ANALYTICAL CHEMISTRY

Introduction to Titration

by
Wan Norfazilah Wan Ismail
Faculty of Industrial Sciences & Technology
norfazilah@ump.edu.my

Chapter Description

- Expected Outcomes
  - Describe the principles of equilibria involved in chemical analysis particularly gravimetry and volumetry.
  - Understand and apply the equilibrium constant based on concentration of species (Kc) to predict how far a reaction will proceed.
  - State the factors that affect equilibrium and the Le Chateliar's principle.
  - Understand and apply the concept of titration.

Contents

- Equilibrium
- Le Chateliar's Principles
- Introduction to titration
- Types of Titrimetry
- Titrant and Titrand
- Volumetric Calculations

EQUILIBRIUM

$$aA + bB \rightleftharpoons cC + dD$$

reactants products

At equilibrium: forward rate of reaction = reverse rate of reaction

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K' = \frac{[A]^a[B]^b}{[C]^c D^d} = \frac{1}{K}$$

A, B, C, D : *chemical species*
a, b, c, d : *stoiciometry coefficients*
K : *equilibrium constant*
[ ] : *concentration of* A, B, C *and* D

EQUILIBRIUM IN AQUEOUS SOLUTION & GASEOUS STATE

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

** An equilibrium that involves pressure, concentration is equivalent to the partial pressure or (mol ratio × P_{total}).

$$P = \frac{nRT}{V} = CRT$$ → Ideal gas law

$$K_P = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$$

$C = molar\ concentration$
$P = pressure$

** Concentration of pure solid or pure liquid is constant. Therefore:

$$K_P = K_C$$

$C = molar\ concentration$
$P = partial\ pressure$

HETEROGENEOUS EQUILIBRIUM

** Heterogeneous equilibrium occurs when the species in equilibrium exist in different phase.

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

$$K = [CO_2]$$

LE CHATELIAR'S PRINCIPLE

When a change is applied to disturb a system at equilibrium, the reaction will favor to reduce the effect of the change.

Factors that affect equilibrium systems are:

- Temperature
- Pressure or volume
- Concentration of the reactant or product

EFFECT OF CONCENTRATION

$$N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

** To find the effect of change in concentration, use reaction quotient, Q.

$$Q = \frac{[NH_3]_o^2}{[N_2]_o[H_2]_o^3}$$

"o" = *original concentration*

- Q = K_c : system will be in equilibrium
- Q > K_c : system will shift to the left
- Q < K_c : system will shift to the right until Q = K_c is achieved

EFFECT OF TEMPERATURE

- For endothermic reactions – the K_c value increases
- For exothermic reactions – the K_c value decreases

EFFECT OF TEMPERATURE

- A catalyst does not change the direction of reaction of K_c value
- A catalyst changes only the rate of reaction, not the equilibrium position

INTRODUCTION TO TITRATION

- Definition:

  Titration = a method to determine the quantity of a reagent **(known concentration)** required to react with a known volume of sample **(unknown concentration)**.

TYPES OF TITRIMETRY

- Volumetric titrimetry

  involves calculating the amount of a sample by a known volume of standard solution until the end point.

- Gravimetric titrimetry

  the mass of a product is used to calculate the quantity of the original analyte

- Coulometric titrimetry

  the concentration of a species is measured using a constant direct electrical current that consumes the analyte

TYPES OF VOLUMETRIC TITRATION

- Volumetric titration can be divided into:
  i. Acid-base or neutralization
  ii. Precipitation
  iii. Complex formation
  iv. Oxidation-reduction (redox)

TERMS USED IN TITRIMETRY

- **Standard solution**: a reagent of known concentration used to carry out a titrimetric analysis
- **Equivalence point**: a point in a titration when the mole of titrant is equivalent to the mole of analyte
- **Back titration** : a technique where the excess of a reagent used to neutralize the sample is determined by a titration with a second reagent

TERMS USED IN TITRIMETRY

- **End point**: the point where the titration is terminated which is determined by changes of indicator.

- **Titration error**: the difference between the equivalence point and the end point

  V_{ep} = actual volume of reagent

  V_{eq} = theoretical volume to reach the equivalence point

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

TERMS USED IN TITRIMETRY

- **Indicator**: reagent added to the analyte solution to produce an observable physical change (the end point) at or near the equivalence point

- **Primary standard**: ultrapure compound that is used to determine the concentration of the standard solution in volumetric & mass titrimetric methods

- **Secondary standard**: less pure compound whose composition is reliably known and serves as reference material for a titrimetric method of analysis

REQUIREMENTS FOR PRIMARY STANDARD

- Highest purity
- Good stability
- High solubility
- High formula weight
- Easily available at reasonable cost
- Free from hydrated water and unable to absorb moisture

