Analytical chemistry
(Quantitative Analysis)

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Analytical chemistry

Introduction

Analytical chemistry: Branch of chemistry that deals with the determination of the chemical composition of substances.

Qualitative analysis determines the identities of the substances in a given sample.

Quantitative analysis determines how much of a particular substance is present.

Simple qualitative techniques exploit the specific, easily observable properties of elements or compounds – for example, the flame test makes use of the different flame colours produced by metal cations when their compounds are held in a hot flame. More sophisticated methods, such as those of spectroscopy, are required where substances are present in very low concentrations or where several substances have similar properties.

Most quantitative analyses involve initial stages in which the substance to be measured is extracted from the test sample, and purified. The final analytical stages (or ‘finishes’) may involve measurement of the substance's mass (gravimetry) or volume (volumetry, titrimetry), or a number of techniques initially developed for qualitative analysis, such as fluorescence and absorption spectroscopy, chromatography, and polarography. Many modern methods enable quantification by means of a detecting device that is integrated into the extraction procedure (as in gas–liquid chromatography).
Part(I)  Volumetric analysis:

In volumetric analysis, a known volume of a standard solution (one whose concentration is known) reacts with a known volume of a solution of unknown concentration. This procedure standardizes the latter solution, by allowing a calculation of its concentration.

**Concentration Expressions:**

**Strength(S):** \( S = \frac{\text{weight of solute (g)}}{\text{volume of solution (L)}} = (g/L) \)

**Part per million (ppm):** \( \text{ppm} = \frac{\text{weight of solute (µg)}}{\text{volume of solution (mL)}} \)

\( \text{ppm} = \left[ \frac{\text{weight of solute (g)}}{\text{weight of sample (g)}} \right] \times 10^6 \)

**Example:** 2ppm = 2 µg/ml = 2 mg/L

**Weight Percent(%w/w):** \( = \left[ \frac{\text{weight of solute (g)}}{\text{weight of solution (g)}} \right] \times 100 \)

**Volume Percent(%v/v):** \( = \left[ \frac{\text{vol. of solute (ml)}}{\text{vol of solution (ml)}} \right] \times 100 \)

**Weight Volume Percent(%w/v):** \( = \left[ \frac{\text{weight of solute (g)}}{\text{volume of solution (ml)}} \right] \times 100 \)

**Molarity (M):** no of mol. solute / vol. of solution(l)

no of m.mol. solute / vol. of solution(ml)
n.b: no. of moles = no. of grams(mass,g)/M.wt(g.f.wt)(g/mole)

Example: Calculate the f.wt of CH₃OH

g.f.wt(CH₃OH)=(12 g + 4 g + 16 g)/1 molCH₃OH=32 g/mol

Example: Calculate the no. of moles present in 250 mg of CaSO₄·7H₂O(f.wt=262.3)

No. of mmoles= no.of mg/f.wt(mg/mmol)

No. of mmoles CaSO₄·7H₂O=0.250/262.3=9.33×10⁻⁴ moles

Example: Calculate the Molarity(M) of 1.50 g of K₂SO₄(f.wt=174.2) dissolved in a volume of 250 ml.

no. of moles of K₂SO₄= no. of mgs/f.wt(mg/mmole)

=1.5×1000/174.2=8.61 mmoles

Molarity (M) = no. of moles of K₂SO₄/ vol.(ml)

= 8.61 mmoles/250 (ml)=0.034 mmoles/ml=0.034 M

Example: Calculate the Molarity(M) of 1.00 ppm of Na

1.00 ppm of Na=1.0 µg/ml Na=1.0 mg/l Na

M Na = 0.001/23 = 4.35×10⁻⁵ moles/l

**Normality(N):** no of equiv. of solute / vol. of solution(L)

= no of mequiv. Solute / vol. of solution(ml)

i.e. (meq/ml) or (eq/l).
equiv.wt of an acid = f.wt / no. of replaceable H

Example:
equiv.wt of $\text{H}_2\text{SO}_4$ = f.wt $\text{H}_2\text{SO}_4$/ 2 = 98/2 = 49 g/equiv

Example:
equiv.wt of $\text{H}_3\text{PO}_4$= f.wt $\text{H}_3\text{PO}_4$/3=32.67 g/equiv

equiv.wt of a base = f.wt / no. of OH

Example:
equiv.wt of NaOH = f.wt NaOH/ no. of OH=40/1=40 g/equiv

**Density and Specific Gravity of Solutions:**

Density(d)=mass(g)/vol.(ml)

Specific Gravity of Solutions(sp.gr) = mass of a certain volume of substance / mass of the same volume of water.

