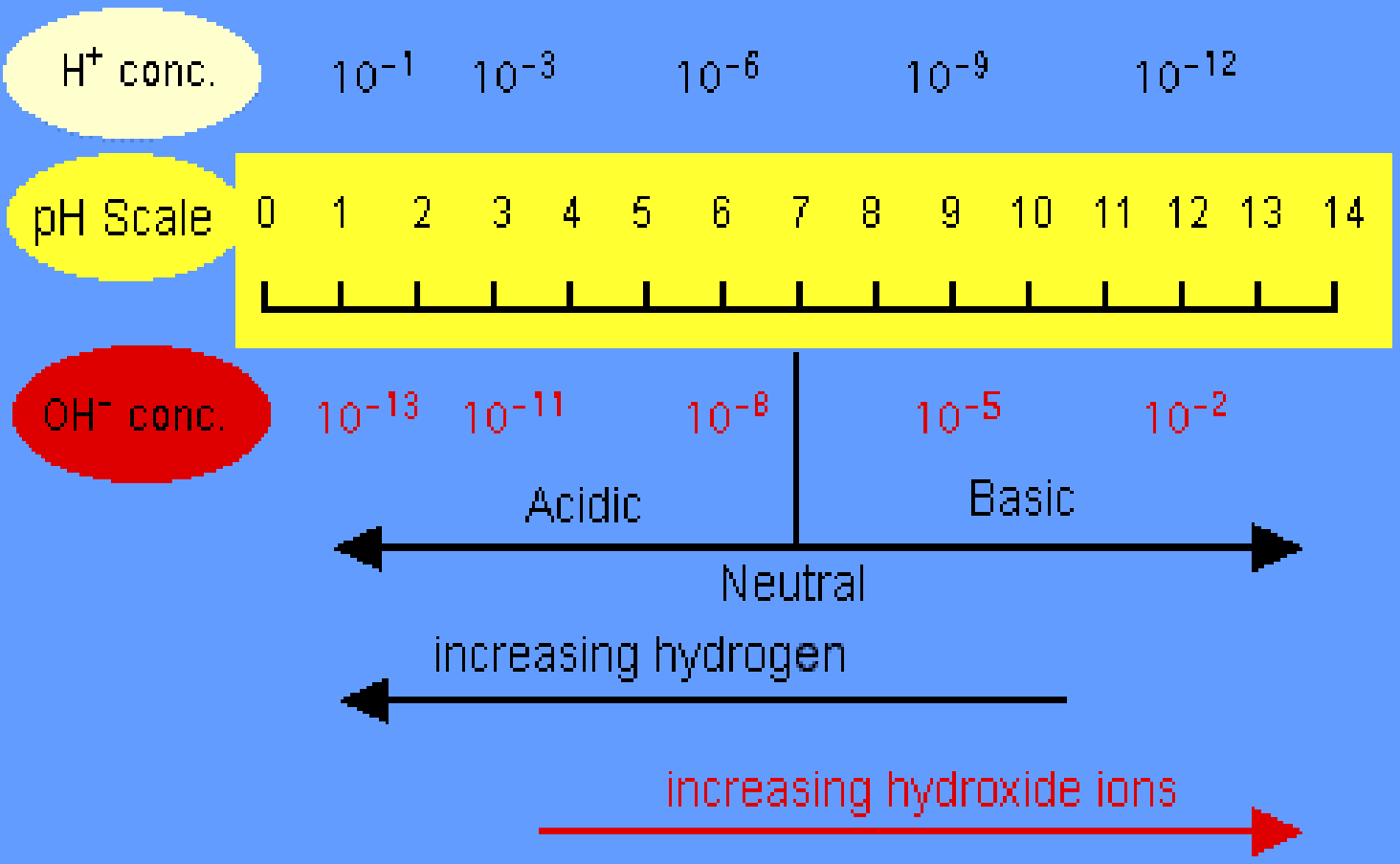
$$\log[H_3O^+] + \log[OH^-] = \log 10^{-14}$$

$$\log[H_3O^+] + \log[OH^-] = 14$$

$$-\log[H_3O^+] - \log[OH^-] = 14$$

$pH + pOH = 14$

pH Scale



C. Ophardt, c. 2003

Example: If an acid has an H^+ concentration of 0.0001 M, find the pH.

Solution:

First convert the number to exponential notation, find the log, then solve the pH equation.

$H^+ = 0.0001M = 10^{-4}$; log of $10^{-4} = -4$;

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

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

$= - (-4)$

$= +4 = pH$

Example:

If the base has an OH^- concentration of 0.001M, find the pH.

Solution:

First find the pOH, (similar to finding the pH,) then subtract the pOH from 14.

