

Volumetric Analysis (Titration Methods)

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Titrimetric Methods: these include a large powerful group of quantitative procedures, based on measuring the amount of a reagent of known concentration that is consumed by an analyte.

Volumetric titrimetry: these involve measuring the volume of standard solution of known concentration that is needed to react essentially completely with the analyte.

In fact, titration methods are widely used than gravimetric methods for routine determinations because they are;

- rapid
- convenient
- accurate
- automated
- economic

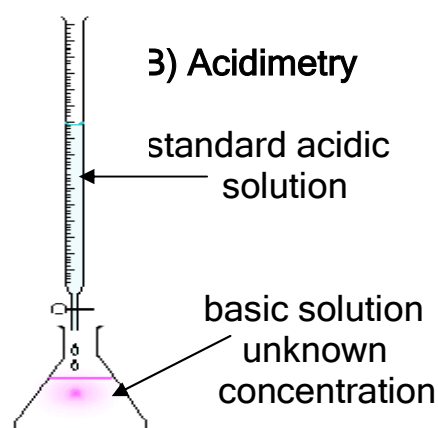
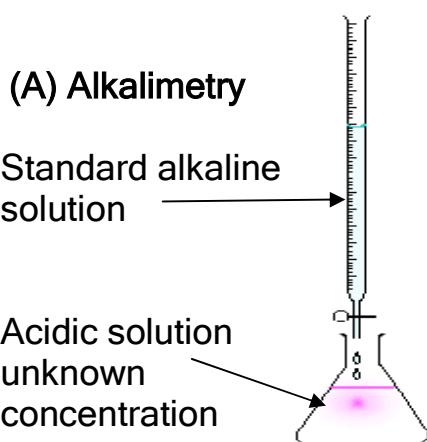
Classification of volumetric methods

These can be subdivided into the following principal methods;

- 1- **Neutralization:** The process in which a solution of one reactant, the titrant, is carefully added to a solution of another reactant, and the volume of titrant required for complete reaction is measured. i.e. these are based on reaction of acids with alkalise and on neutralization;



If it is used for determining the amount of acid in a given solution is called **alkalimetry**, while for base is called **acidimetry**.

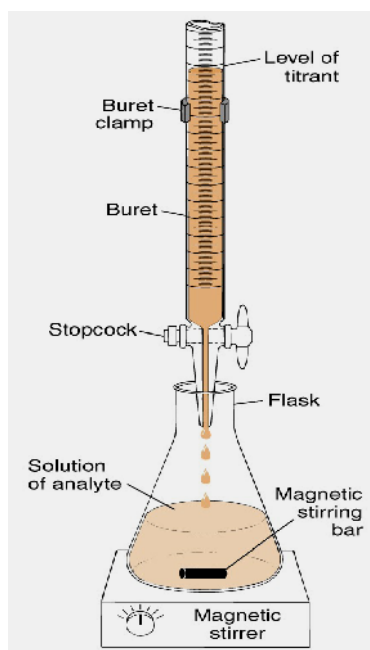


2- Oxidation-reduction methods(Oxidimetry): the commonest of these are;

- Permanganometry: the method based on reactions of oxidation with KMnO_4
- Iodometry: a technique in which an oxidant is treated with I^- to produce I_3^- which is then titrated (usually with thiosulfate).
- Chromatometry: in which oxidation by the action of $\text{K}_2\text{Cr}_2\text{O}_7$ is used.
- Bromatometry: involving oxidation an analyte with potassium bromate KBrO_3 .
- Cerimetry: involves the oxidation occur by cerium (IV) ion.
- Vanadometry: involves the oxidation of an analyte occur by VO_3^- ions.
- Titanometry: involves the reduction of an analyte by Ti (III) ions.

3- Complexometric titrations: one in which the reaction between analyte and titrant involves complex formation.**4- Precipitation titrations:** Based on reactions that yield ionic compounds of limited solubility.**Some General Aspect for Volumetric Titrimetry**

1. **Titration:** a procedure in which one substance (titrant) is carefully added to another (analyte) until complete reaction has occurred. The quantity of titrant required for complete reaction tells how much analyte is present.



2. **Standard solution** (titrant): a reagent of exactly known concentration that is used in a titrimetric analysis.
3. **Equivalent point**: when the quantity of added titrant (i.e. the exact stoichiometric amount) reacts with the quantity of analyte. It cannot be determined experimentally. Can be estimated by observing some physical change associated with the condition of equivalence (i.e., the end point). For example, (a) the equivalent point in the titration of NaCl with AgNO₃ occur after exactly 1 mole of Ag⁺ ions has been added for each mole of Cl⁻ ions in the sample (b) the equivalent point in the titration of H₂SO₄ with NaOH is reached after introduction of 2 mole of base for each mole of acid.
4. **End-point**: When a physical and chemical change occur that are associated with the condition of chemical equivalence. We choose an indicator with an end point close to the equivalence point, so that the color change in the indicator corresponds to the point at which the acid has been neutralized.
5. **Titration error**: The difference in volume or mass between the equivalence point and the end point as a result of inadequacies in the physical changes in our ability to observe them. The titration error is given by;

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

When V_{eq} is the theoretical volume of reagent required to reach the equivalent point and V_{ep} is the actual volume to arrive at the end-point.