Molarity(M) of acid= [sp.gr x %w/w x 1000] / M.wt.

Example: Calculate the Molarity(M) of HNO\textsubscript{3}:

M.wt=63 g/mole , sp.gr =1.42 , %w/w=70

Molarity(M) of HNO\textsubscript{3}= (1.42x0.70x1000)/63=16 M.

Example:

Calculate the volume required to prepare 100 ml of HCl 6.0M starting from conc. HCl 37%w/w ,sp.gr =1.18 and f.wt HCl = 36.5

$M_{\text{HCl}}$=(1.18x0.37x1000)/36.5=12 mol/l=12M

$V_{\text{conc.}} \times M_{\text{conc.}} = V_{\text{dil.}} \times M_{\text{dil.}}$

$V_{\text{conc}} \times 12 = 100 \times 6.00$

$V_{\text{conc}} = 50$ ml
**Volumetric Terminology:**

- **End point:** a point during the addition of titrant signalling particular conditions have been reached.
- **Equivalence point:** the point when stoichiometry is satisfied.
- **Titration error:** the difference between the end and equivalence points.
- **Indicators:** A compound with at least two distinct coloured forms
- **Titrant:** The fluid added from a burette
- **Titre:** The volume of fluid added from a burette
- **Aliquot:** The volume of fluid being titrated
- **Anolyte:** The substance being determined

**Principles of Volumetric Analysis**

Volumetric procedures are applicable to all four types of reactions (i.e., acid/base reactions, redox reactions, precipitation reactions and complex formation reaction).

Most common volumetric technique is (titration)

**Requirements for titrimetric analysis are:**

1. Titrant solution of known concentration
2. Accurate volumetric measurement
3. “Clear” endpoint signal
4. Known endpoint-equivalence point relationship

**Primary Standards**

**Definition:**

*A highly purified compound that serves as a reference material in volumetric methods.*

1. Obtainable in high purity
2. Stable in air, can be stored
3. Absence of hydrated water
4. Low cost
5. Moderate solubility
6. Large molar mass
7. Reacts stoichiometrically and rapidly

E.g. potassium hydrogen phthalate, benzoic acid

*A primary standard can be used to produce a standard solution in two ways.*

1. A known mass is dissolved in a known volume of water. ‘Primary standard solution’
2. A known mass is dissolved and titrated with an unknown solution. ‘Secondary standard solution’.
The preparation and dispensing of solutions requires the use of calibrated glassware such as burettes, pipettes, and volumetric flasks. In this experiment, you will prepare and standardize a sodium hydroxide solution. You will then use this solution to analyze a solution containing an unknown concentration of hydrochloric acid, using phenolphthalein as the indicator in the titration.

**Titration**

In a titration, a burette is used to dispense measured increments of one solution into a known volume of another solution. The object of the titration is the detection of the equivalence point, that point in the procedure where chemically equivalent amounts of the reactants have been mixed. Whether or not the equivalence point comes when equimolar amounts of reactants have been mixed depends on the stoichiometry of the reaction. In the reaction of HCl and NaOH, the equivalence point does occur when one mole of HCl has reacted with one mole of NaOH. However, in the reaction of H₂SO₄ and
NaOH, the equivalence point occurs when two moles of NaOH have reacted with one mole of H$_2$SO$_4$.

The titration technique can be applied to many types of reactions, including oxidation-reduction, precipitation, complexation, and acid-base neutralization reactions. Although a variety of instrumental methods for detecting equivalence points are now available, it is frequently more convenient to add an indicator to the reaction mixture. An indicator is a substance that undergoes a distinct color change at or near the equivalence point. The point in the titration at which the color change occurs is called the end point. Obviously, the titration will be accurate only if the end point and the equivalence point coincide fairly closely.

For this reason, the indicator used in a titration must be selected carefully. Fortunately, a large number of indicators are commercially available and finding the right one for a particular titration is not a difficult task.

