Analytical chemistry

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Solution Composition

- Solution: A solute dissolved in a solvent.

- Solute: The substance which is dissolved.

- Solvent: The substance in which it is dissolved.

- Aqueous solutions: A solution in water.

- **Molarity:** Moles of solute per litre of solution.

- If we know the molarity and litres of solution, we can calculate the moles (and mass) of solute present.

VOLUMETRIC ANALYSIS

- Volumetric Analysis is a method of analysis based on titration.

- Titration is a procedure for determining the amount of a particular substance A by adding a carefully measured volume of a solution with a known concentration of B until the reaction is complete.

Stoichiometric calculations in volumetric analysis
Volumetric titration

A solution of accurately known concentration (Standard solution) is gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.
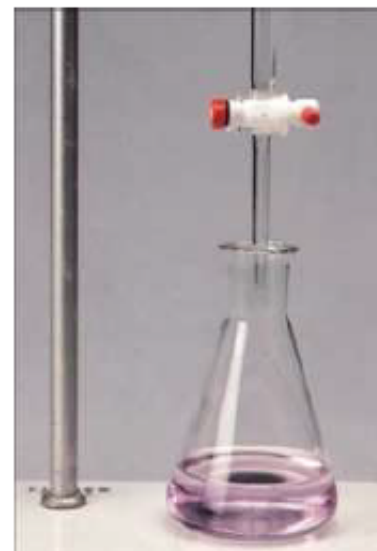
Equivalence point– the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point

Endpoint –the point at which the color of indicator changes
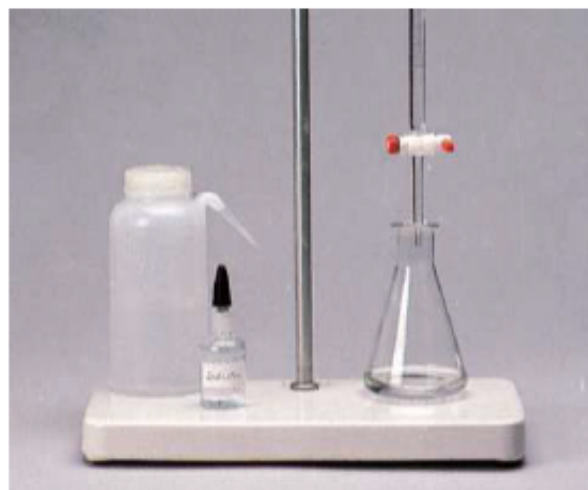
The titrant is add Slowly until

The indicator changes color (pink)

- The reaction must be **stoichiometric**. That is, there must be a well-defined and known reaction between the analyte and the titrant.

  $NaOH + HCl \rightarrow NaCl + H_2O$

- The reaction should be *rapid*. Most ionic reactions are very rapid.

- There should be *no side reactions,* and the reaction should be specific.

- There should be a *marked change in some property of the solution when the reaction is complete.* This may be a **change in color** of the solution.

- A color change is usually brought about by addition of an indicator, whose color is dependent on the properties of the solution, for example, the pH.

Standard Solutions

- A solution that contains a known concentration of an analyte
- It is prepared by dissolving accurately weighed quantity of highly pure material called Primary Standard material.
- The primary standard material should fulfill the following requirements:

1. It should be *100.00% pure*, although 0.01 to 0.02% impurity is tolerable if it is accurately known.

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]

3. It should be *readily available* and fairly inexpensive.

4. Although not necessary, it should have a *high formula weight*. This is so that a relatively large amount of it will have to be weighed to get enough to titrate. The relative error in weighing a greater amount of material will be smaller than that for a small amount.

5. If it is to be used in titration, it should possess the *properties required for a titration* listed above. In particular, the equilibrium of the reaction should be far to the right so that a very sharp end point will be obtained.

Analytical chemistry

There are two ways for prepare standard solution :

1)   Directly , by dissolving a carefully weight   quantity of pure reagent and diluting to an exactly known volume .

2)   Indirectly , by titrating a weighed quantity of pure substance with the reagent solution .