6. **Indicators**: They are often added to the analyte solution to produce an observable physical change (the end point) at or near the equivalence point.
 - These are the chemical compounds that exhibit a change in color as a result of concentration changes in the relative concentration of analyte or titrant occur in the equivalent point region.
 - Typical indicator changes include appearance or disappearance of a color, a change in color or the appearance or disappearance of turbidity.
 - Most of these indicators used in volumetric analysis are weak organic acids and weak organic bases.

Primary & Secondary Standard Solutions

Primary Standards - Highly purified compound that serves as a reference material in volumetric and mass titrimetric methods.

- Important requirements:

- High purity (99.999%).
- Atmospheric stability.
- Absence of hydrate water so that the composition of the solid does not change with variations in humidity.
- Modest cost.
- Reasonable solubility in the titration medium.
- Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

- Desirable properties:

- be sufficiently stable so that it is necessary to determine its concentration only once;
- react rapidly with the analyte so that the time required between additions of reagent is minimized;
- react more or less completely with the analyte so that satisfactory end points are realized;
- Undergo a selective reaction with the analyte that can be described by a balanced equation.
- It should be nontoxic

Secondary standards: A compound whose purity has been established by chemical analysis and that serves as the reference material for a titrimetric method of analysis.

Some requirements which must be required in volumetric analysis:

1. The reaction should be rapid.
2. The reaction must be preceding forward completion.
3. The reaction must be describing balance chemical equation.
4. The absence of side reaction.
5. There must be available method for the detection of the end-point.

End-point Detections:

1. Color change : using Indicators
2. Turbidity change: resulting from the formation or disappearance of solid phase.

3. Electrical conductivity change.
4. Refractive index change.
5. Electrical potential change between two pairs of electrodes.
6. Temperature change
7. Using the so-called titration curves to determine the end-point of titration. It is stated as a graph of the pH of a solution as a function of the volume of titrant added.

Expressing the concentration of standard solutions

It is generally expressed in units of either; molarity (M) or normality (N);

Molarity (M): it is defined as the number of moles of reagent contained in one litre of solution.

$$M = \frac{\text{No. of moles of A}}{V \text{ (L)}} \quad \text{or} \quad \frac{\text{No. of mmoles of A}}{V \text{ (mL)}} \quad \text{---- (1)}$$

$$M = \frac{\text{Weight of A(g)}}{\text{M.wt (g/ mol).}} \times \frac{1000 \text{ mL/ L}}{V \text{ (mL)}} \quad \text{----(2)}$$

Normality (N): defined as the number of equivalents of reagent in one litre of solution or the number of milliequivalents in one mL of solution.

$$N = \frac{\text{No. of eq. of A}}{V \text{ (L)}} \quad \text{or} \quad \frac{\text{No. of meq. of A}}{V \text{ (mL)}} \quad \text{----(3)}$$

$$N = \frac{\text{Weight of A(g)}}{\text{Eq.wt (g/eq.wt.)}} \times \frac{1000 \text{ mL/ L}}{V \text{ (mL)}} \quad \text{---- (4)}$$

Volumetric Calculations Using Molraity:

For the chemical species A , we may write;

$$\text{Amount of A (mol)} = \frac{\text{mass of A (g)}}{\text{molar mass A (g/mol)}} \quad \text{---- (5)}$$

We may derive from the definition of molar concentration . that is;

$$\text{Amount of A (mol)} = V \text{ (L) } \times C_A \text{ (mol A/L)} \quad \text{----(6)}$$

or,

$$\text{Amount of A (mmol)} = V \text{ (mL) } \times C_A \text{ (mmol A/mL)} \quad \text{----(7)}$$

Example 1: Describe the preparation of 2.0 L of 0.050 M AgNO₃ (169.87 g/mol) from the primary standard grade solid.

Solution:

Since the volume is in liters , we base our calculations one the mole rather than the millimole. Thus , to obtain the amount of AgNO₃ needed, we write;

$$\begin{aligned} \text{Amount AgNO}_3 &= V_{\text{sol}} \text{ (L)} \times C_{\text{AgNO}_3} \text{ (mol/L)} \\ &= 2.0 \text{ L} \times 0.050 \text{ mol/L} = 0.10 \text{ mol AgNO}_3 \end{aligned}$$

To obtain the mass of AgNO₃ ;

$$\text{Mass AgNO}_3 = 0.10 \text{ mol} \times 169.87 \text{ g/mol} = 16.98 \text{ g}$$

Therefore , the solution is prepared by dissolving 16.98 g of AgNO₃ in water and diluting to exactly 2.0 L.

We can also use the formula to find out the mass of AgNO₃

$$M = \frac{\text{mass . solute}}{\text{Molar mass}} \times \frac{1}{V \text{ (L)}}$$

$$0.050 = \frac{\text{mass AgNO}_3}{169.87} \times \frac{1}{2}$$

$$\text{mass AgNO}_3 = 16.98 \text{ g}$$

Example 2: A standard 0.010 M solution of Na^+ is required to calibrate a flame photometric method to determine the element. Describe how 500 mL of this solution can be prepared from primary standard Na_2CO_3 (105.99 g/mol) .