**Chapter (1)**

**Acid- Base Titrations**

Acids and Bases Although several definitions of acids and bases may be given, the classical Arrhenius concept will suffice for this experiment. According to this concept, an acid is a substance that dissociates in water to produce hydrogen ions; a base is a substance that dissociates in water to produce hydroxide ions. Thus, the acid, HCl, and the base, NaOH, dissociate according to the following equations:
The hydrated proton, $\text{H}^+$ (aq), has been named the hydronium ion and is often written $\text{H}_3\text{O}^+$. The dissociation of HCl, using this convention, is shown in Equation 3.

$$\text{HCl} \rightleftharpoons \text{H}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \quad (1)$$

$$\text{NaOH} \rightleftharpoons \text{Na}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \quad (2)$$

Water itself is partially dissociated into ions, as represented by Equation 4.

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- (\text{aq}) \quad (4)$$

In pure water, the concentrations of hydronium ions and hydroxide ions are equal; each is present at a concentration of $1.0 \times 10^{-7}$ mole/liter at $25^\circ\text{C}$. In acid solutions, the hydronium ion concentration is higher than $10^{-7}$ M and the hydroxide ion concentration is less than $10^{-7}$ M. In basic solutions, the situation is reversed. When an acidic solution and an alkaline (basic) solution are mixed, neutralization occurs:

$$\text{H}_3\text{O}^+ + \text{Cl}^- (\text{aq}) + \text{Na}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow 2\text{H}_2\text{O} + \text{Na}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \quad (5)$$

The $\text{Cl}^- (\text{aq})$ and $\text{Na}^+ (\text{aq})$ are not appreciably affected by the reaction. If these spectator ions are omitted, the general neutralization expression shown in Equation 6 is obtained.

$$\text{H}_3\text{O}^+ + \text{OH}^- (\text{aq}) \rightleftharpoons 2\text{H}_2\text{O} \quad (6)$$
Although neutralization is essentially the reaction between hydronium ions and hydroxide ions to form water, the titration mixture may not be neutral at the equivalence point. It is the nature of the other ions present in the mixture that determines whether the concentrations of the hydronium ion and the hydroxide ion are equal. Because NaCl dissolves in water to give a neutral solution, the equivalence point for the reaction between hydrochloric acid and sodium hydroxide is reached when the concentrations of both the hydronium ions and the hydroxide ions are equal to $1.0 \times 10^{-7}$ mole/liter (at 25°).

**Indicators:**

**Theory of indicators:**

An acid-base indicator is a weak acid($H^+In^-$) or a weak base($In^{+}OH$). The undissociated form of the indicator is a different color than the iogenic 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.

The dissociation of the indicator $HIn$ maybe represented as shown in Equation 7.

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^- \quad \text{(7)}$$

In acid solutions the indicator exists predominately as $HIn$. 
In basic solutions it is present mainly as In$^-$ ions, which impart a different color to the solution. At a specific point in the titration, the indicator will be approximately equally distributed between the HIn and In$^-$ forms and, thus, will show an intermediate color which we can interpret as the end point.

**How is an indicator used?**

Weak acids are titrated in the presence of indicators which change under slightly alkaline conditions. Weak bases should be titrated in the presence of indicators which change under slightly acidic conditions.

