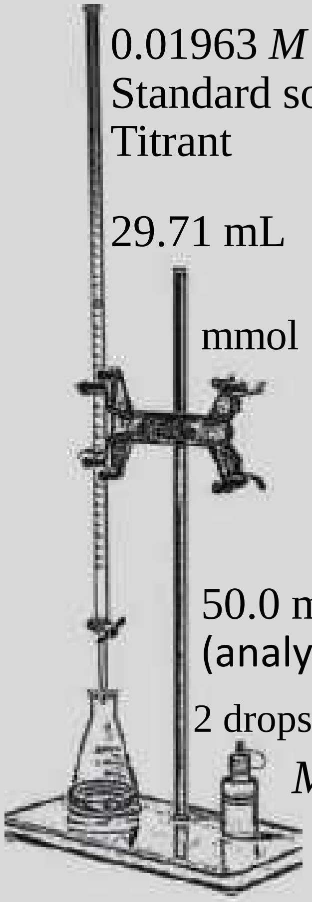
Al-Rasheed University College
Department of Medical Laboratory Technique

Medical Chemistry
Lecture 2

Prepared by
Dr. Kutaiba Ibrahim Alzand

TITRATION

- In a **titration**, the test substance (analyte) reacts with an added reagent of known concentration, generally instantaneously.
- The reagent of known concentration is referred to as a **standard solution**. It is typically delivered from a buret; the solution delivered by the buret is called the **titrant**.
- The volume of titrant required to just completely react with the analyte is measured.
- Since we know the reagent concentration as well as the reaction stoichiometry between the analyte and the reagent, we can calculate the amount of analyte.



$0.01963\ M\ Ba(OH)_2$
Standard solution
Titrant

29.71 mL

mmol = M x mL

50.0 mL of HCl
(analyte)

2 drops of indicator

$M_{HCl} = ?$

mmol = M x mL
M = mmol / mL

$$\mathbf{2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O}$$

At equivalent point

$$\text{2 mmol HCl} = \text{1 mmol } Ba(OH)_2$$

$$x \qquad 0.01963 \times 29.71 = 0.582$$

$$x = 2 \times 0.582 = 1.16463 \text{ mmol HCl}$$

$$M_{HCl} = \text{mmol}_{HCl} / \text{mL}_{HCl}$$

$$M_{HCl} = 1.16463 / 50 = 0.02329\ M$$

We calculate the moles of analyte titrated from the moles of titrant added and the ratio in which they react.

The requirements of a titration are as follows:

1. The reaction must be stoichiometric.
2. The reaction should be rapid.
3. There should be no side reactions; the reaction should be specific.
4. There should be a marked change in some property of the solution when the reaction is complete.
5. The point at which an equivalent or stoichiometric amount of titrant is added is called the **equivalence point**. The point at which the reaction is observed to be complete is called the **end point**, that is, when a change in some property of the solution is detected. The end point should coincide with the equivalence point or be at a reproducible interval from it.
6. The reaction should be quantitative.

- The ***equivalence point*** is the theoretical end of the titration where the number equivalents of the analyte exactly equals the number of equivalents of the titrant added.
- The ***end point*** is the observed end of the titration. The difference is the titration error.

STANDARD SOLUTIONS—THERE ARE DIFFERENT KINDS

- A standard solution is prepared by dissolving an accurately weighed quantity of a highly pure material called a **primary standard** and diluting to an accurately known volume in a volumetric flask.
- Alternatively, if the material is not sufficiently pure, a solution is prepared to give approximately the desired concentration, and this is **standardized** by titrating a weighed quantity of a primary standard.
- For example, sodium hydroxide (NaOH) is not sufficiently pure to prepare a standard solution directly. It is therefore standardized by titrating a primary standard acid, such as potassium acid phthalate (KHP). Potassium acid phthalate is a solid that can be weighed accurately.
- A solution standardized by titrating a primary standard is itself a **secondary standard**. It will be less accurate than a primary standard solution due to the errors of titrations.

A **primary standard** should fulfill these requirements:

1. It should be *100.00% pure*
2. It should be *stable to drying temperatures,* and it should be stable indefinitely at room temperature. The primary standard is always dried before weighing.
3. It should be *readily* and relatively inexpensively *available.*
4. Although not essential, it should have a *high formula weight.*
5. If it is to be used in titration, it should *possess the properties required for a titration*.

