Lec.I & II

Analytical Chemistry

For Pharmacy Students

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Review of Elementary Concepts.

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.

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.

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 disappear 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 affect 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 lower the freezing point of the solvent. Pure water freezes at 0°C, while the presence of sugar for example it freezes at -1.86°C.

Electrolytes & 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).

Table 1.1 Classification of electrolytes

Strong electrolytes	Weak electrolytes
1- Inorganic acids HNO_3, $HClO_4$, H_2SO_4, HCl, HI, HBr, $HClO_3$, $HBrO_3$	1- Many inorganic acids such as H_2CO_3, H_3PO_4, H_2S, H_2SO_3, H_3BO_3
2- Alkali and alkaline-earth hydroxides	2- Most organic acids
3- Most salts	3- Ammonia and most organic bases

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.

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:

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

$2CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$

$2HCOOH \rightleftharpoons HCOOH_2^+ + HCOO^-$

$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

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

Acids & 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:

$HCl \longrightarrow H^+ + Cl^-$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

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

$NaOH \longrightarrow Na^+ + OH^-$

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

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 CH_3COOH. 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:

$H_2O + \text{acid} \rightleftharpoons \text{conjugate base} + H_3O^+$

$$\text{acid 1} + \text{base 2} \rightleftharpoons \text{base 1} + \text{acid 2}$$

$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

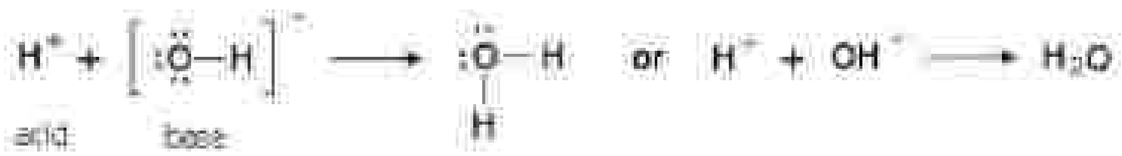
$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

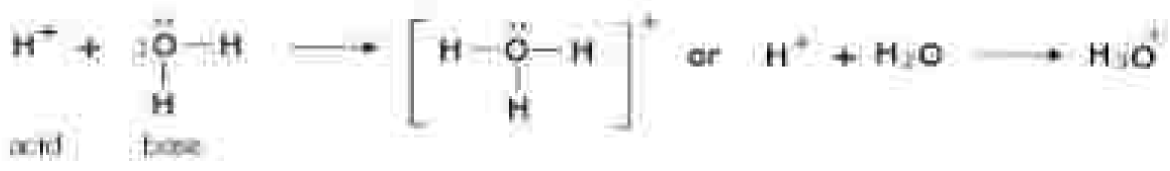
$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

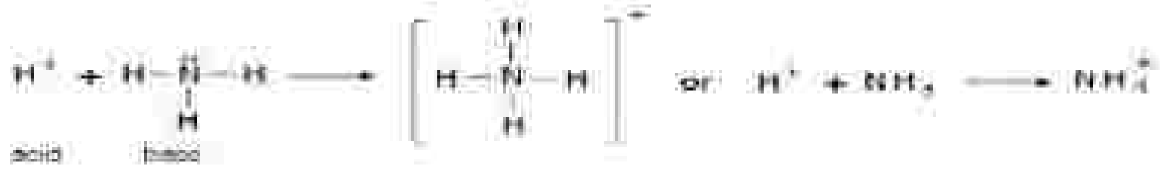
Note that acids can be anionic, cationic, or electrically neutral. It is also seen that water acts as a proton acceptor (a base) with respect to the first three solutes and as a proton donor or acid with respect to the last one; solvents that possess both acidic and basic properties are called amphiprotic.

*** *Lewis acids and bases***

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







$$SO_3 + O^{2-} \longrightarrow SO_4^{2-}$$
acid base

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

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

Salts *

Salts are formed by the reactions of cations and anions. Some of the salts are anhydrous like NaCl, KCl, $KMnO_4$ and $K_2Cr_2O_7$. Other salts are hydrous such as $CaCl_2.2H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$. Salts exist in its solid state as ions, therefore, sodium chloride is ionized in its crystalline case into Na^+ which is surrounded by six ions of Cl^-, and each Cl^- is surrounded by six ions of Na^+. These ions are attached to each other by electrostatic strengths. Thus, these salts are completely ionized in solvents of dielectric constant like water.

