جامعة الانبار كلية : الصيدلة قسم : الكيمياء الصيدلانية اسم المادة باللغة العربية: الكيمياء التحليلية اسم المادة باللغة الإنكليزية: Analytical Chemistry المرحلة: الاولى التدريسي: نغم خيري كريم عنوان المحاضرة باللغة العربية: مراجعة المفاهيم الاساسية

عنوان المحاضرة باللغة الإنكليزية: Review of Elementary of Concepts

1.1 Analytical Chemistry

Analytical chemistry deals with methods for the identification of one or more of the components in a sample of matter and the determination of the relative amounts of each. The identification process is called a qualitative analysis while the determination of amount is termed a quantitative analysis. We will deal largely with the latter.

The results of a quantitative analysis are expressed in such relative terms as the percent of the analyte (the substance being determined) in the sample, the parts of analyte per thousand, per million, or even per billion parts of sample, the grams or milliliters of analyte per liter of sample, or the mole fraction of the analyte in the sample.

Most quantitative analytical measurements are preformed on solutions of the sample, therefore the study of analytical chemistry makes use of solution concepts with which the student should have considerable familiarity.

Quantitative analysis is classified into two types of analysis:

1- *Volumetric analysis*, which concentrates on the exact volume measurement of the solution during titration. The volumetric methods of analysis include acid-base titration, precipitation titration, oxidation-reduction titration, and complex formation titration.

2- *Gravimetric analysis*, which based upon the measurement of the weight of a substance of known composition that is chemically related to the analyte. There are two types of gravimetric analysis, precipitation methods and volatilization method.

1.2 The Chemical Composition of Solutions

Both aqueous and organic solvents find widespread use in chemical analysis. Nonpolar solvents, such as hydrocarbons and halogenated hydrocarbons, are employed when the analyte itself is nonpolar. Organic solvents, such as alcohols, ketones, and ethers, which are intermediate in polarity and which form hydrogen bonds with solutes, are considerably more useful than their less polar counterparts because they dissolve a larger variety of both organic and inorganic species. Aqueous solvents, including solutions of the common inorganic acids and bases, are perhaps the most widely used of all for analytical purposes. Our discussion will therefore focus on the behavior of solutes in water: reactions in nonaqueous polar media will be considered in less detail.

Solutions are classified according to the nature of particles of the solute to: true solution, suspended solution, and colloidal solution. 1- *True solution*, in which the solute disappears between the molecules

of the solvent, like NaCl in water.

2- *Suspended solution*, in which the particles of the solute can be distinguished. The solute particles are separated and settled in the bottom of the container, and do not pass through filter paper.

3- *Colloidal solution*, in which the particles of solute are suspended but do not settle in the bottom of the container, and pass through filter paper.

The presence of the solutes affects the properties of the solvent. They lower the vapour pressure, therefore the temperature increases above its boiling point to reach its usual vapour pressure. The boiling points of the solvent also increase in the presence of the solute, and if the solute is ionic its effect will doubled. Pure water boils at 100°C, but in the presence of the solute it boils at higher temperature. The presence of the solute also lowers the freezing point of the solvent. Pure water freezes at 0^{0} C, while the presence of sugar for example it freezes at - 1.86°C.

1.3 Electrolytes and Non-electrolytes

Electrolytes are solutes which ionize in a solvent to produce an electrically conducting media. Strong electrolytes ionize completely whereas weak electrolytes are only partially ionized in the solvents (Table 1.1).

Strong electrolytes	Weak electrolytes
1- Inorganic acids HNO ₃ , HClO ₄ , H ₂ SO ₄ , HCl, HI, HBr, HClO ₃ , HBrO ₃	
2- Alkali and alkaline-earth hydroxides	2- Most organic acids
3- Most salts	3- Ammonia and most organic bases
	4- Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

Table 1.1 Classification of electrolytes

Non-electrolytes are solutes which do not ionize in their solvents, and therefore the solution does not conduct electricity. Examples are solutions of sugar, and alcohol in water.

1.4 Self-ionization of Solvents

Many common solvents are weak electrolytes which react with themselves to form ions (this process is termed autoprotolysis). Some examples are:

 $2H_{2}O \longrightarrow H_{3}O^{+} + OH^{-}$ $2CH_{3}OH \longrightarrow CH_{3}OH_{2}^{+} + CH_{3}O^{-}$ $2HCOOH \longrightarrow HCOOH_{2}^{+} + HCOO^{-}$ $2NH_{3} \longrightarrow NH_{4}^{+} + NH_{2}^{-}$

The positive ion formed by the autoprotolysis of water is called the hydronium ion, the proton being bonded to the parent molecule via a covalent bond involving one of the unshared electron pairs of the oxygen. Chemists use the term H^+ instead of H_3O^+ .

1.5 Acids and Bases

The classification of substances as acids or bases was founded upon several characteristic properties that these compounds impart to an aqueous solution. Typical properties include the red and blue colors that are associated with the reaction of acids and bases with litmus, the sharp taste of a dilute acid solution, the bitter taste and slippery feel of a basic solution, and the formation of a salt by interactions of an acid with a base.

