

# Analytical Chemistry

Lecture No. 3

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## Titrimetric Methods

Titrimetric analysis consists in determining the number of moles of reagent (titrant), required to react quantitatively with the substance being determined. The titrant can be added (a) volumetrically, with a glass or automatic burette or with a low flow-rate pump, or (b) coulometrically, with an electrochemical generation from a proper electrolyte.

There are many different types of titrations that differ by the titrant used and substances that can be determined. While every titration is different, they all share similar characteristic - but before we will start to discuss them let's define several important terms.

### Titrant

Titrant is a substance added from the burette. Titrant used and reaction that proceeds usually defines name of the titration - like acid-base (or alkalimetric) titration if we use strong acid (or strong base) as a titrant, or redox when the reaction that proceeds is of a redox type. Name can be also much more specific - like permanganometric titration (also known as manganometry or permanganometry) when titrant is potassium permanganate.

### Titration

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

### Back-titration

A process in which the excess of a standard solution used to react with an analyte is determined by titration with a second standard solution.

## End point

Related to the physical sign that associate with the condition of chemical equivalence. The end point is express in range, the range should address to the equivalence point

End point is where the titration ends in practice. The closer the end point to the equivalence point the better, but it is often not easy to find a good method of equivalence point detection. However, very often we can easily spot a point very close to the equivalence point - and that's where the end point will be.

## Equivalence point

Equivalence point is where the titration should really end - titration fraction equals exactly 1, we have added stoichiometric amount of titrant to titrated substance. That's not necessarily where we end titration.

**Equivalent weight:** Equivalent weight of the substance is defined as the weight of the substance that contains or reacts with 1.0078 g of hydrogen or 8 g of oxygen, or 35.45 g of chlorine. This generalized definition is used for the calculation of equivalent weight. But depending upon the reaction involved, equivalent weight can be simplified as below.

Equivalent weight in Neutralization Reactions: Equivalent weight of an acid is that weight of it which contains one g atom of replaceable hydrogen e.g. 1.0078 g of hydrogen. Equivalent weight of monobasic acids is equal to its molecular weight

Molecular weight

Equivalent weight = -----

Basicity

Equivalent weight of a dibasic or a tribasic acid is  $\frac{1}{2}$  and . respectively of its molecular weight. Similarly, equivalent weight of a base is the weight of the substance, which contains one replaceable hydroxyl group.

Molecular weight

Equivalent weight = -----

Acidity

Molecular weight

Ex. (a) HCl EW = ----- = 36.5

1

Molecular weight

(b) H<sub>2</sub>SO<sub>4</sub> EW = -----

Acidity

98

= ----- = 49

2

Molecular Weight

(c) NaOH EW = -----

Basicity

40

= ----- = 40

1

Molecular weight

(d) Ca(OH)<sub>2</sub> EW = -----

Acidity

74

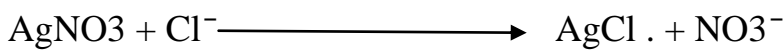
= ----- = 37

2

Equivalent weight in Complexation Reactions: The equivalent weight is the weight of the substance, which contains or reacts with 1 g atom of a univalent cation  $M^+$  (equivalent to 1.0078 g of hydrogen),  $\frac{1}{2}$  g atom of a bivalent cation  $M^{+2}$ ,  $\frac{1}{3}$  g atom of a trivalent cation  $M^{+3}$  etc. Equivalent weight of complexing agent is calculated on the basis of above definition.

For cations, equivalent weight is the atomic weight divided by the valency of atom. Equivalent weight in Precipitation Reactions: Equivalent weight of a salt in a precipitation reaction is the gram molecular weight of the salt divided by the valency of the reacting ions.

1.  $AgNO_3$



Molecular Weight

$$E.W. = \frac{\text{-----}}{\text{-----}}$$

Valency of reacting ions

Mol. Wt.

$$= \frac{\text{-----}}{\text{-----}}$$

1

2.  $NaCl$



Molecular weight

$$E.W. = \frac{\text{-----}}{\text{-----}}$$

1

Equivalent weight in Oxidation-Reduction Reactions: Equivalent weight of an oxidant or reductant can be defined as that weight of the substance, which reacts or contains 1.0078 g of available hydrogen or 8.0 g of available oxygen. Equivalent weight can be calculated by:

a) Ion-electron balance method.

b) Oxidation number method.

a) Ion-electron balance Method: Ion electron balance method is based on following steps:

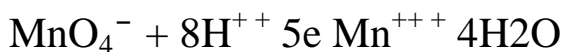
1. Ascertain the reactants and products of the reaction.
2. Determine oxidizing agent. Write down partial equation for oxidizing agent.
3. Determine reducing agent. Write down partial equation for reducing agent.
4. Add both partial equations and cancel out common substances after multiplying

both partial equations by suitable coefficient.