Solution:

We wish to compute the mass of reagent required to give a species molarity of 0.010. Here, we will use millimole, since the volume is in millimetres. Because Na_2CO_3 dissociates to give two Na^+ ions, we can write that the number of millimoles of Na_2CO_3 needed is;

$$\begin{aligned} \text{Amount Na}_2\text{CO}_3 &= 500 \text{ mL} \times 0.010 \text{ mmol Na}^+ / \text{mL} \times \frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol Na}^+} \\ &= 2.50 \text{ mmol} \end{aligned}$$

From the definition of millimole, we write;

$$\begin{aligned} \text{Mass Na}_2\text{CO}_3 &= 2.50 \text{ mmol Na}_2\text{CO}_3 \times 0.10599 \text{ g Na}_2\text{CO}_3 / \text{mmol Na}_2\text{CO}_3 \\ &= 0.265 \text{ g} \end{aligned}$$

The solution is therefore prepared by dissolving 0.265 g of Na_2CO_3 in water and diluting to 500 mL.

Example 3: How would you prepare 50.0-mL portions of standard solutions that are 0.005 M, 0.002 M, and 0.001 M in Na from the solution in example 2.

Solution :

The number of millimoles of Na:

amount of Na from conc sol = amount of Na^+ in dil soln

since, $V_{\text{concd}} \times C_{\text{concd}} = V_{\text{dil}} \times C_{\text{dil}}$

where V_{concd} and V_{dil} are the volumes in milliliters of the concentrated and diluted solutions, respectively, and C_{concd} and C_{dil} are their molar Na^+ concentrations.

- For the 0.005 M solution, this equation rearranges to;

$$V_{\text{conc}} = \frac{V_{\text{dil}} \times C_{\text{dil}}}{C_{\text{concd}}} = \frac{50.0 \times 0.005}{0.01} = 25.0 \text{ mL}$$

To produce 50.0 mL of 0.00500 M Na, 25.0 mL of the concentrated solution should be diluted to exactly 50.0 mL.

Volumetric Calculations Using Normality:

For the chemical species A, we may write;

$$\text{amount A (eq.)} = \frac{\text{mass A (g)}}{\text{eq.mass A (g/eq.)}}$$

$$\begin{aligned} \text{amount A (meq.)} &= V \text{ (mL)} \times C_A \text{ (meq A/mL)} \\ \text{amount A (eq.)} &= V \text{ (L)} \times C_A \text{ (eq.A/L)} \end{aligned}$$

The amount of substance contained in one equivalent can be vary from reaction to reaction.

Equivalent weights in Neutralization reaction:

Eq.wt. of acid : is the weight of acid that liberated 1 g formula weight of H^+ ion (one proton).

Eq.wt. of base: is the weight of base that can be accepted or reacted with one proton.

Material	Chemical equation	Equivalent weight
For acids		
HCl	$\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$	mol. weight
HI	$\text{HI} \longrightarrow \text{H}^+ + \text{I}^-$	mol. weight
HNO_3	$\text{HNO}_3 \longrightarrow \text{H}^+ + \text{NO}_3^-$	mol. weight
HClO_4	$\text{HClO}_4 \longrightarrow \text{H}^+ + \text{ClO}_4^-$	mol. weight
CH_3COOH	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	mol. weight

H ₂ SO ₄	$\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}^+ + \text{SO}_4^{2-}$	mol. weight/2
H ₂ C ₂ O ₄	$\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$	mol. weight/2
H ₃ PO ₄	$\text{H}_3\text{PO}_4 \rightleftharpoons 3\text{H}^+ + \text{PO}_4^{3-}$	mol. weight/3
H ₃ PO ₄	$\text{H}_3\text{PO}_4 \rightleftharpoons 2\text{H}^+ + \text{HPO}_4^{2-}$	mol. weight/2
H ₃ PO ₄	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	mol. weight
For Bases		
NaOH	$\text{NaOH} + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{Na}^+$	mol. weight
KOH	$\text{KOH} + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{K}^+$	mol. weight
Ba(OH) ₂	$\text{Ba(OH)}_2 + 2\text{H}^+ \longrightarrow 2\text{H}_2\text{O} + \text{Ba}^{2+}$	mol. weight/2
Al(OH) ₃	$\text{Al(OH)}_3 + 3\text{H}^+ \longrightarrow 3\text{H}_2\text{O} + \text{Al}^{3+}$	mol. weight/3
Fe ₂ O ₃	$\text{Fe}_2\text{O}_3 + 6\text{H}^+ \longrightarrow 3\text{H}_2\text{O} + 2\text{Fe}^{3+}$	mol. weight/6

Equivalent weight of acidic and basic salts

- **eq.wt. of acidic salts:** is the weight of salt that accepted or liberated one proton.
- **eq.wt. of basic salts:** is the weight of salt that reacted with one proton.