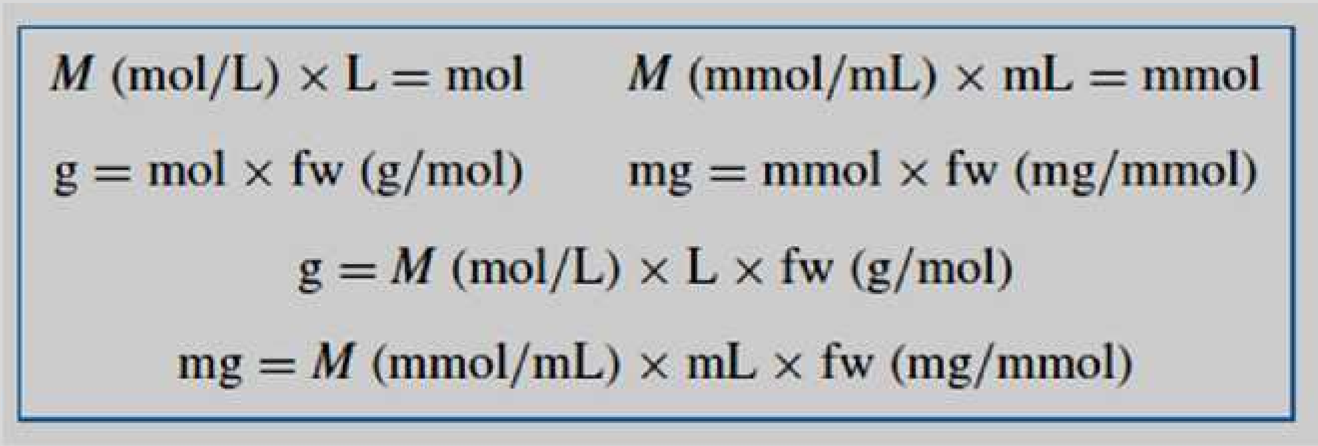
Why a primary standard it should have a high formula weight?

A high formula weight means a larger weight must be taken for a given molar concentration of titrant to be made. This reduces the relative error in weighing.

CLASSIFICATION OF TITRATION METHODS

1. Acid–Base
2. Precipitation
3. Complexometric
4. Reduction–Oxidation

Volumetric Calculations—Let’s Use Molarity



$$M\ (\text{mol/L}) \times \text{L} = \text{mol} \qquad M\ (\text{mmol/mL}) \times \text{mL} = \text{mmol}$$

$$\text{g} = \text{mol} \times \text{fw}\ (\text{g/mol}) \qquad \text{mg} = \text{mmol} \times \text{fw}\ (\text{mg/mmol})$$

$$\text{g} = M\ (\text{mol/L}) \times \text{L} \times \text{fw}\ (\text{g/mol})$$

$$\text{mg} = M\ (\text{mmol/mL}) \times \text{mL} \times \text{fw}\ (\text{mg/mmol})$$

- We usually work with millimole (mmol) and milliliter (mL) quantities in titrations; therefore, the right-hand equations are more useful.
- Note that the expression for formula weight contains the same numerical value whether it be in g/mol or mg/mmol.

Example 5.19

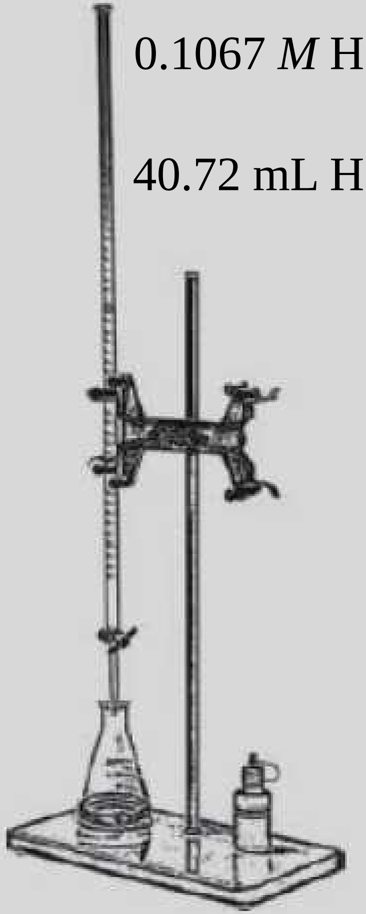
(f.wt = 84. 01 g/mol)

A 0.4671-g sample containing sodium bicarbonate was dissolved and titrated with standard 0.1067 *M* hydrochloric acid solution, requiring 40.72 mL. The reaction is

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Calculate the percent sodium bicarbonate in the sample.

% (w/w) = g solute/g sample x 100%



0.1067 *M* HCl

40.72 mL HCl

0.4671 g $NaHCO_3$

Solution

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

mmol = *M* x mL
mmol = mg/f.wt
mg = mmol x f.wt

At equivalent point

1 mmol $NaHCO_3$ = 1 mmol HCl

x 0.1067 x 40.72 = 4.344

x = 4.344 mmol $NaHCO_3$

mg = mmol x f.wt

mg = 4.344 x 84.01 = 365.01 mg $NaHCO_3$

g = 365.01 x 0.001 = 0.3650 g $NaHCO_3$

% $NaHCO_3$ = 0.3650 g $NaHCO_3$ / 0.4671 g $_{Sample}$ x 100%

= 78.14 % $NaHCO_3$

Example 5.20

(f.wt = 105.99 g/mol)

A 0.2638-g soda ash sample is analyzed by titrating the sodium carbonate with the standard 0.1288 *M* hydrochloride solution, requiring 38.27 mL. The reaction is

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

Calculate the percent sodium carbonate in the sample.