Chemical Units of Weight:

In the laboratory, the mass of a substance is ordinarily determined in such metric units as the kilogram (kg), the gram (g), the milligram (mg), the microgram (μg), the nanogram (ng), or the picogram (pg).

$$g = 10^3\ mg = 10^6\ \mu g = 10^9\ ng = 10^{12}\ pg = 10^{-3}\ kg$$

For chemical calculations, however, it is more convenient to employ mass units that express the weight relationship or stoichiometry among reacting species in terms of small whole numbers. The gram formula weight, the gram molecular weight, and the gram equivalent weight are employed in analytical work for this reason. These terms are often shortened to the formula weight, the molecular weight and the equivalent weight.

1.7 Chemical Formula, Formula Weight and Molecular Weight

An empirical formula expresses the simplest combination of atoms in a substance. It is also serves as the chemical formula unless experimental evidence exists to indicate that the fundumental aggregate is actually some multiple of the empirical formula. For example, the chemical formula for hydrogen is H_2 because the gas exists as diatomic molecules under ordinary conditions. In contrast, Ne serves adequately to describe the composition of neon, which is observed to be monatomic.

The entity expressed by the chemical formula may or may not actually exist. For example, no evidence has been found for sodium chloride molecules, as such in the solid state or in aqueous solution. Rather, this substance consists of sodium ions and chloride ions, no one of which can be shown to be in simple combination with any other single ion. Nevertheless, the formula NaCl is convenient for stoichiometric accounting and is so used. It is also necessary to note that the chemical formula is frequently that of the principal species only. Thus, for example, water in the liquid state contains small amounts of such entities as H_3O^+, OH^-, H_4O_2 (and undoubtedly others), in addition to H_2O. Here the

One molecular weight of a species contains 6.02×10^{23} particles of that species; this quantity is frequently referred to as the ***mole***. In a similar way, the formula weight represents 6.02×10^{23} units of the substance, whether real or not, represented by the chemical formula.

Example 1

A 25.0 g sample of H_2 contains:

$$\frac{25.0\ \text{g}}{2.016\ \text{g/mole}} = 12.4 \text{ moles of } H_2$$

$$12.4 \text{ moles} \times \frac{6.02\times10^{23} \text{ molecules}}{\text{Mole}} = 7.47\times10^{24} \text{ molecules } H_2$$

The same weight of NaCl contains:

$$\frac{25.0\ \text{g}}{58.44\ \text{g/fw}} = 0.428 \text{ fw NaCl}$$

which corresponds to 0.428 mole Na^+ and 0.428 mole Cl^-

1.8 Equivalent Weight

For acids:

It is the weight of acid that contains 1g ion of alternative hydrogen.

$$\text{equivalent weight} = \frac{\text{molar mass}}{\text{no. of alternative hydrogen ions}}$$

Example 2

Calculate the equivalent weights for the following acids: HCl, H_2SO_4, H_3PO_4. Atomic weights for H = 1, O = 16, Cl = 35.5, S = 32, P = 31.

$$\text{equivalent weight for HCl} = \frac{\text{molar mass}}{\text{no. of alternative hydrogen ions}}$$

$$= \frac{1 + 35.5}{1} = 36.5 \text{ gram/equivalent}$$

$$\text{for } H_2SO_4 = \frac{(2\times1) + 32 + (16\times4)}{2} = 49$$

$$\text{for } H_3PO_4 = \frac{(3\times1) + 31 + (16\times4)}{3} = 32.67$$

For bases:

It is the weight of base that contains 1g ion of alternative hydroxide.

$$\text{equivalent weight} = \frac{\text{molar mass}}{\text{no. of alternative hydroxide ions}}$$

Example 3

Calculate the equivalent weights for the following bases: NaOH, $Ca(OH)_2$, $Al(OH)_3$. Atomic weights for H = 1, O = 16, Na = 23, Ca = 40, Al = 26.98.

$$\text{equivalent weight for NaOH} = \frac{\text{molar mass}}{\text{no. of alternative hydroxide ions}}$$

$$= \frac{23 + 16 + 1}{1} = 40 \text{ gram/equivalent}$$

$$\text{for } Ca(OH)_2 = \frac{40 + [(16 + 1)]2}{2} = 37$$

$$\text{for } Al(OH)_3 = \frac{26.98 + [(16 + 1)]3}{3} = 25.99$$

For salts:

It is the weight of the salt that contains the equivalent weight of one of its ions.

$$\text{equivalent weight for salt} = \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}}$$

$$= \frac{\text{molar mass}}{\text{no. of acidic radical ions} \times \text{oxidation no.}}$$

Example 4

Calculate the equivalent weights for the following salts: Na_2O, Na_2CO_3, $Al_2(SO_4)_3$. Atomic weights for O = 16, C = 12, Na = 23, S = 32, Al = 26.98.