Types of titration reactions

Types of titration reactions :

1) Acid-base titration(neutralization titration):

$$HA + OH^- \longrightarrow A^- + H_2O$$

$$H^+ + B \longrightarrow BH^+$$

2) Precipitation titration :

$$Ag^+ + Cl^- \longrightarrow AgCl_{(s)}$$

3) Complex formation :

$$Cu^{+2} + 4NH_3^+ \longrightarrow [Cu(NH_3)_4]^{+2}$$

4) Oxidation-reduction reaction :
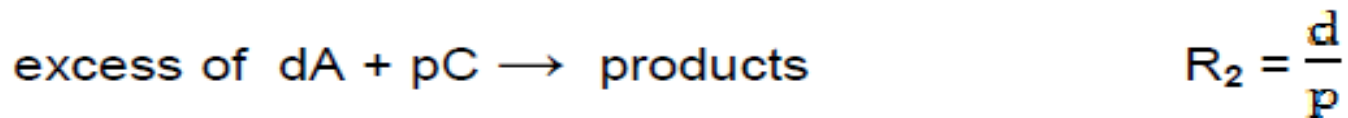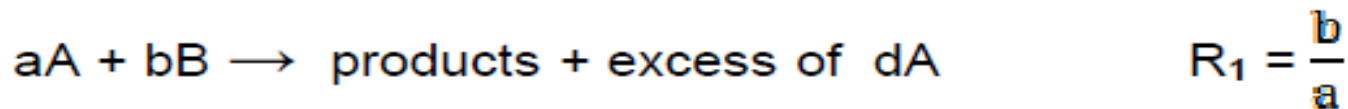
$$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

Back titration

Back- titration :

In this type of titration , when the reaction is slow and the end point is not clear and when we need to determine analyte like B , it is convenient or necessary to added an excess amount from A , and the excess amount will be determine by back-titration with a second (another) standard sol. like C .

aA + bB $\longrightarrow$ products + excess of dA $\qquad$ $R_1 = \dfrac{b}{a}$

excess of dA + pC $\longrightarrow$ products $\qquad$ $R_2 = \dfrac{d}{p}$

mg B = $[N_A V_A - N_C V_C]$ x eq.wt. B x R_1

Dilution calculations :

$M_1V_1 = M_2V_2$

$N_1V_1 = N_2V_2$

**EX.** Prepare 250ml of 0.05N HCl , from a sol. of 0.1N ?

$N_1V_1 = N_2V_2$

$0.1 \times V_1 = 0.05 \times 250$

$V_1 = 125$ ml

Volumetric analysis

What is an acid-base indicator?

- An acid-base indicator is a weak acid or a weak base.

- The undissociated form of the indicator is a different color than the associated form of the indicator.

- An Indicator does not change color from pure acid to pure alkaline at specific hydrogen ion concentration, but rather, color change occurs over a range of hydrogen ion concentrations.

- This range is termed the *color change interval*. It is expressed as a pH range.

