ANALYTICAL CHEMISTRY

Introduction to Titration

by

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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 Chatelier’s principle.
  – Understand and apply the concept of titration.
Contents

- Equilibrium
- Le Chatelier’s Principles
- Introduction to titration
- Types of Titrimetry
- Titrant and Titrand
- Volumetric Calculations
EQUILIBRIUM

\[ aA + bB \rightleftharpoons cC + dD \]

reactants \hspace{1cm} \text{products}

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

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

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

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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 \times P_{\text{total}}).

\[ P = \frac{nRT}{V} = CRT \quad \text{Ideal gas law} \]

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

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

\[ K_P = K_C \]

\[ C = \text{molar concentration} \]
\[ P = \text{partial pressure} \]
**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.

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

"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
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

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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
  
  \[ V_{ep} = \text{actual volume of reagent} \]
  
  \[ V_{eq} = \text{theoretical volume to reach the equivalence point} \]

  \[ E_t = V_{ep} - V_{eq} \]
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

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TITRATION METHOD

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In titrimetry we add a reagent, called the **titrant**, to a solution containing another reagent, called the **titrand**, and allow them to react.

- **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

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

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

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

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)

\[ \text{Ba(OH)}_2 + 2\text{HCl} \rightarrow \text{BaCl}_2 + 2\text{H}_2\text{O} \]

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 AgNO₃. The analytical reaction is

$$2\text{Ag}^+ + \text{S}^2- \rightarrow \text{Ag}_2\text{S} \text{ (s)}$$

Calculate the concentration of H₂S in the water in ppm. (Ag: 107.86 g/mol, S: 32.07 g/mol)

Ans: H₂S = 64.8 ppm
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