Material	Chemical equation	Equivalent weight
Basic salt		
Na ₂ CO ₃	$\text{Na}_2\text{CO}_3 + \text{HCl} \xrightarrow{\text{Ph.ph.}} \text{NaHCO}_3 + \text{NaCl}$	mol. weight
Na ₂ CO ₃	$\text{Na}_2\text{CO}_3 + 2\text{HCl} \xrightarrow{\text{M.O.}} \text{H}_2\text{CO}_3 + 2\text{NaCl}$	mol. weight/2
Na ₂ B ₄ O ₇	$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \longrightarrow 2\text{NaCl} + 4\text{H}_3\text{BO}_3$	mol. weight/2
KCN	$\text{KCN} + \text{HCl} \longrightarrow \text{HCN} + \text{KCl}$	mol. weight
Acidic salt		
KHSO ₄	$\text{KHSO}_4 \rightleftharpoons \text{H}^+ + \text{K}^+ + \text{SO}_4^{2-}$	mol. weight
KHC ₈ H ₄ O ₄	$\text{KHC}_8\text{H}_4\text{O}_4 \rightleftharpoons \text{H}^+ + \text{K}^+ + \text{C}_8\text{H}_4\text{O}_4^{2-}$	mol. weight
KH(IO ₃) ₂	$\text{KH(IO}_3)_2 \rightleftharpoons \text{H}^+ + \text{K}^+ + 2\text{IO}_3^-$	mol. weight

Equivalent weights for oxidation /reduction reaction

The equivalent weights of a participant in an oxidation/reduction reaction are that the amount that directly or indirectly produces or consumes 1 mole of electrons.

Eq.wt. of reducing agent: that is the weight of substance divided by the number of electron lost.

Eq.wt. of oxidizing agent: that is the weight of substance divided by the number of electron gained.

Material	Chemical equation	Equivalent weight
KMnO ₄	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \xrightarrow{\text{acidic}} \text{Mn}^{2+} + 4\text{H}_2\text{O}$	mol. Weight/5
KMnO ₄	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \xrightarrow{\text{neutral}} \text{Mn}^{2+} + 4\text{H}_2\text{O}$	mol. Weight/3
KMnO ₄	$\text{MnO}_4^- + \text{e}^- \longrightarrow \text{MnO}_4^{2-}$	mol. weight
KCr ₂ O ₇	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	mol. Weight/6
KCr ₂ O ₇	$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	mol. weight
KIO ₃	$\text{IO}_3^- + 6\text{H}^+ + 6\text{e}^- \longrightarrow \text{I}^- + 3\text{H}_2\text{O}$	mol. weight/6
KIBrO ₃	$\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \longrightarrow \text{Br}^- + 3\text{H}_2\text{O}$	mol. weight/6
Mn	$\text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{e}^- \longrightarrow \text{MnO}_4^- + 8\text{H}^+$	mol. weight/5

Equivalent weights in precipitation and complex formation reaction

- Stated as the weight that reacts with or provides one mole of the reacting cation if it is univalent, one-half if it is bivalent, one-third if it is trivalent and so on.

Material	Chemical equation	Equivalent weight
AgNO ₃	$\text{AgNO}_3 \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$	mol. Weight
KCl	$\text{KCl} + \text{Ag}^+ \rightleftharpoons \text{AgCl} + \text{K}^+$	mol. Weight
KBr	$\text{KBr} + \text{Ag}^+ \rightleftharpoons \text{AgBr} + \text{K}^+$	mol. weight
Co	$\text{Co}^{2+} + 4\text{C}_5\text{H}_5\text{N}^+ + 2\text{SCN}^- \longrightarrow [\text{Co}(\text{C}_5\text{H}_5\text{N})](\text{SCN})_2$	mol. Weight/2
Ni	$\text{Ni}^{2+} + 4\text{C}_5\text{H}_5\text{N}^+ + 2\text{SCN}^- \longrightarrow [\text{Ni}(\text{C}_5\text{H}_5\text{N})](\text{SCN})_2$	mol. Weight/2
HgCl ₂	$\text{Hg}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{HgCl}_2$	mol. weight/2

Titer (T) :

The titer of a solution is the weight of a substance that is chemically equivalent to one millilitre of that standard solution.

$$T = N \times \text{eq.wt} = \text{mg/mL}$$

Example 4: what will be the sulphuric acid titer for complete neutralization when the normality of NaOH is 0.1 N?

Solution:

$$T = N \times \text{eq.wt} = \text{mg/mL}$$

$$T_{\text{H}_2\text{SO}_4} = 0.1 \text{ meq/mL} \times 49.04 \text{ mg/meq} = 4.904 \text{ mg/mL}$$

Example 5: Calculate the normality for each of NaOH and AgNO₃ solutions which have an HCl titer of 4.0 mg/mL.