colorless

red
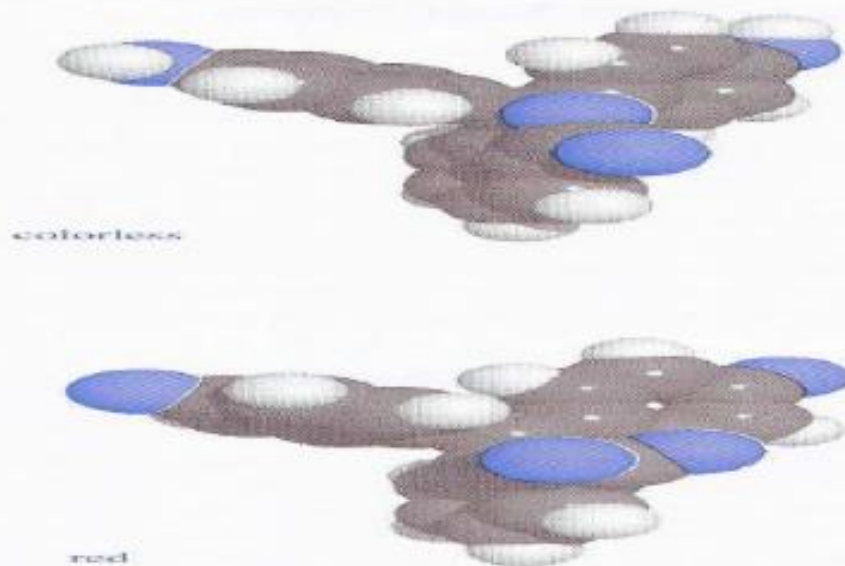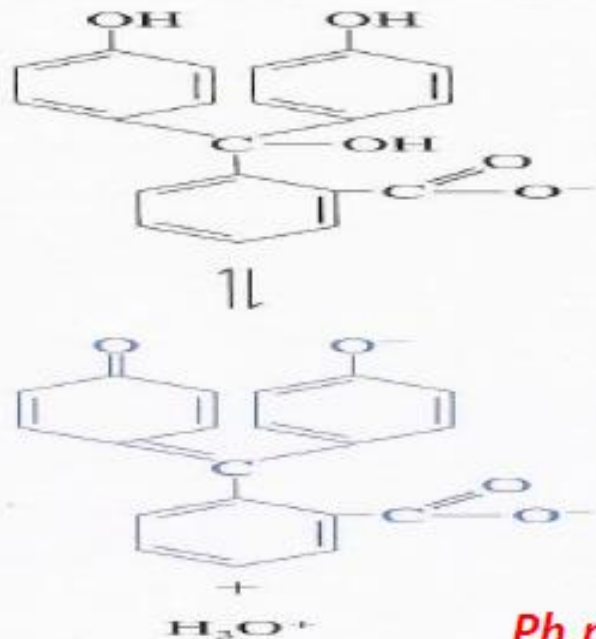
Ph.ph Indicator for acid – base titration

TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†
Thymol blue	1.2–2.8	1.65§	R–Y
	8.0–9.6	8.96§	Y–B
Methyl yellow	2.9–4.0		R–Y
Methyl orange	3.1–4.4	3.46§	R–O
Bromocresol green	3.8–5.4	4.66§	Y–B
Methyl red	4.2–6.3	5.00§	R–Y
Bromocresol purple	5.2–6.8	6.12§	Y–P
Bromothymol blue	6.2–7.6	7.10§	Y–B
Phenol red	6.8–8.4	7.81§	Y–R
Cresol purple	7.6–9.2		Y–P
Phenolphthalein	8.3–10.0		C–R
Thymolphthalein	9.3–10.5		C–B
Alizarin yellow GG	10–12		C–Y

The equivalence point of a titration

- When you carry out a simple acid-base titration, you use an indicator to tell you when you have the acid and alkali mixed in exactly the right proportions to "neutralise" each other. When the indicator changes color, this is often described as the *end point* of the titration.

- In an ideal world, the color change would happen when you mix the two solutions together in exactly equation proportions. That particular mixture is known as the *equivalence point*.

