

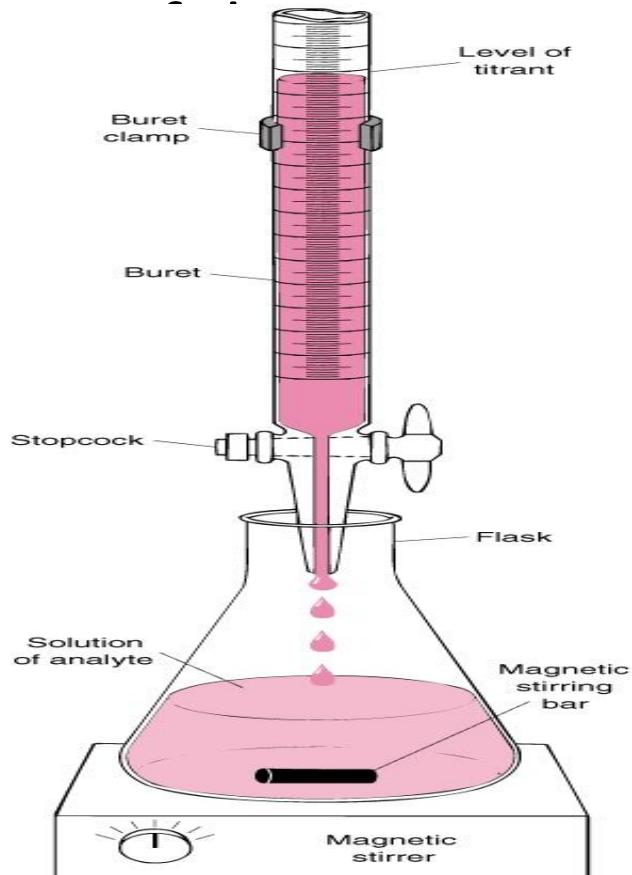
# **Volumetric Analysis: ( Titrimetric Methods):**

By Dr.mohammed.J.Hamzah

## **Volumetric Analysis: ( Titrimetric Methods):**

A titration is a process whereby a known standard reagent is delivered from a buret to the analyte until the reaction is complete. Titrations may be based on a variety of chemical reactions such as acid/base, redox, complexation, or precipitation.

**Volumetric titrimetry:** is a type of titrimetry in which the volume of a standard reagent is the measured quantity. Generally an indicator is required to signal when the end point of the reaction has occurred and tells the analyst to stop the addition



# **SOME TERMS USED IN**

# **VOLUMETRIC TITRIMETRY**

**A standard solution:** is a reagent of exactly known concentration that is used in a titrimetric analysis.

**Titration** is a process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete.

**The equivalence point** is the point in a titration when the amount of added standard reagent is exactly equivalent to the amount of analyte.

**The end point** is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

In volumetric methods, the **titration error  $E_t$**  is given by

$$E_t = V_{ep} - V_{eq}$$

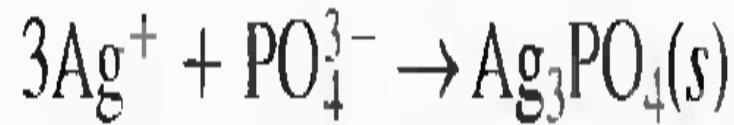
where  $V_{ep}$  is the **actual volume** of reagent required to reach the end point and  $V_{eq}$  is the **theoretical volume** to reach the equivalence point.

**Indicators** are organic materials (almost weak acid or weak base) are often added to the analyte solution to produce an observable physical change (the end point) at or near the equivalence point.