Solution:

For NaOH solution ;

$$4.0 \text{ mg/mL} = N \times 40 \text{ mg / meq}$$
$$N = 4.0/40 = 0.1 \text{ meq/mL} = 0.1 \text{ N}$$

For AgNO₃ solution;

$$4.0 \text{ mg/mL} = N \times 169.89 \text{ mg / meq}$$
$$N = 0.0236 \text{ meq/mL}$$
$$= 0.0236 \text{ N}$$

Calculation of the normality and molarity of standard solutions:

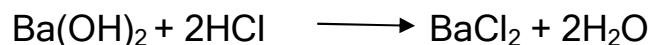
The normality of a standard solution is calculated either from the;

- Data from the titration of a primary standard(indirect method)
- The data related to its actual preparation (direct method).
-

Example 6: A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 N Ba(OH)₂ to reach an end point with bromocresol green indicator. Calculate the normality of the HCl.

Solution:

1 mmol of $\text{Ba}(\text{OH})_2$ reacts with 2 mmol of HCl as in the following equation;



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

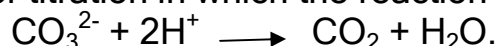
$$2(\text{No. meq. HCl}) = \text{No. meq. Ba}(\text{OH})_2$$

$$\text{No. meq. Ba}(\text{OH})_2 = 29.71 \text{ mL} \times 0.01963 \text{ meq/mL} = 0.5832$$

$$1/2 (50 \text{ mL} \times N) = 0.5832$$

$$N = 0.0233 \text{ meq/L}$$

Example 7: Describe the preparation of 5L of 0.1N Na_2CO_3 (105.99 g/mol) from the primary standard solid assuming that the solution is to be used for titration in which the reaction is;

**Solution:**

$$\begin{aligned} \text{No. of eq. of Na}_2\text{CO}_3 &= 5 \text{ L} \times 0.1 \text{ eq/L} \\ &= 0.5 \text{ eq.} \end{aligned}$$

$$\text{No. eq.} = w (\text{mass}) / \text{eq.wt.}$$

$$0.5 = w / 105.99/2$$

$$w = 0.5 \times 105.99/2 = 26.50 \text{ g of Na}_2\text{CO}_3$$

We have to dissolve 26.50 g of Na_2CO_3 in H_2O and dilute to 5 L .

Another method can be used to calculate the mass of Na_2CO_3

$$N = \frac{\text{mass . solute}}{\text{eq.wt}} \times \frac{1}{V(\text{L})}$$

$$0.1 = \frac{\quad}{105.99/2} \times \frac{\quad}{5}$$

mass $\text{AgNO}_3 = 26.50 \text{ g}$ Na_2CO_3 must be dissolved in 5 L H_2O

Example 8: Titration of 0.2121 g of pure $\text{Na}_2\text{C}_2\text{O}_4$ (m.wt. 134 g/mol) required 43.31 mL KMnO_4 . What is the molarity of KMnO_4 solution. The chemical reaction is;



Solution:

From the above equation, we see that,

$$\text{stoichiometric ratio} = \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}$$

The amount of primary standard $\text{Na}_2\text{C}_2\text{O}_4$ is given by equation 5;

$$\text{amount Na}_2\text{C}_2\text{O}_4 = 0.2121 \text{ g Na}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mmol Na}_2\text{C}_2\text{O}_4}{0.134 \text{ g Na}_2\text{C}_2\text{O}_4}$$

To obtain the number of millimoles of KMnO_4 , we multiply this result by stoichiometric ratio:

$$\begin{aligned} \text{amount KMnO}_4 &= \frac{0.2121}{0.1340} \text{ mmol Na}_2\text{C}_2\text{O}_4 \times \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4} \\ &= 0.6331 \text{ mmol} \end{aligned}$$

The molarity is then obtained by dividing the volume of KMnO_4 consumed. Thus,

$$C_{\text{KMnO}_4} = 0.6331 \text{ mmol KMnO}_4 / 43.31 \text{ mL KMnO}_4 = 0.01462 \text{ M}$$

Calculation the quantity of analyte from titration data

Example 9: A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{2+} and titrated with 47.22 mL of 0.02242 M KMnO_4 solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 g/mol) and (b) % Fe_3O_4 (231.54 g/mol).

Solution:

The reaction is:



$$\text{Stoichiometric ratio} = \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4}$$

$$\text{amount KMnO}_4 = 47.22 \text{ mL} \times 0.02242 \text{ mmol/mL} = 1.05867 \text{ mmol}$$

hence,

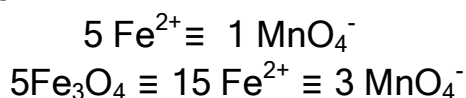
$$\text{amount Fe}^{2+} = 1.05867 \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4} = 5.299 \text{ mmol}$$