Titration Curve

A titration curve is a plot of pH vs. the amount of titrant added. Typically the titrant is a strong (completely) dissociated acid or base. Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.
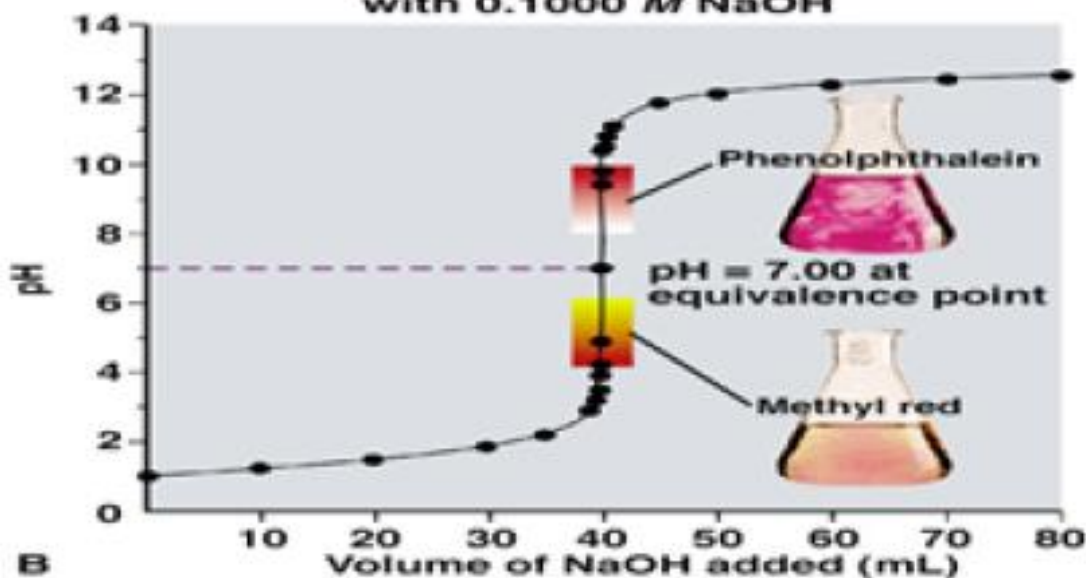
Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Strong Acid-Base Titration Curve

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

A

B

Titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH

Phenolphthalein

pH = 7.00 at equivalence point

Methyl red

Volume of NaOH added (mL)

Experimental techniques

burette filled with base

flask filled with acid and indicator
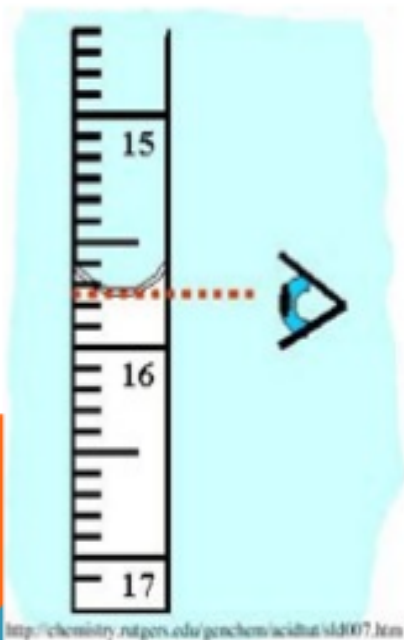
burette