% (wt/wt) = g solute/g sample x 100%

Solution

mmol = *M* x mL
mmol = mg/f.wt
mg = mmol x f.wt

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

At equivalent point

$$1 \text{ mmol } Na_2CO_3 = 2 \text{ mmol HCl}$$

$$x \qquad\qquad 0.1288 \text{x } 38.27 = 4.929$$

$x = 4.929 / 2 = 2.464$ mmol Na_2CO_3

mg = mmol x f.wt

mg Na_2CO_3 = 2.464 x 105.99 = 261.21 mg Na_2CO_3

g Na_2CO_3 = 261.21 x 0.001 = 0.2612 g Na_2CO_3

% Na_2CO_3 = 0.2612 g Na_2CO_3 / 0.2638 g $_{\text{Sample}}$ x 100%

= 99.02 % Na_2CO_3

0.1288 *M* HCl

38.27 mL HCl

0.2638 g Na_2CO_3

A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 M $Ba(OH)_2$ to reach an end point with bromocresol green indicator. Calculate the molar concentration of the HCl.

$$2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O$$

At equivalent point

2 mmol HCl = 1 mmol $Ba(OH)_2$
x 0.01963 x 29.71 = 0.582

x = 2 x o.582 = 1.16463 mmol HCl

$M_{HCl} = mmol_{HCl} / mL_{HCl}$

$M_{HCl} = 1.16463 / 50 = 0.02329\ M$

0.01963 M $Ba(OH)_2$

29.71 mL

50.0 mL of HCl

Example 5.21

How many milliliters of 0.25 *M* solution of H_2SO_4 will react with 10 mL of a 0.25 *M* solution of NaOH?

Solution

The reaction is

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

mmol = *M* x mL
M = mmol / mL
mL = mmol / *M*

1 mmol H_2SO_4 = 2 mmol NaOH

x 0.25 *M* x 10 mL = 2.5

x = 2.5 / 2 = 1.25 mmol H_2SO_4

mmol = *M* x mL

mL H_2SO_4 = mmol H_2SO_4 / *M* H_2SO_4

= 1.25 / 0.25 = 5.0 mL H_2SO_4

STANDARDIZATION AND TITRATION CALCULATIONS

- When a titrant material of high or known purity is not available, the concentration of the approximately prepared titrant solution must be accurately determined by **standardization;** that is, by titrating an accurately weighed quantity (a known number of millimoles) of a primary standard.
- From the volume of titrant used to titrate the primary standard, we can calculate the molar concentration of the titrant.
- In standardization, generally it is the concentration of the titrant that is unknown and the moles of analyte (primary standard) are known.

Example 5.23

An approximate 0.1 *M* hydrochloric acid solution is prepared by 120-fold dilution of concentrated hydrochloric acid. It is standardized by titrating 0.1876 g of dried primary standard sodium carbonate: The f.wt of Na_2CO_3 = 105.99 g/mol

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

The titration required 35.86 mL acid. Calculate the molar concentration of the hydrochloric acid.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

At equivalent point

Solution

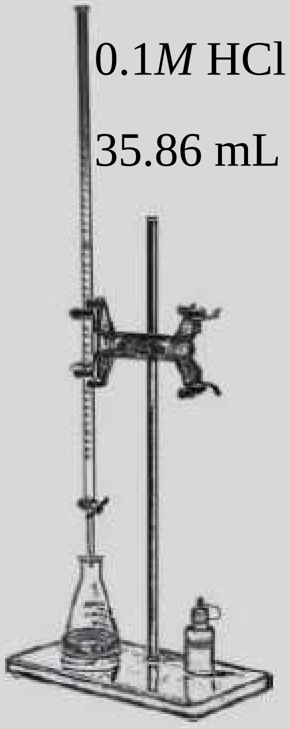
M = mmol / mL
mmol = *M* x mL
mmol = mg/f.wt
mg = mmol x f.wt

2 mmol HCl = 1 mmol Na_2CO_3
x 187.6 / 105.99 = 1.77

x = 1.77 x 2 = 3.54 mmol HCl

M = mmol / mL

M HCl = 3.54 / 35.86 = 0.0987 *M*



0.1*M* HCl

35.86 mL HCl

0.1876 g Na_2CO_3