Example: Reduction of potassium permanganate by ferrous sulphate in presence of dilute sulphuric acid.

The first partial (reduction) is  $\text{MnO}_4^- \rightarrow \text{Mn}^{++}$

To balance atomically and electrically



The second partial (oxidation) is  $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$

To balance electrically  $\text{Fe}^{+2} - \text{e}^- \rightarrow \text{Fe}^{+3}$

Molecular weight

Equivalent weight = -----

Number of electrons transferred

M W                      158

E.W.  $\text{KmnO}_4$  = ----- = ----- = 31.6

5                              5

M W

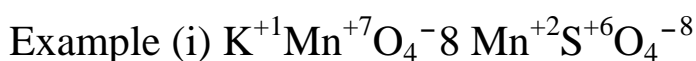
$$\text{E.W. FeSO}_4 = \frac{\text{Molecular weight}}{\text{Change in O.N.}} = 278$$

1

(b) Oxidation number method: Oxidation and reduction are the processes involving the changes in the valency. Oxidation number (O.N.) indicates the amount of oxidation or reduction, which is required to convert one atom of the element from free state to that in the compound. If oxidation is taking place the oxidation number is positive and if reduction is necessary oxidation number is negative.

Following general rules apply in determination of O.N.

- a) O.N. of free or uncombined element is zero.
- b) O.N. of hydrogen (except hydrides) is + 1.
- c) O.N. of oxygen except peroxides is -2.
- d) O.N. of metal in combination is generally positive.
- e) O.N. of radical or ion is equal to its electrovalency with correct sign.
- f) O.N. of compound is zero and is determined by sum of O.N. of individual atoms.



Change in oxidation number of manganese is from + 7 to + 2.

Molecular weight

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Change in O.N.}}$$

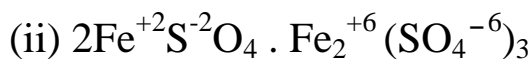
Change in O.N.

Mol. weight

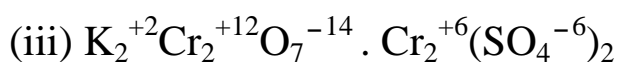
$$= \frac{\text{Molecular weight}}{\text{Change in O.N.}}$$

$$= \frac{\quad}{5} = 31.6$$

5



Change in O.N. per atom of iron is from +2 to +3 i.e. by 1 unit. Hence equivalent weight of ferrous sulphate is equal to its molecular weight.



The change in oxidation number is from +12 to +6 i.e. by 6 units and hence equivalent is 1/6 the molecular weight of potassium dichromate.

Titer: Solution concentration is expressed in the form of titer in quantitative analysis involving volumetric methods particularly. The titer gives the weight of some particular substances with which the solute in 1 ml of solution will react.

When the normality of solution is known in relation to a specific reaction titer of the solution can be calculated as

$$\text{Titer} = \text{Normality} \times \text{equivalent weight}$$

The titer of the solution changes with volume changes associated with temperature. Parts per Million and parts per billion: Parts per Million is frequently used to express the concentration of very dilute solutions and is expressed as 'ppm'.

Mass of solute

$$C_{\text{ppm}} = \frac{\quad}{\text{Mass of solution}} \times 10^6 \text{ ppm}$$

Mass of solution

For every dilute solution the concentration is expressed in parts per billion (ppb). These terms are also employed to express the concentration of impurities in pharmaceuticals.

## Titration curve

Titration curve is a plot of changes of some selected solution property during titration. Property selected depends on the titration. In the case of alkali metric titration we look for the changes in solution pH, in the case of complex metric titration we will usually trace changes in metal concentration (using its logarithm or minus logarithm on the plot, as concentration can change even 10<sup>10</sup> times), during redox titrations we are interested in the redox potential in the solution and so on. Most titration curves have the same shape - plateau in the first part, sharp rise (or fall) near equivalence point (inflection point of the curve), followed by the second flat part. The most important part of the curve is the one where the changes are the fastest - close to the inflection point.