$OH^- = 0.001M = 10^{-3}$;

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

$= -\log (10^{-3})$

$= +3 = pOH$

$pH = 14 - pOH$; $pH = 14 - 3 = 11 = pH$

BRIEF REVIEW OF TOPIC

- **IONIC EQUILIBRIUM**
- **TYPES OF EQUILIBRIUM**
- TERMS USED IN IONIC EQUILIBRIUM
- **Arrhenius Theory of Ionization**
- **FACTORS INFLUENCING THE DEGREE OF IONIZATION**
- Ionic equilibrium in Aq solution(derivation of ostwald dilution law)

$$K = C\alpha^{2.}$$

. Ionization of water

. Concept of pH

BUFFER SOLUTIONS

1. a) What is a buffer solution?

   b) Give an example of a buffer solution with a pH less than 7.

   c) Give an example of a buffer solution with a pH greater than 7.

2. This question is about a buffer solution made by mixing together solutions containing ethanoic acid and sodium ethanoate.

   a) If you add a small amount of an acid such as dilute hydrochloric acid to this, the pH doesn't change much. Explain what happens to the extra hydrogen ions you have added.

   b) If you add a small amount of an alkali such as sodium hydroxide solution to the buffer solution, again the pH doesn't change much. There are two ways in which the extra hydroxide ions can be removed. What are they?

3. This question is about a buffer solution made by mixing together solutions containing ammonia and ammonium chloride.

   a) If you add a small amount of an acid such as dilute hydrochloric acid to this, the pH doesn't change much. There are two ways in which the extra hydrogen ions can be removed. What are they?

   b) If you add a small amount of an alkali such as sodium hydroxide solution to the buffer solution, again the pH doesn't change much. Explain what happens to the extra hydroxide ions you have added.

4. In all these questions, K_a for ethanoic acid = 1.74×10^{-5} mol dm^{-3}.

   a) Calculate the pH of a buffer solution containing 0.100 mol dm^{-3} ethanoic acid and 0.100 mol dm^{-3} sodium ethanoate.

   b) Calculate the pH of a buffer solution containing 0.500 mol dm^{-3} ethanoic acid and 0.250 mol dm^{-3} sodium ethanoate.

   c) In what proportions would you have to mix solutions of ethanoic acid and sodium ethanoate of the same concentration in order to produce a buffer solution of pH 5.00?

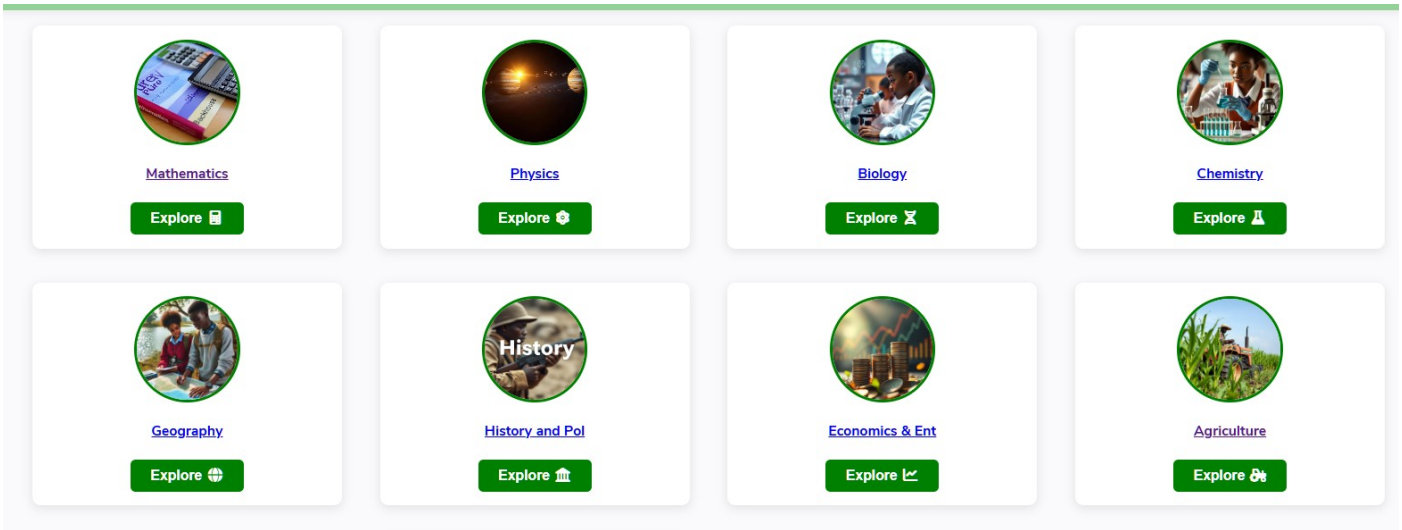
5. In all these questions, K_a for the ammonium ion, NH_4^+, is 5.62×10^{-10} mol dm^{-3}.

   a) Calculate the pH of a buffer solution containing 0.200 mol dm^{-3} ammonia and 0.200 mol dm^{-3} ammonium chloride.

   b) Calculate the pH of a buffer solution containing 0.100 mol dm^{-3} ammonia and 0.200 mol dm^{-3} ammonium chloride.

   c) In what proportions would you have to mix solutions of ammonia and ammonium chloride of the same concentration in order to produce a buffer solution of pH 10.00?

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