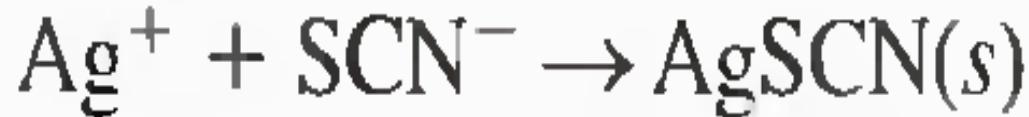
Titration between . . .	Indicator	Explanation
strong acid and strong base	any	
strong acid and weak base	methyl orange	changes color in the acidic range (3.2 - 4.4)
weak acid and strong base	phenolphthalein	changes color in the basic range (8.2 - 10.6)
Weak acid and weak base	No suitable	

**Back-titration** is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

It is sometimes necessary to add an excess of the standard titrant and then determine the excess amount by back-titration with a second standard titrant. For example, the amount of phosphate in a sample can be determined by adding a measured excess of standard silver nitrate to a solution of the sample, which leads to the formation of insoluble silver phosphate:



The excess silver nitrate is then back-titrated with a standard solution of potassium thiocyanate



**A primary standard** is an ultrapure compound that serves as the reference material for a titrimetric method of analysis.

**The accuracy of a method** is critically dependent on the properties of this compound. Important requirements for a primary standard are the following:

- 1. High purity.** Established methods for confirming purity should be available.
- 2. Atmospheric stability.**
- 3. Absence of hydrate water** so that the composition of the solid does not change with variations in humidity.
- 4. Modest cost.**
- 5. Reasonable solubility in the titration medium.**
- 6. Reasonably large molar mass** so that the relative error associated with weighing the standard is minimized.

Very few compounds meet or even approach these criteria, and only a limited number of primary-standard substances are available commercially. As a consequence, less pure compounds must sometimes be used in place of a primary standard.

The purity of such a **secondary standard must be established** by careful analysis.

**A secondary standard** is a compound whose purity has been established by chemical analysis and that serves as the reference material for a titrimetric method of analysis.

## **STANDARD SOLUTIONS :**

Standard solutions play a central role in all titrimetric methods of analysis.

Therefore, we need to consider the desirable properties for such solutions, how they are prepared, and how their concentrations are expressed. The ideal standard solution for a titrimetric method will :

- 1. Be sufficiently stable** so that it is necessary to determine its concentration only once;
- 2. React rapidly with the analyte** so that the time required between additions of reagent is minimized;
- 3. React more or less completely with the analyte** so that satisfactory end points are realized; and
- 4. Undergo a selective reaction with the analyte** that can be described by a balanced equation.

***Few reagents meet all these ideals perfectly.***

The accuracy of a titrimetric method can be no better than the accuracy of the concentration of the standard solution used in the titration. **Two basic methods are used to establish the concentration of such solutions.** The **first** is the direct method, in which a carefully weighed quantity of a primary standard is dissolved in a suitable solvent and diluted to an exactly known volume in a volumetric flask.

**The second** is by standardization, in which the titrant to be standardized is used to titrate

- (1) a weighed quantity of a primary standard,
- (2) a weighed quantity of a secondary standard. Or
- (3) a measured volume of another standard solution.

# **Classification 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 end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH with a pH meter here are four general classes of volumetric or titrimetric methods.



**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 to form silver chloride precipitate



**3. *Complexometric*.** In complexometric titrations, the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion.



**4. *Reduction-Oxidation*.** These "redox" titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.





## **VOLUMETRIC CALCULATIONS:**

we express the concentration of solutions in several ways. For standard solutions used in titrimetry, either molarity (CM) or normality (CN) is usually employed. The first term gives the number of moles of reagent contained in one liter of solution, and the second gives the number of equivalents of reagent in the same volume.

## Some Useful Algebraic Relationships

Most volumetric calculations are based on two pairs of simple equations that are derived from definitions of the millimole, the mole, and the molar concentration. For the chemical species A, we may write.

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g/mmol)}} \quad (13-1)$$

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} \quad (13-2)$$

The second pair is derived from the definition of molar concentration. That is,

$$\text{amount A (mmol)} = V(\text{mL}) \times c_A (\text{mmol A/mL}) \quad (13-3)$$

$$\text{amount A (mol)} = V(\text{L}) \times c_A (\text{mol A/L}) \quad (13-4)$$

where  $V$  is the volume of the solution.

