

# Introduction to Analytical Chemistry

**ANALYTICAL CHEMISTRY:** The Science of Chemical Measurements.

**ANALYTE:** The compound or chemical species to be measured, separated or studied

## **TYPES of ANALYTICAL METHODS:**

- 1.) **Classical Methods** (Earliest Techniques)
  - a.) **Separations:** precipitation, extraction, distillation
  - b.) **Qualitative:** boiling points, melting points, refractive index, color, odor, solubilities
  - c.) **Quantitative:** titrations, gravimetric analysis
- 2.) **Instrumental Methods** (~post-1930's)
  - a.) **Separations:** chromatography, electrophoresis, etc.
  - b.) **Qualitative or Quantitative:** spectroscopy, electrochemical methods, mass spectrometry, NMR, radiochemical methods, etc.

## **Classification of volumetric methods:**

There are four general classes of volumetric methods:

## **1-Acid-Base:**

Many compounds, both inorganic and organic, are either acids or bases and can be titrated with a standard solution of a strong base or a strong acid. The reactions involve the combination of hydrogen and hydroxide ions to form water. The end points of these titrations are easy to detect, either by means of indicator or by following the change in pH with a pH meter. The acidity and basicity of many organic acids and bases can be enhanced by titrating in nonaqueous solvent, so the weaker acids and bases can be titrated.

## **2- Precipitation:**

In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution.

## **3- Complexometric:**

In complexometric titrations, the titrant is a complexing agent and forms a water-soluble complex with the analyte, a metal ion. The titrant is often a chelating agent.

## **4- Reduction-oxidation:**

These "redox" titration involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing

agent gains electrons and a reducing loses electrons in a reaction between them.

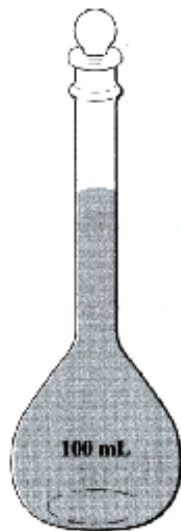
## **Expressions of concentration:**

### **Concentration:**

The quantity of substance in a defined volume of solution.



**Graduated  
cylinder**



**Volumetric  
flask**



**Buret**



**Pipet**



**Syringe**

## **Measurement of Volume**

### **Concentrations of solutions:**

Standard solutions are expressed in terms of molar concentrations or molarity (M).

Molar solution is defined as one that contains one mole of substance in each liter of a solution.

Molarity of a solution is expressed as moles per liter or as millimoles per milliliters.

$$\text{moles} = (\text{moles/liter}) \times \text{liters} = \text{molarity} \times \text{liters}$$

$$\text{millimoles} = \text{molarity} \times \text{milliliters}$$

$$\text{mmole} = M \times \text{ml}$$

$$\text{Molarity (M)} = \frac{\text{Mole of solute}}{\text{Volume of solution in liters}}$$

### **The equivalent weight:**

The equivalent weight is that weight of a substance in grams that will furnish one mole of the reacting unit. Thus, for HCl, the equivalent weight is equal to the formula weight:

$$\text{eq.wt.HCl} = \frac{\text{Formula wt. HCl (g/mol)}}{1 \text{ (eq / mol)}}$$

The milliequivalent weight is one thousandth of the eq.wt.

A normal solution contains one gram eq.wt of solute in one liter of solution:

No. of gram-equivalents

$$N = \frac{\text{No. gram - equivalent s}}{\text{No. of liters}}$$

$$= \frac{\text{No. milligram - equivalent s}}{\text{No. of milliliter s}}$$

By rearrangement of these equations we obtain the expression for calculating other quantities:

$$\therefore \text{No of gram eq.} = N \times \text{No. of liters}$$

$$\text{No. of milligram eq.} = N \times ml = N \times V$$

### **Back titration:**

In back-titrations, a known number of millimoles of reactant is taken in excess of the analyte. The unreacted portion is titrated for example, in the titration of antacid tablets with a strong acid such as HCl.

**Lecture 1 (2 hrs) ..../...../.....: (Acid-base)**

Theoretical bases of neutralization reactions, Electrolyte and the theory of electrolytic Dissociation, Strong and weak electrolytes, Law of mass action , The dissociation of water, Hydrogen ion exponent (pH), Acids and bases, Acid–base equilibrium (pH calculations), Solution of strong acids and strong bases, Solution of weak acids and bases, pH of salts

## **Theoretical bases of neutralization reactions**

### **Electrolyte and the theory of electrolytic Dissociation:**

Aqueous solutions of substances differ in their behavior when submitted to an electric current. Some of them allow the current to pass, i.e. they conduct the electric current, these are termed "*electrolytes*"; while other do not allow the current to pass, i.e. they yield non-conducting solutions, and are called "*non-electrolytes*". The first class includes mineral acid, caustic alkalies and salts, while the second class is exemplified by cane sugar, glycerin and ethyl acetate.