$$\text{equivalent weight for } Na_2O = \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}}$$

$$= \frac{(23 \times 2) + 16}{2 \times 1} = 31 \text{ gram/equivalent}$$

$$\text{for } Na_2CO_3 = \frac{(23 \times 2) + 12 + (16 \times 3)}{2 \times 1} = 53$$

$$\text{for } Al_2(SO_4)_3 = \frac{(26.98 \times 2) + [32 + (16 \times 4)]\,3}{2 \times 3} = 56.99$$

For salts in precipitation reactions:

The equivalent weight of salts in precipitation reactions is the weight of substance in gram that precipitates quantity equivalent to quantity of 1 gram of hydrogen. or the equivalent weight of another substance in the same reaction.

$$\text{equivalent weight for salt} = \frac{\text{molar mass}}{\text{sum of oxidation numbers of the part participates in precipitate formation}}$$

Example 5

Calculate the equivalent weight for the substances participate in the reaction of AgCl precipitation. Atomic weights for Ag = 108, N = 14, O = 16, Na = 23, Cl = 35.5.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$\text{equivalent weight for } AgNO_3 = \frac{\text{molar mass for } AgNO_3}{\text{oxidation number of Ag}}$$

$$= \frac{108 + 14 + (16 \times 3)}{1} = 170 \text{ gram/equivalent}$$

$$\text{equivalent weight for NaCl} = \frac{\text{molar mass for NaCl}}{\text{oxidation number of Cl}}$$

$$= \frac{35.5 + 23}{1} = 58.5$$

For oxidation-reduction agents:

The oxidation-reduction reactions involve transfer of electrons from one substance to another.

$$\text{equivalent weight for oxidation or reduction agent} = \frac{\text{molar mass}}{\text{the difference between oxidation numbers}}$$

1.9 Concentration Units

1- *Mass percentage w/w%* $= \dfrac{\text{g solute}}{\text{g solution}} \times 100$

5% solution of NaCl means that 5 g of NaCl dissolved in 95 g water.

Example 7

Calculate the mass percentage for a solution prepared by dissolving 15 g of $AgNO_3$ in 100 cm^3 water. The density of water is 1 g/cm^3.

$$\text{weight of solvent} = \text{volume} \times \text{density}$$
$$= 100\ cm^3 \times 1\ g/cm^3$$
$$= 100\ g$$
$$\text{weight of solution} = 100\ g\ \text{solvent} + 15\ g\ \text{solute}$$
$$= 115\ g$$
$$\text{mass percentage w/w\%} = \frac{\text{g solute}}{\text{g solution}} \times 100$$
$$= \frac{15}{115} \times 100$$
$$= 13.04\%$$

2- *Volume percentage v/v%* $= \dfrac{\text{ml solute}}{\text{ml solution}} \times 100$

10% solution of alcohol means that 10 ml alcohol is added to enough solvent in order to reach 100 ml volume (addition of 90 ml solvent).

Example 8

10 g of organic solvent (density 1.5 g/cm^3) was added to 90 g water, the density of the solution become 1.1 g/cm^3. Calculate the v/v% and the w/w% concentrations of the organic substance in the solution.

$$\text{weight of solution} = 90\text{ g} + 10\text{ g} = 100\text{ g}$$

$$\text{mass percentage w/w\%} = \frac{10\text{ g}}{100\text{ g}} \times 100$$

$$= 10\%$$

$$\text{volume of solution} = \frac{\text{weight}}{\text{density}} = \frac{100}{1.1} = 90.90\text{ ml}$$

$$\text{volume of solute} = \frac{\text{weight}}{\text{density}} = \frac{10}{1.5} = 6.67\text{ ml}$$

$$\text{volume percentage v/v\%} = \frac{6.67\text{ ml}}{90.90\text{ ml}} \times 100$$

$$= 7.3\%$$

3- *Mass/volume percentage w/v%* $= \dfrac{\text{g solute}}{\text{ml solution}} \times 100$

It is the weight of the solute in 100 ml solution, this means:

$$\text{weight of solute (g)} = \text{percentage} \left(\frac{\text{g}}{100\text{ ml}}\right) \times \text{volume (ml)}$$

Example 9

Calculate the weight of sodium chloride salt in 500 ml solution of a 0.85 %w/v concentration.