The mass of Fe^{2+} is then given by;

$$\text{Mass Fe}^{2+} = 5.299 \text{ mmol} \times 0.05587 \text{ g/mmol} = 0.2957 \text{ g}$$

$$\% \text{ Fe}^{2+} = \frac{0.2957}{0.8040} \times 100 = 36.78\%$$

Correct stoichiometric ratio

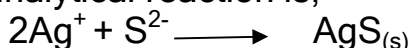


$$\text{Stoichiometric ratio} = \frac{5 \text{ mmol Fe}_3\text{O}_4}{3 \text{ mmol KMnO}_4}$$

$$\begin{aligned}\text{amount Fe}_3\text{O}_4 &= 1.05867 \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Fe}^{2+}}{3 \text{ mmol KMnO}_4} \\ &= 1.7645 \text{ mmol} \\ \text{Mass Fe}_3\text{O}_4 &= 1.7645 \text{ mmol} \times 0.23154 \text{ g/mmol} = 0.40854 \text{ g}\end{aligned}$$

$$\% \text{ Fe}_3\text{O}_4 = \frac{0.40854}{0.08040} \times 100 = 60.37\%$$

Example 10: A 100 mL sample of brackish water was made ammoniacal, and the sulphide it contained was titrated with 16.47 mL of 0.02310 M AgNO_3 . the analytical reaction is;



Calculate the concentration of H_2S in the water in part per million.

Solution:

$$\text{Stoichiometric ratio} = \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3}$$

$$\text{amount AgNO}_3 = 16.47 \text{ mL} \times 0.02310 \text{ mmol/mL} = 0.3804 \text{ mmol}$$

$$\text{amount H}_2\text{S} = 0.3804 \text{ mmol AgNO}_3 \times \frac{1 \text{ mmol H}_2\text{S}}{2 \text{ mmol AgNO}_3} = 0.1902 \text{ mmol}$$

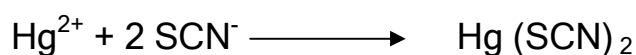
$$\text{mass H}_2\text{S} = 0.1902 \text{ mmol} \times 0.034081 \text{ g/mmol} = 6.483 \times 10^{-3} \text{ g}$$

$$\text{Conc. H}_2\text{S} = \frac{6.483 \times 10^{-3} \text{ g H}_2\text{S}}{100 \text{ mL} \times 1.0 \text{ g sample / mL sample}} \times 10^6 \text{ ppm} = 64.8 \text{ ppm}$$

Example 11: The organic matter in a 3.776 g sample of a mercuric ointment is decomposed with HNO_3 . After dilution, the Hg^{2+} is titrated with 21.30 mL of a 0.1144 M solution of NH_4SCN . Calculate the %Hg (200.5 g/mol) in ointment.

Solution:

This titration involves the formation of a stable neutral complex $\text{Hg}(\text{SCN})_2$;



Stoichiometric ratio:
$$\frac{1 \text{ mmol Hg}^{2+}}{2 \text{ mmol NH}_4\text{SCN}}$$

$$\begin{aligned} \text{Amount (mmol) NH}_4\text{SCN} &= 21.30 \text{ mL} \times 0.1144 \text{ mmol/mL} \\ &= 2.4367 \text{ mmol} \end{aligned}$$

$$\text{Amount (mmol) Hg}^{2+} = 2.4367 \times \frac{1}{2} = 1.21836$$

$$\begin{aligned} \text{mass (g) Hg}^{2+} &= 1.21836 \text{ mmol} \times 0.20059 \text{ g/mmol} \\ &= 0.2444 \text{ g} \end{aligned}$$

$$\% \text{ Hg} = \frac{0.2444}{3.776} \times 100 = 6.47$$

or

$$\begin{aligned} \% \text{Hg} &= \frac{V_{\text{NH}_4\text{SCN}} \times M_{\text{NH}_4\text{SCN}} \times \frac{a}{b} \times \text{m.wt} \times 10^{-3}}{W_{\text{sample}}} \times 100 \\ &= \frac{21.30 \times 0.1144 \times \frac{1}{2} \times 200.59 \times 10^{-3}}{3.776} \times 100 \\ &= 6.47 \end{aligned}$$

Back-titration:

The titration of an excess of a standard solution that has reacted completely with an analyte, or is the process in which the excess of 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 e.g. as in Volhard method.

Example 12: A 0.4755 g sample containing $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and inert compounds was dissolved in water and made alkaline with KOH. The liberated ammonia was distilled into a flask containing 50 mL of 0.1007 N (0.05035 M) H_2SO_4 . The excess of acid was back-titrated with 11.31 mL of 0.1214 N NaOH. Calculate the %N (14.007 g/mol) and of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (124.10 g/mol) in the sample.

Solution:

At equivalent point, the meq. of acid and base are equal. In this titration, however two bases are involved NaOH and NH_3 .

$$\text{no. meq. H}_2\text{SO}_4 = \text{no. meq. NH}_3 + \text{no. meq. NaOH}$$

$$\text{no. meq. NH}_3 = \text{no. meq. N} = \text{no. meq. H}_2\text{SO}_4 - \text{no. meq. NaOH}$$

$$\frac{\text{mass N (g)}}{\text{meq.wt. N(g/meq)}} = 50 \text{ mL} \times 0.1007 \text{ meq/mL} - 11.31 \text{ mL} \times 0.1214 \text{ meq/mL}$$

$$\text{mass N (g)} = (50 \times 0.1007 - 11.31 \times 0.1214) \times 0.014007 = 0.0513 \text{ g}$$

$$\begin{aligned} \%N &= \frac{(50 \times 0.1007 - 11.31 \times 0.1214) \times 0.014007}{0.4755} \times 100 \\ &= 10.85\% \end{aligned}$$

$$\text{Wt. } (\text{NH}_4)_2\text{C}_2\text{O}_4 = \text{wt. (N)} \times \frac{\text{f.w } (\text{NH}_4)_2\text{C}_2\text{O}_4}{4 \times \text{At.wt (N)}}$$