Pure water is a bad conductor of electricity, but when acid like HCl, a base such as KOH or a salt like  $\text{Na}_2\text{SO}_4$  is dissolved in water its conductivity is greatly improved. At the same time, it is noticed that the solute decomposes by the passage of the electric current into its components at the cathode and the anode. These components of the electrolyte are called "*ions*".

The whole phenomenon was called by Arrhenius in 1887 "ionisation" or "dissociation"

### **Strong and weak electrolytes:**

According to the theory of ionisation, the extent of ionisation increases with dilution, and at very great dilution it is practically complete. On the other hand, for each concentration there is a state of equilibrium between the undissociated molecules and the ions; the process being a reversible one.



and the balance can be shifted to the right or the left according to conditions.

Arrhenius therefore introduced a quantity "a", called "the degree of dissociation" defined as follows

$$a = \frac{\text{Number of solute molecules dissociated}}{\text{Total number of solute molecules before dissociation}}$$

When the ionisation is complete, i.e. when all molecules have dissociated, the value of "a" will be unity or very nearly so. The electrolyte will be then called "strong electrolyte". On the other hand this value for weak electrolytes is very far from unity.

## Law of mass action

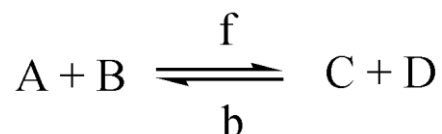
The law is concerned with reactions involving equilibrium between the reactants and productants. Since this the case in the dissociation of most electrolytes, this law is the basis for many calculations in neutralimetric analysis.

### The law reads:

***"The rate of a chemical reaction is proportional to the active masses of the reacting substances."***

In dilute solutions, where conditions approach ideal state "active mass" may be expressed by the concentrations of the reacting species, that is gram-molecules or gram-ions per liter.

In a reaction:



The velocity of the forward reaction  $[V_f]$  and of the backward reaction  $[V_b]$  can expressed.

$$V_f = [A].[B]. K_f$$

$$V_b = [C]. [D]. K_b$$

Where  $K_f$  and  $K_b$  are the proportionality constants called "Velocity constant" and brackets indicate concentration, at equilibrium that is when  $V_f = V_b$

$$K_f [A]. [B] = K_b [C]. [D]$$



And

$$\frac{K_f}{K_b} = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

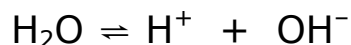
Since  $K_f$  and  $K_b$  are both constants, the fraction  $K_f / K_b$  must also be constant. Hence:

$$K = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

Where  $K$  denotes the "**equilibrium constant**" of the reaction (constant at a given temperature).

### The dissociation of water

The dissociation of water is reversible and to a very limited extent as illustrated by its very weak conductivity to an electric current, and can be represented by the equation:



According to the law of mass action:

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} = K \dots\dots\dots (1)$$

Since the fraction of water ionised is very minute or negligible, the value of  $[\text{H}_2\text{O}]$  is equal to (1) can be regarded as equation 1, and the equation can be written therefore:

$$[\text{H}^+] \cdot [\text{OH}]^- = K_w \dots\dots\dots(2)$$

$K_w$  is known as "**The ionic product of water**"

Under ordinary experimental conditions and at about 25°C; the value of  $K_w$  is taken to be  $1 \times 10^{-14}$  and it follows that;

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

Furthermore, since the dissociation of water gives rise to equal number of hydrogen and hydroxyl ions. Equation (2) could be written:

$$[H^+]^2 = K_w = 1 \times 10^{-14} \dots\dots\dots(3)$$

and in other words;

$$[H^+] = \sqrt{10^{-14}} = 10^{-7}$$

it follows that, if the  $[H^+] = [OH^-] = 10^{-7}$  the solution is described as "neutral", if  $[H^+]$  is more than  $10^{-7}$ , that is  $10^{-6}$ ,  $10^{-5}$ ..., etc. the solution is said to be "acidic" and if  $[H^+]$  is less than  $10^{-7}$ , that is  $10^{-8}$ ,  $10^{-9}$  ..etc., the solution is called "alkaline".

### **Hydrogen ion exponent (pH):**

The hydrogen ion exponent was introduced as an easy method for representing small changes in the ion concentrations, and was called the "pH". *pH is defined as equal to the logarithm of the hydrogen ion concentration with a negative sign.*

i.e  $pH = -\log [H^+]$

$$\text{if } [\text{H}^+] = 1 \times 10^{-10}$$
$$\text{pH} = -\log 10^{-10} = 10$$

This method of stating hydrogen ion concentration has the advantage that all degree of acidity and alkalinity between that of a solution molar (or normal) with respect to hydrogen and hydroxyl ions can be expressed by a series of positive numbers between 0 and 14. A neutral solution is one in which  $\text{pH} = 7$ , an acid solution is one in which  $\text{pH}$  is less than 7 and an alkaline solution in which  $\text{pH}$  is more than 7.