**For example, a 0.1 M solution contains 0.1 mol of a species per liter or 0.1 mmol per milliliter.**

**Use Equations 13-1 and 13-3 when volumes are measured in milliliters and Equations 13-2 and 13-4 when the units are liters.**

See pages 342 -347 in chapter 13 by Skooge.  
Text book

## EXAMPLE 13-1

Describe the preparation of 2.000 L of 0.0500 M AgNO<sub>3</sub> (169.87 g/mol) from the primary-standard-grade solid.

Since the volume is in liters, we base our calculations on the mole rather than the millimole. Thus, to obtain the amount of AgNO<sub>3</sub> needed, we write

$$\begin{aligned}\text{amount AgNO}_3 &= V_{\text{soln}}(\text{L}) \times c_{\text{AgNO}_3}(\text{mol/L}) \\ &= 2.000 \text{ L} \times \frac{0.0500 \text{ mol Na}_2\text{CO}_3}{\text{L}} = 0.1000 \text{ mol AgNO}_3\end{aligned}$$

To obtain the mass of AgNO<sub>3</sub>, we rearrange Equation 13-2 to give

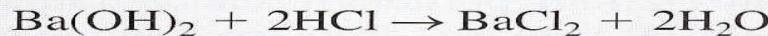
$$\begin{aligned}\text{mass AgNO}_3 &= 0.1000 \cancel{\text{mol AgNO}_3} \times \frac{169.87 \text{ g AgNO}_3}{\cancel{\text{mol AgNO}_3}} \\ &= 16.98 \text{ g AgNO}_3\end{aligned}$$

Therefore, the solution is prepared by dissolving 16.98 g of AgNO<sub>3</sub> in water and diluting to exactly 2.000 L.

## EXAMPLE 13-4

A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 M Ba(OH)<sub>2</sub> to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl.

In the titration, 1 mmol of Ba(OH)<sub>2</sub> reacts with 2 mmol of HCl:



Thus, the stoichiometric ratio is

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

The number of millimoles of the standard is obtained by substituting into Equation 13-3:

$$\text{amount Ba}(\text{OH})_2 = 29.71 \text{ mL Ba}(\text{OH})_2 \times 0.01963 \frac{\text{mmol Ba}(\text{OH})_2}{\text{mL Ba}(\text{OH})_2}$$

To obtain the number of millimoles of HCl, we multiply this result by the stoichiometric ratio determined initially:

$$\text{amount HCl} = (29.71 \times 0.01963) \text{ mmol Ba}(\text{OH})_2 \times \frac{2 \text{ mmol HCl}}{1 \text{ mmol Ba}(\text{OH})_2}$$

To obtain the number of millimoles of HCl per mL, we divide by the volume of the acid. Thus,

$$\begin{aligned} c_{\text{HCl}} &= \frac{(29.71 \times 0.01963 \times 2) \text{ mmol HCl}}{50.0 \text{ mL HCl}} \\ &= 0.023328 \frac{\text{mmol HCl}}{\text{mL HCl}} = 0.02333 \text{ M} \end{aligned}$$

## **Expressions of the Analytical Results :**

Results are reported as concentration, on either weight or volume basis the quantity of analyte per unit weight or per volume of sample . the units used for the analyte will vary.

Weights Units: mass unit , the gram(for macro analyses)  
.for sample or trace constituents, chemists used small unit

:

$$( \text{mg} = 10^{-3} \text{g} , \mu\text{g} = 10^{-6} \text{ g} , \text{ng(nano gram)} = 10^{-9} \text{ g} )$$

Volume unit: the Liter; mL=10<sup>-3</sup> L ,  $\mu\text{L}=10^{-6}$  L ,nL(nano liter)=10<sup>-9</sup>

The mL is used mostly in volumetric analysis Common term:

k = kilo =  $10^3$

d = deci =  $10^{-1}$

c = centi =  $10^{-2}$

m = milli =  $10^{-3}$

$\mu$  = micro =  $10^{-6}$

n = nano =  $10^{-9}$

p = pico =  $10^{-12}$

f = femto =  $10^{-15}$

$10^{-18}$

# **Normality(N)**

The No. of equivalent weights in 1 L of solution

1N solution contains 1 equivalent / 1 L

**Equivalent**= is the mass of material providing Avogadros number of reacting units. The No of reacting units depends on the chemical reaction.