*Arrhenius acids and bases

Arrhenius defined acids as hydrogen-containing substances that dissociate into hydrogen ions and anions when dissolved in water:

HCl \longrightarrow H⁺ + Cl⁻ CH₃COOH \longleftarrow H⁺ + CH₃COO⁻

and bases as compounds containing hydroxyl groups that give hydroxides ions and cations upon the same treatment:

NaOH \longrightarrow Na⁺ + OH⁻ Al(OH)₃ \longrightarrow Al³⁺ + 3OH⁻

The relative strengths of acids and bases could be compared by measuring the degree of dissociation in aqueous solution. A completely ionized acid called strong acid, like HCl, and a partially ionized acid called weak acid, like CH₃COOH. The same rule applied for strong and weak bases.

* Bronsted and Lowry acids and bases

Bronsted and Lowry proposed independently in 1932 that an acid *is any substance that is capable of donating a proton:* a base is *any substance that can accept a proton.* The loss of a proton by an acid gives rise to an entity that is a potential proton acceptor and thus a base; it is called the conjugated base of the parent acid. The reaction between an acid and water is a typical example:

 $H_2O + acid$ \longrightarrow conjugate base + H_3O^+

It is important to recognize that the acidic character of a substance will be observed only in the presence of a proton acceptor; similarly basic behavior requires the presence of a proton donor. Neutralization in the Bronsted-Lowry sense can be expressed as:

acid 1 + base 2 \longrightarrow base 1 + acid 2

This process will be spontaneous in the direction that favors production of the weaker acid and base. The dissolving of many solutes can be regarded as neutralizations, with the solvent acting as either a proton donor or acceptor. Thus:

> acid 1 + base 2 \longrightarrow base 1 + acid 2 HCl + H₂O \longleftarrow Cl⁻ + H₃O⁺ CH₃COOH + H₂O \longleftarrow CH₃COO⁻ + H₃O⁺ NH₄⁺ + H₂O \longleftarrow NH₃ + H₃O⁺ H₂O + NH₃ \longleftarrow OH⁻ + NH₄⁺

Note that acids can be anionic, cationic, or electrically neutral. It is also seen that water acts as a proton acceptor (a base) with respect to the first three solutes and as a proton donor or acid with respect to the last one; solvents that possess both acidic and basic properties are called amphiprotic.

Acids and bases differ in the extent to which they react with solvents. The reaction between hydrochloric acid and water is essentially complete; this solute is thus classed as acid in the solvent water. Acetic acid and ammonium ion react with water to a lesser degree, with the result that these substance are progressively weaker acids.

The extent of reaction between a solute acid or base and a solvent is also dependent upon the tendency of the latter to donate or accept protons. Thus, for example perchloric, hydrochloric and hydrobromic acids are all classed as strong acid in water. If glacial acetic acid, a poorer proton acceptor is used as the solvent instead, only perchloric acid undergoes complete dissociation and remains a strong acid, the process can be expressed by the equation:

HClO₄ + CH₃COOH
$$\leftarrow$$
 ClO₄⁻ + CH₃COOH₂⁺
Acid 1 base 2 base 1 acid 2

Because they undergo only partial dissociation, hydrochloric acid and hydrobromic acids are weak acids in glacial acetic acid.

A consequence of the Bronsted theory is that the most effective proton donors (that is the strongest acids) give rise, upon loss of their protons to the least effective proton acceptors (the weakest conjugate bases).

The general solvent theory includes not only species that qualify as acids or bases in the Bronsted-Lowry sense but also extends the concept of acid-base behavior to solvents that do not necessarily contain protons.

* Lewis acids and bases

Lewis defined an acid as *an electron-pair acceptor* and a base as *an electron-pair donor*.

$$H^{+} + \begin{bmatrix} : \ddot{\Theta} - H \end{bmatrix} \longrightarrow : \ddot{\Theta} - H \quad \text{or} \quad H^{+} + OH^{-} \longrightarrow H_{2}O$$

acid base H

$$\begin{array}{ccc} H^{+} + & \stackrel{"}{\overset{"}{\underset{H}{}}} & \stackrel{\longrightarrow}{\underset{H}{}} & \left[\begin{array}{c} H - \stackrel{"}{\overset{"}{\underset{H}{}}} - H \\ & \stackrel{H}{\underset{H}{}} \end{array} \right]^{+} \text{ or } H^{+} + H_{2}O \longrightarrow H_{3}O^{+} \\ \text{acid base} \end{array}$$

$$H^{+} + H - \overset{\overset{\overset{\overset{}}{\mathsf{N}}}{\overset{\overset{}}{\mathsf{H}}} H \longrightarrow \begin{bmatrix} H \\ H \\ H \\ H \end{bmatrix}^{+} \text{ or } H^{+} + \mathsf{N}\mathsf{H}_{3} \longrightarrow \mathsf{N}\mathsf{H}_{4}^{+}$$
acid base
$$SO_{3} + O^{2-} \longrightarrow SO_{4}^{2-}$$
Acid-

base

 $SO_3 + OH^- \longrightarrow HSO_4^-$

 $AlCl_3 + Cl^- \longrightarrow AlCl_4^-$

acid base