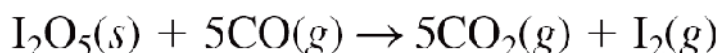
$$124.10$$

$$= 0.0531 \times \frac{\quad}{56.028} = 0.1176 \text{ g}$$

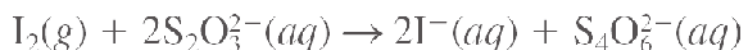
$$\% (\text{NH}_4)_2\text{C}_2\text{O}_4 = \frac{\text{Wt. } (\text{NH}_4)_2\text{C}_2\text{O}_4}{\text{Wt. sample}} \times 100$$

$$\% (\text{NH}_4)_2\text{C}_2\text{O}_4 = \frac{0.1176}{0.4755} \times 100 = 24.73$$

Homework1: The CO in a 20.3-L sample of gas was converted to CO₂ by passing the gas over iodine pentoxide heated to 150°C:



The iodine was distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M Na₂S₂O₃.

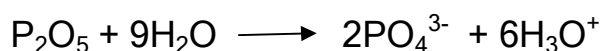


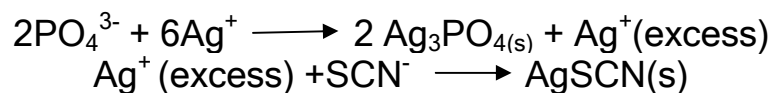
The excess Na₂S₂O₃ was back-titrated with 2.16 mL of 0.00947 M I₂ solution. Calculate the concentration in milligrams of CO (28.01 g/mol) per litre of sample.

Homework 2: A mixture weighing 27.73 mg containing only FeCl₂ (FM = 126.75) and KCl (FM = 74.55) required 18.49 mL of 0.02237 M AgNO₃ for complete titration of the chloride. Find the mass of FeCl₂ and the weight percent of Fe in the mixture.

Example 13: The phosphorous in a 4.258 g sample of a plant food was converted to PO₄³⁻ and precipitated as Ag₃PO₄ through the addition of 50.00 mL of 0.0820 M AgNO₃. The excess AgNO₃ was back-titrated with 4.06 mL of KSCN. Express the results of this analysis in terms of %P₂O₅.

Solution:





Thus the stoichiometric ratios are;

$$\frac{1 \text{ mmol P}_2\text{O}_5}{6 \text{ mmol AgNO}_3} \quad \text{and} \quad \frac{1 \text{ mmol KSCN}}{1 \text{ mmol AgNO}_3}$$

$$\text{total amount AgNO}_3 = 50.00 \text{ mL} \times 0.0820 \frac{\text{mmol AgNO}_3}{\text{mL}} = 4.100 \text{ mmol}$$

$$\begin{aligned} \text{amount AgNO}_3 \text{ consumed by KSCN} &= 4.06 \text{ mL} \times 0.0625 \frac{\text{mmol KSCN}}{\text{mL}} \\ &\quad \times \frac{1 \text{ mmol AgNO}_3}{\text{mmol KSCN}} \\ &= 0.2538 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{amount P}_2\text{O}_5 &= (4.100 - 0.254) \text{ mmol AgNO}_3 \times \frac{1 \text{ mmol P}_2\text{O}_5}{6 \text{ mmol AgNO}_3} \\ &= 0.6410 \text{ mmol P}_2\text{O}_5 \end{aligned}$$

$$\begin{aligned} \text{wt of P}_2\text{O}_5 &= 0.6410 \text{ mmol P}_2\text{O}_5 \times 0.1419 \text{ gP}_2\text{O}_5 / \text{mmol} \\ &= 0.0909 \text{ g} \end{aligned}$$

$$\% \text{P}_2\text{O}_5 = \frac{0.0909 \text{ g}}{4.258 \text{ g}} \times 100 = 2.14\%$$