**What are some common acid-base indicators?**

Several acid-base indicators are listed below, some more than once if they can be used over multiple pH ranges. Quantity of indicator in aqueous (aq.) or alcohol (alc.) solution is specified. Tried-and-true indicators include: thymol blue, tropeolin OO, methyl yellow, methyl orange, bromphenol blue, bromcresol green, methyl red, bromthymol blue, phenol red, neutral red, phenolphthalein, thymolphthalein, alizarin yellow, tropeolin O, nitramine, and trinitrobenzoic acid. Data in this table are for sodium salts of thymol blue, bromphenol blue, tetrabromphenol blue, bromcresol green, methyl red, bromthymol blue, phenol red, and cresol red.
<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH Range</th>
<th>Quantity per 10 ml</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thymol Blue</td>
<td>1.2-2.8</td>
<td>1-2 drops 0.1% soln. in aq.</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Pentamethoxy red</td>
<td>1.2-2.3</td>
<td>1 drop 0.1% soln. in 70% alc.</td>
<td>red-violet</td>
<td>colorless</td>
</tr>
<tr>
<td>Tropeolin OO</td>
<td>1.3-3.2</td>
<td>1 drop 1% aq. soln.</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>2.4-4.0</td>
<td>1-2 drops 0.1% soln. in 50% alc.</td>
<td>colorless</td>
<td>yellow</td>
</tr>
<tr>
<td>Methyl yellow</td>
<td>2.9-4.0</td>
<td>1 drop 0.1% soln. in 90% alc.</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>3.1-4.4</td>
<td>1 drop 0.1% aq. soln.</td>
<td>red</td>
<td>orange</td>
</tr>
<tr>
<td>Bromphenol blue</td>
<td>3.0-4.6</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow</td>
<td>blue-violet</td>
</tr>
<tr>
<td>Tetrabromphenol blue</td>
<td>3.0-4.6</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow</td>
<td>blue</td>
</tr>
<tr>
<td>Alizarin sodium sulfonate</td>
<td>3.7-5.2</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow</td>
<td>violet</td>
</tr>
<tr>
<td>□-Naphthyl red</td>
<td>3.7-5.0</td>
<td>1 drop 0.1% soln. in 70% alc.</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>p-Ethoxychrysoidine</td>
<td>3.5-5.5</td>
<td>1 drop 0.1% aq. soln.</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Indicator</td>
<td>pH</td>
<td>Amount</td>
<td>Color Change</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------</td>
<td>------------</td>
<td>-----------------------</td>
<td></td>
</tr>
<tr>
<td>Bromcresol green</td>
<td>4.0-5.6</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → blue</td>
<td></td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.4-6.2</td>
<td>1 drop 0.1% aq. soln.</td>
<td>red → yellow</td>
<td></td>
</tr>
<tr>
<td>Bromcresol purple</td>
<td>5.2-6.8</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → purple</td>
<td></td>
</tr>
<tr>
<td>Chlorphenol red</td>
<td>5.4-6.8</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → red</td>
<td></td>
</tr>
<tr>
<td>Bromphenol blue</td>
<td>6.2-7.6</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → blue</td>
<td></td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>5.0-7.0</td>
<td>1-5 drops 0.1% aq. soln.</td>
<td>colorless → yellow</td>
<td></td>
</tr>
<tr>
<td>Azolitmin</td>
<td>5.0-8.0</td>
<td>5 drops 0.5% aq. soln.</td>
<td>red → blue</td>
<td></td>
</tr>
<tr>
<td>Phenol red</td>
<td>6.4-8.0</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → red</td>
<td></td>
</tr>
<tr>
<td>Neutral red</td>
<td>6.8-8.0</td>
<td>1 drop 0.1% soln. in 70% alc.</td>
<td>red → yellow</td>
<td></td>
</tr>
<tr>
<td>Rosolic acid</td>
<td>6.8-8.0</td>
<td>1 drop 0.1% soln. in 90% alc.</td>
<td>yellow → red</td>
<td></td>
</tr>
<tr>
<td>Cresol red</td>
<td>7.2-8.8</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → red</td>
<td></td>
</tr>
<tr>
<td>p-Naphtholphthalein</td>
<td>7.3-8.7</td>
<td>1-5 drops 0.1% soln. in 70% alc.</td>
<td>rose → green</td>
<td></td>
</tr>
<tr>
<td>Tropeolin OOO</td>
<td>7.6-8.9</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → rose-red</td>
<td></td>
</tr>
<tr>
<td>Thymol blue</td>
<td>8.0-9.6</td>
<td>1-5 drops 0.1% aq. soln.</td>
<td>yellow → blue</td>
<td></td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.0-10.0</td>
<td>1-5 drops 0.1% soln. in 70% alc.</td>
<td>colorless → red</td>
<td></td>
</tr>
<tr>
<td>p-Naphtholbenzein</td>
<td>9.0-11.0</td>
<td>1-5 drops 0.1% soln. in 90% alc.</td>
<td>yellow → blue</td>
<td></td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>9.4-10.6</td>
<td>1 drop 0.1% soln. in 90% alc.</td>
<td>colorless → blue</td>
<td></td>
</tr>
<tr>
<td>Nile blue</td>
<td>10.1-11.1</td>
<td>1 drop 0.1% aq. soln.</td>
<td>blue → red</td>
<td></td>
</tr>
<tr>
<td>Alizarin yellow</td>
<td>10.0-12.0</td>
<td>1 drop 0.1% aq. soln.</td>
<td>yellow → lilac</td>
<td></td>
</tr>
<tr>
<td>Salicyl yellow</td>
<td>10.0-12.0</td>
<td>1-5 drops 0.1% soln. in 90% alc.</td>
<td>yellow → orange-brown</td>
<td></td>
</tr>
</tbody>
</table>
Titration of an Unknown