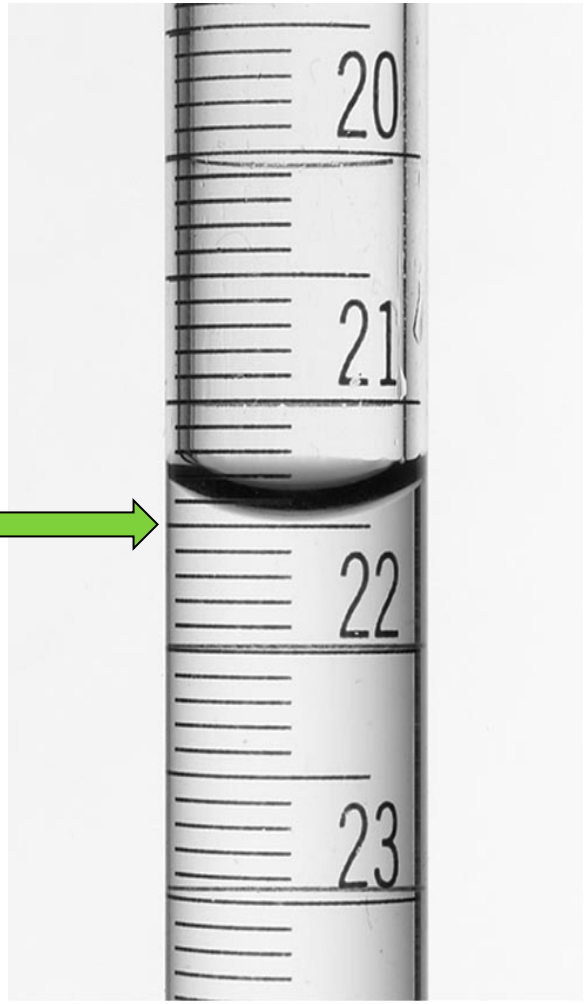
DESIRABLE PROPERTIES OF STANDARD SOLUTIONS

- Stable
- React rapidly and completely with the analyte
- Undergo a selective reaction with the analyte

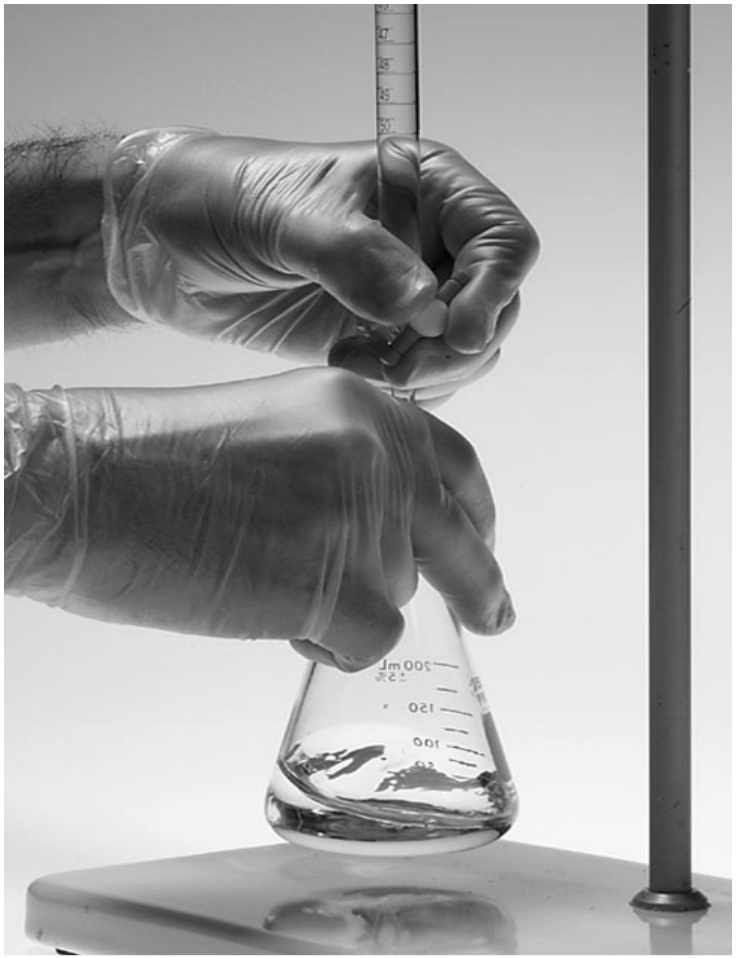
APPARATUS OF VOLUMETRIC TITRIMETRY

MEASURING THE VOLUME IN THE BURETTE

21.50 mL



TITRATION METHOD



TITRANT & TITRAND

- In titrimetry we add a reagent, called the **titrant**, to a solution containing another reagent, called the **titrand**, and allow them to react.
- In acid–base titrations, an acidic or basic titrant reacts with a titrand that is a base or an acid
- Complexometric titrations: metal–ligand complexation
- Redox titrations: titrant is an oxidizing or reducing agent
- Precipitation titrations: titrand and titrant form a precipitate.

VOLUMETRIC CALCULATIONS

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

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

$$\text{amount A (mol)} = \text{volume (L)} \times \text{concentration A} \left(\frac{\text{mol}}{\text{L}} \right)$$

$$\text{amount A (mmol)} = \text{volume (mL)} \times \text{concentration A} \left(\frac{\text{mmol}}{\text{mL}} \right)$$

VOLUMETRIC CALCULATIONS

- Calculate the molarity of standard solutions

  Refer to Chapter 2

- Treating titration data

Example:

A 50.00mL portion of HCl solution required 29.71mL of 0.01963M $Ba(OH)_2$ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl. (Ba: 137.327 g/mol, Cl: 35.5 g/mol)

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

Ans: HCl = 0.02333M

VOLUMETRIC CALCULATIONS

- Calculate the quantity of analyte from titration data

Example:

A 100.0mL sample of brackish water was made ammoniacal, and the sulfide it contained was titrated with 16.47mL of 0.02310M $AgNO_3$. The analytical reaction is

$$2Ag^+ + S^{2-} \rightarrow Ag_2S\ (s)$$

Calculate the concentration of H_2S in the water in ppm. (Ag: 107.86 g/mol, S: 32.07 g/mol)

Ans: H_2S = 64.8ppm

Universiti Malaysia PAHANG

Engineering • Technology • Creativity

Editor: Wan Norfazilah Wan Ismail

Author: Siti Maznah Kabeb

Industrial Chemistry Programme
Faculty of Industrial Sciences & Technology
Universiti Malaysia Pahang