N.B. this method of expressing the concentration of hydrogen ions as its negative exponent ( $\text{pH}$ ) has been extended to express other numerically small values as  $[\text{OH}^-]$ ,  $K_w$  ..... etc.

$$\text{Thus } \text{pOH} = -\log [\text{OH}^-]$$
$$\text{p}K_w = -\log K_w$$

The ionic product of water ( $1 \times 10^{-14}$ ) could be thus expressed:

$$\text{p}K_w = \text{pH} + \text{pOH}$$
$$\therefore \text{pH} = \text{p}K_w - \text{pOH}$$
$$\text{or } \text{pH} = 14 - \text{pOH}$$
$$\text{or } \text{pOH} = 14 - \text{pH}$$

### **Acids and bases:**

According to the classical theory of **Arrhenius** all acids when dissolved in water dissociate giving rise to hydrogen ions as positive ions. Bases, on the other hands, undergo dissociation with the formation of hydroxyl ions  $[\text{OH}^-]$  as the only negative ions. The old definition of both acids and bases

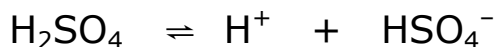
was laid, therefore, on that observation. The acidity of a solution or its basicity can also be determined by measuring the amount of either hydrogen ions or hydroxyl ions it contains, respectively. The degree of dissociation of the dissolved acid or base can be used to calculate the concentration of the ions present in the solution.

According to the degree of dissociation acids can be divided into two groups:

- A) Strong acids, having a high degree of dissociation and
- B) Weak acids, which are feebly dissociated.

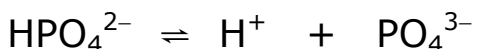
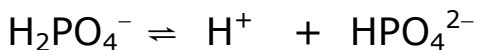
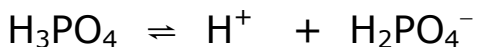
Similarly strong bases have a high degree of ionisation. While weak bases dissociate feebly.

Apart from monbasic acids, which dissociate in one stage, polybasic acids dissociate in consecutive stages. Sulphuric acid, for example, dissociate in two stages, in the first stage one hydrogen is almost completely ionised, thus:



In the second stage, the other hydrogen is only partially ionised.

Phosphoric acid dissociates in three stages:



These stages are called the primary, secondary and tertiary dissociations, respectively, the first stage is the most complete while the others are smaller and smaller.

The equilibrium, which exists in a dilute solution of an acid like acetic acid (HAc) at constant temperature, is



Applying the law of mass action

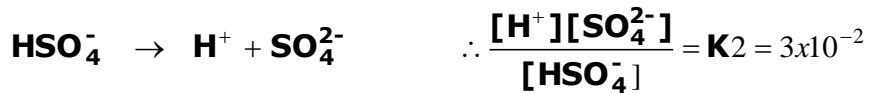
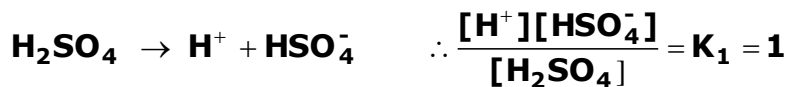
$$K = \frac{[\text{H}^+] \times [\text{Ac}^-]}{[\text{HAc}]}$$

Where K is called "dissociation" "ionisation" or "acidity constant"

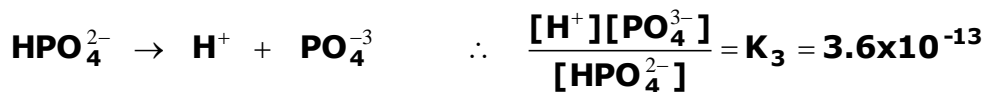
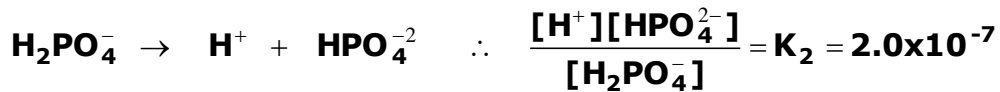
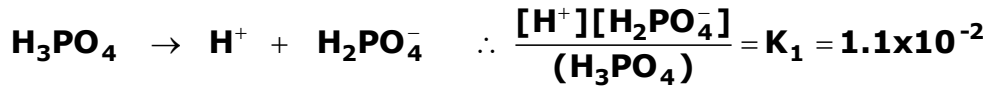
The stronger the acid, the larger the acidity constant. For a completely ionised acid, the acidity constant is assumed to be 1, and the mass action law does not help much in this case.

In considering acids with more than one replaceable hydrogen, such as sulphuric or phosphoric acids the dissociation takes place on stages and not on one stage.

The corresponding mass action expressions are:



Also



In the same case of phosphoric acid, it may be considered that three acids are present. The first,  $\text{H}_3\text{PO}_4$ , corresponds to a moderately strong acid, the second is a weak acid, while the third is an extremely weak acid.