$$\text{weight of solute (g)} = \text{percentage} \left(\frac{\text{g}}{100\text{ ml}}\right) \times \text{volume (ml)}$$

$$= \left(\frac{0.85\text{ g}}{100\text{ ml}}\right) \times 500\text{ml}$$

$$= 4.25\text{ g}$$

4- ***Parts per million (ppm)*** $= \dfrac{\text{mg solute}}{\text{kg solvent}}$

and there are:

$$\text{Parts per thousand (ppt)} = \frac{\text{g solute}}{\text{kg solvent}}$$

$$\text{Parts per billion (ppb)} = \frac{\mu\text{g solute}}{\text{kg solvent}}$$

5- *Molar concentration (M)*

It is the number of molar weights of the solute in 1 liter of solvent.

$$\text{Molarity (M)} = \frac{\text{no. of molar weights of solute}}{\text{volume of solution in liter}}$$

$$\text{no. of molar weights} = \frac{\text{weight of substance in g}}{\text{molar mass}}$$

$$\text{Molar concentration (M)} = \frac{\dfrac{\text{weight of substance in g}}{\text{molar mass}}}{\dfrac{\text{volume of solution in ml}}{1000}}$$

$$= \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$\text{weight of substance} = \text{M} \times \text{molecular weight} \times \frac{\text{volume ml}}{1000}$$

Example 10

Calculate the molar concentration (M) of a solution prepared by dissolving 29.35 g of NaCl in 200 ml water. Atomic weights for Na = 23.99, Cl = 35.45.

$$M = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$= \frac{29.35 \times 1000}{200 \times 58.44} = 2.5 \text{ molar}$$

6- Normal concentration (N)

It is the number of equivalent weights of the solute dissolved in liter of the solvent.

$$\text{Normality (N)} = \frac{\text{no. of equivalent weights of solute}}{\text{volume of solution in liter}}$$

$$\text{no. of equivalent weights} = \frac{\text{weight of substance in g}}{\text{equivalent weight}}$$

$$\text{Normal concentration (N)} = \frac{\dfrac{\text{weight of substance in g}}{\text{equivalent weight}}}{\dfrac{\text{volume of solution in ml}}{1000}}$$

$$= \frac{\text{weight of substance in g} \times 1000}{\text{equivalent weight} \times \text{volume of solution in ml}}$$

$$\text{weight of substance} = N \times \text{equivalent weight} \times \frac{\text{volume ml}}{1000}$$

*** Relationship between Molarity (M) and Normality (N)***

$$N = M \times \text{no. of equivalents}$$

Example 11

Calculate the molar (M) concentration of H_3PO_4 solution of 0.250 N, to produce phosphate ion PO_4^{3-}.

$$N = M \times \text{no. of equivalents}$$

$$0.25 = M \times 3 \;,\; \text{so} \quad M = 0.0833 \text{ Molar}$$

**** The mole fraction***

The mole fraction for solvent is the number of moles of solvent relative to the total number of moles, and the mole fraction for solute is the number of moles of solute relative to the total number of moles. If we multiply the mole fraction by 100 the product is mole percent.

Example 13

Calculate the mole fraction for ethanol C_2H_5OH and water in a solution prepared by dissolving 13.80 g of ethanol in 27 g water. Atomic weight for O=16, C=12, H=1.

$$\text{no. of moles of ethanol} = \frac{\text{weight}}{\text{molecular weight}} = \frac{13.80}{46} = 0.30 \text{ mole}$$

$$\text{no. of moles of water} = \frac{\text{weight}}{\text{molecular weight}} = \frac{27}{18} = 1.50 \text{ mole}$$

$$\text{the total number of moles} = 0.30 + 1.50 = 1.80 \text{ mole}$$

$$\text{mole fraction for ethanol} = \frac{\text{moles of ethanol}}{\text{total no. of moles}} = \frac{0.30}{1.80} = 0.167$$

$$\text{mole fraction for water} = \frac{\text{moles of water}}{\text{total no. of moles}} = \frac{1.50}{1.80} = 0.833$$

The highest value for mole fraction is 1, so it is possible to calculate mole fraction for water by determining mole fraction for ethanol:

mole fraction for water = 1 – mole fraction for ethanol

= 1- 0.167 = 0.833

**** Solutions Normality***

$$N = \frac{D \times \% \times 1000}{\text{equivalent weight} \times 100}$$

D = density.

To dilute a solution we use the law:

$$\underbrace{N_1 \times V_1}_{\text{before dilution}} = \underbrace{N_2 \times V_2}_{\text{after dilution}}$$

For solutions:

no. of milliequivalents (meq) = V of solution × Normality (N)

For solids:

$$\text{no. of milliequivalents} = \frac{\text{wt. of solids (g)}}{\text{equivalent weight}} \times 1000$$

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