Exercises No. 1

1. Distinguish between terms end point and equivalent point.
2. define (a) titration error (b) millimole (c) titration
3. Distinguish between a primary standard and a secondary standard.
4. How many milligrams of oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (FM 126.07), will react with 1.00 mL of 0.0273 M ceric sulfate ($\text{Ce}(\text{SO}_4)_2$) if the reaction is; $\text{H}_2\text{C}_2\text{O}_4 + 2\text{Ce}^{4+} \rightarrow 2\text{CO}_2 + 2\text{Ce}^{3+} + 2\text{H}^+$? (Ans: 1.72 mg)
5. A mixture weighing 27.73 mg containing only FeCl_2 (FM 126.75) and KCl (FM 74.55) required 18.49 mL of 0.02237 M AgNO_3 for complete titration of the chloride. Find the mass of FeCl_2 and the weight percent of Fe in the mixture. (Ans: 17.26 mg ; 28.0% Fe)
6. A typical protein contains 16.2 wt% nitrogen. A 0.500 mL aliquot protein solution was digested and liberated NH_3 was distilled into 10.00 mL of 0.02140 M HCl . The unreacted HCl required 3.26 mL of 0.0198 M NaOH for complete titration. Find the concentration of protein (mg/mL) in the original sample. (Ans: 25.8 mg protein/mL)
7. If 3.00 g of solid KOH and 5.00 g of solid NaOH are mixed, dissolved in water, and the solution made up to 1500 mL. What is the normality of the solution as a base? (Ans; 0.119 N).
8. How much 0.600 N base must be added to 759 mL of a 0.200 N base in order to be 0.300? (Ans: 250 mL).
9. A sample of pure oxalic acid weighs 0.20 g and required 30.12 mL of KOH solution for complete neutralization. What is the normality of KOH solution? (Ans; 0.1053 N).
10. A sample of meat scrap weighing 2.0 g is digested with concentrated H_2SO_4 and a catalyst. the resulting solution is made alkaline with NaOH and the liberated ammonia distilled into 50.0 mL of 0.6700N H_2SO_4 . the excess acid then requires 30.10 mL of 0.6520 N NaOH for neutralization. Calculate the percentage of nitrogen in the meat? (Ans; 9.72%) .
11. Choose one alternative that best complete the statement or answer the questions;
A- The total concentration of ions in a 0.250 M solution of HCl is -----
(1) 0.750 M (2) essentially zero (3) 0.250 M (4) 0.500 M (5) 0.125 M
B- A strong electrolyte is one that -----completely in solution.
(1) Ionizes (2) decomposes (3) disappears (4) reacts
C- A weak electrolyte exists predominately as ----- in solution.
(1) Electron (2) an isotope (3) molecules (4) atoms (5) ions

- D- The balanced net ionic equation for precipitation of CaCO_3 when aqueous solutions of Na_2CO_3 and CaCl_2 are mixed is -----
- (1) $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \longrightarrow \text{CaCO}_3$
(2) $\text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{NaCl}$
(3) $\text{Na}_2\text{CO}_3(\text{aq}) + \text{CaCl}_2(\text{aq}) \longrightarrow 2\text{NaCl}(\text{aq}) + \text{CaCO}_3(\text{s})$
(4) $2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-} \longrightarrow \text{Na}_2\text{CO}_3(\text{aq})$
(5) $2\text{Na}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \longrightarrow 2\text{NaCl}(\text{aq})$
- E- Combining aqueous solution of BaI_2 and Na_2SO_4 affords a precipitate of BaSO_4 . Which ion(s) is /are spectator ions in the following reactions.
(1) SO_4^{2-} and I^- (2) Ba^{2+} and SO_4^{2-} (3) Ba^{2+} only (4) Na^+ only (5) Na^+ and I^-
- F- When H_2SO_4 is neutralized by NaOH in aqueous solution, the net ionic equation is -----
- (1) $\text{SO}_4^{2-}(\text{aq}) + 2\text{Na}^+(\text{aq}) \longrightarrow \text{Na}_2\text{SO}_4(\text{aq})$
(2) $\text{SO}_4^{2-}(\text{aq}) + 2\text{Na}^+(\text{aq}) \longrightarrow \text{Na}_2\text{SO}_4(\text{s})$
(3) $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$
(4) $\text{H}_2\text{SO}_4(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{SO}_4^{2-}(\text{aq})$
(5) $2\text{H}^+(\text{aq}) + 2\text{NaOH}(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{Na}^+$
- G- Which of the following are strong acids?
(1) HNO_3 , HF , HBr (2) HF , HBr (3) HI , HNO_3 , HF , HBr (4) HI , HF , HBr (5) HI , HNO_3 , HBr
- H- Of the species below, only ----- is not an electrolyte.
(1) KOH (2) Ar (3) Rb_2SO_4 (4) NaCl (5) HCl
- I- What is the concentration (M) of NaCl solution prepared by dissolving 9.3 g of NaCl in sufficient water to give 350 mL solution?
(1) 0.16 (2) 0.45 (3) 18 (4) 27 (5) 2.7×10^{-2}
- J- There are ----- mole of bromide ions in 500 mL of a 0.300 M solution of AlBr_3
(1) 0.500 (2) 0.0500 (3) 0.150 (4) 0.167 (5) 0.450
- K- An aqueous ethanol solution (400 mL) was diluted to 4.00 L giving a concentration of 0.0400 M. the concentration of the original solution was----- M
(1) 4.00 (2) 0.200 (3) 0.400 (4) 2.00 (5) 1.60
- L- The concentration of species in 500 mL of 2.104 M solution of sodium sulphate is ----- M sodium and ----- M sulphate ion.
(1) 1.050, 1.052 (2) 2.104, 2.104 (3) 2.104, 1.052 (4) 2.104, 4.208 (5) 4.208, 2.104
- M- In a titration of 35 mL of 0.737M H_2SO_4 ----- mL of a 0.827 M KOH is required for neutralization.
(1) 62.4 (2) 1.12 (3) 35.0 (4) 39.3 (5) 25.8