acid

conical flask

alkaline solution and indicator
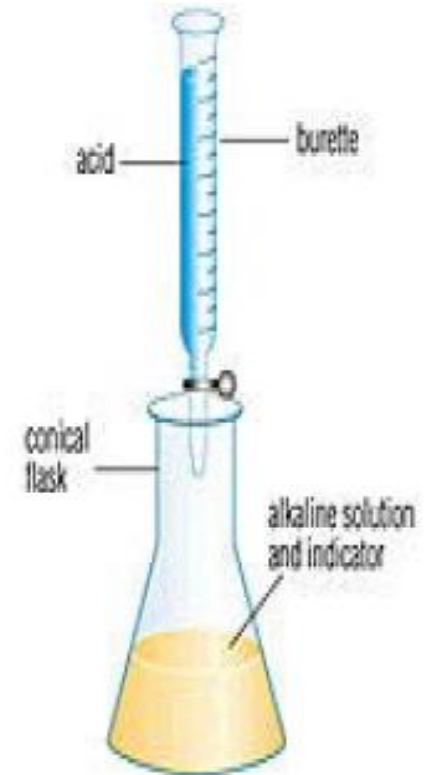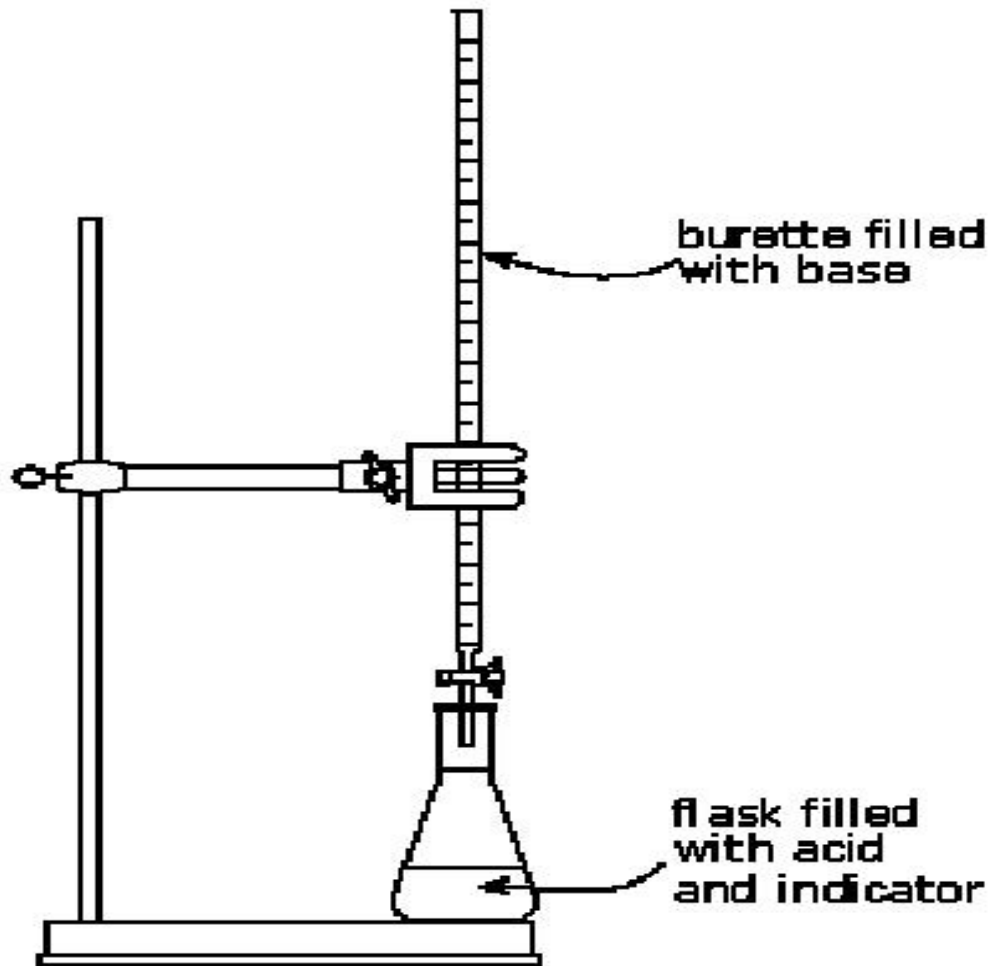
Reading a Burette

- A burette scale is inverted. Individual readings only make sense when compared to a second value.

Experimental techniques

Setup for Titration

Burette is placed in clamp over Conical flask. White paper Beneath flask

1-2 drops of phenolphthalein indicator is added to the 25mL of primary standard solution in the conical flask

Experimental techniques

Slowly add solution to the flask from burette while gently swirling.

After some time , a pink colour will appear and quickly disappear as the solutions are mixed. The longer the pink colour persists, the closer to the end-point(stoichiometric point).

RECORD THE VOLUME OF SOLUTION USED FROM YOUR BURETTE

Analytical chemistry

*Calculate the weight of the solid from the Law:

$$N = \frac{wt}{eq.wt} \times \frac{1000}{V \text{ in ml}} \quad eq \, /L,$$

$$eq.wt = \frac{M.wt}{No. \text{ of } eq}$$

*Calculate the volume of the liquid substance from the laws:

$$N_1 = \frac{\% * sp.gr. * 1000}{eq.wt.}$$

N : the normality of the concentrated acid
$\%$: the weight by weight concentration of the acid
$sp.$ $gr.$: the specific gravity of the acid
$eq.$ $wt.$: the equivalent weight of the acid

$$N_1V_1 = N_2V_2$$

N1 X V1   for the conc.
N2 X V2   for dilution solution