$$\text{Eq.} = \text{wt.g}/(\text{eq.wt.g}/\text{eq})$$

**Equivalent weight** = f.wt/ No of reacting units.

For acids & base , No . of reacting units is based on the number of H+ an acid give or a base reacted with. For oxidation-reduction reaction, it is based on the number of electrons on oxidizing or reducing agent will take on or supply. **No. of**

$$\text{Eq.} = \text{wt.g}/(\text{eq.wt.g}/\text{eq})$$

$\text{g/eq} = \text{mg/meq} = \text{equivalent weight};$   
 $\text{eq/L} = \text{meq/mL} = \text{normality}.$

As with molarity, we usually work with millequivalent quantities, and

$$\text{meq} = \frac{\text{mg}}{\text{eq wt (mg/meq)}} = \text{normality (meq/mL)} \times \text{mL} \quad (5.7)$$

**Example:** calculate the equivalent weight of the followings:

1- Sulfuric acid , $\text{H}_2\text{SO}_4$ , has two reacting units of protons; that is there are two equivalents of protons in each mole therefore.

$$\text{Equivalent weight} = \frac{98.08 \text{ g/mol}}{2 \text{ eq/mol}} = 49.04 \text{ g/eq}$$

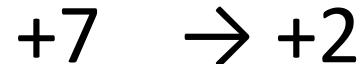
## **2-H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> oxalic acid**

(H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> g/mol) /2eq/mol =90.04/2=45.02g/eq

## **3-KMnO<sub>4</sub>**

when Mn<sup>+7</sup> → Mn<sup>+2</sup> reduction

5 electron change (in this reduction)



Eq.wt.= KMnO4 f.wt (g/mol)/5 eq/mol

$$= 158.04/5 = 31.608\text{g/eq}$$

**4-NH<sub>3</sub>**

**NH<sub>3</sub> g/mol/1 eq = 17/1 = 17 g/eq.**

**5- K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**



$$\begin{aligned}\text{Eq.wt.} &= \text{K}_2\text{Cr}_2\text{O}_7 \text{g/mol} / 6 \text{ eq/mol} = 294.19 / 6 \\ &= 49.03 \text{ g/eq}\end{aligned}$$

Example : calculate the normality of a solution contains 5.267 g/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Cr is reduced to Cr<sup>+3</sup>

$$\text{Cr}^{+6} \rightarrow \text{Cr}^{+3}$$
$$N = 5.267 \text{ g/L} / (294.19/6) \text{ g/eq} = 0.1074 \text{ eq/L}$$

## Note :

For calculation moles & equivalents ,we may use a stoichiometric factor which is  $n =$   
unit of eq/mol

Equivalents = moles  $\times n$  (eq/mol)

$N = M \times n$  (reaction unit)

Eq.wt = f.wt./n

### **3- Formality( F)**

F is the No of formula weight of a solute dissolved in 1 L solution.

$$F = f.wt / L \text{ or } m \text{ f.wt.} / \text{ml}$$

## **Example :**

**Exactly 5.00 g NaCl are dissolved in 100ml distilled water .calculate the formality of this solution**

$$F.wt = 5.00 / 58.44 = 0.0856$$

$$F = 0.0856 / 100 \times 10^{-3} = 0.856 \text{ gf.wt / L}$$

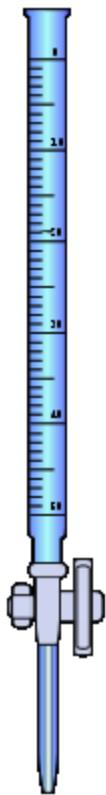
F is numerically the same as M molarity . F is used for ionic salts that do not exist as molecules in the solid or in the solution.

**Formality = Molarity numerically**

F is used for total analytical concentration

M is used for equilibrium concentration.

# Volumetric apparatus



Thank you for your attention