1- Obtain an HCl solution of unknown concentration in your 100-mL volumetric flask.
2- Dilute the solution to exactly 100 mL with distilled water. Mix well and then rinse your second burette with two 5-mL portions of the diluted acid. Fill the burette with the solution, accurately read the initial volume, and then dispense 25 mL into a 125-mL Erlenmeyer flask. (Accurately measure the final volume.)
3- Add 2 or 3 drops of phenolphthalein indicator and then titrate the acid with your 0.1 M NaOH solution until a faint, persistent pink color is obtained.
4- Calculate the Molarity of the HCl solution.
5- Repeat the titration once or twice. Report the results of each titration and the average concentration of your HCl unknown.

Acid-Base Titrations:

For a molecule with a H-X bond to be an acid, the hydrogen must have a positive oxidation number so it can ionize to form a positive +1 ion. For instance, in sodium hydride (NaH) the hydrogen has a -1 charge so it is not an acid but it is actually a base. Molecules like CH₄ with nonpolar bonds also cannot be acids because the H does not ionize. Molecules with strong bonds (large electronegativity differences), are less likely to be strong acids because they do not ionize very well. For a molecule with an X-O-H bond (also called an oxyacid) to be an acid, the hydrogen must again ionize to form H⁺. To be a base, the O-H must break off to form the hydroxide ion (OH⁻). Both of these happen when dealing with oxyacids.

Strong Acids:

These acids completely ionize in solution so they are always represented in chemical equations in their ionized form. There are only seven (7) strong acids:

\[
\text{HCl, HBr, HI, H}_2\text{SO}_4, \text{HNO}_3, \text{HClO}_3, \text{HClO}_4
\]

To calculate a pH value:

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Example Problem: Determine the pH of a 0.25 M solution of HBr.

Answer: \( \text{pH} = - \log [H^+] = - \log[0.25] = 0.60 \)

Weak Acids:

These are the most common type of acids. They follow the equation:

\[
\text{HA(aq)} \rightleftharpoons H^+(aq) + A^-(aq)
\]

The equilibrium constant for the dissociation of an acid is known as Ka. The larger the value of Ka, the stronger the acid.

\[
K_a = \frac{[H^+][A^-]}{[HA]}
\]

Example Problem: Determine the pH of 0.30 M acetic acid (HC_2H_3O_2) with the Ka of 1.8x10^-5.

Answer:

Write the equilibrium equation for the acid:

\[
\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons H^+ + \text{C}_2\text{H}_3\text{O}_2^-
\]

Write the equilibrium expression and the Ka value:

\[
K_a = \frac{[H^+] [C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}
\]

"Start, Change, Equilibrium":

\[
\begin{array}{ccc}
\text{Start} & \text{0.30 M} & \text{0 M} & \text{0 M} \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.30-x & x & x \\
\end{array}
\]

Substitute the variables (disregard the "-x" because it is so small compared to the 0.30) and solve for \([H^+]\):

\[
K_a = 1.8 \times 10^{-5} = \frac{x(x)}{(0.30-x)} = \frac{x^2}{0.30} \\
x = [H^+] = 2.3 \times 10^{-3} \\
\text{pH} = - \log[H^+] = 2.64
\]

Strong Bases:

Like strong acids, these bases completely ionize in solution and are always represented in their ionized form in chemical equations. There are only seven (7) strong bases:
LiOH, NaOH, KOH, RbOH, Ca(OH)$_2$, Sr(OH)$_2$, Ba(OH)$_2$

Example Problem: Determine the pH of a 0.010 M solution of Ba(OH)$_2$.

**Answer:**

\[
\text{Start: } \begin{array}{c} \text{Ba(OH)}_2 \text{(aq)} \rightarrow \text{Ba}^{2+} \text{(aq)} + 2\text{OH}^- \text{(aq)} \\ 0.010 \text{ M} & 0 \text{ M} \end{array} \\
\text{Change: } \begin{array}{c} \text{Ba(OH)}_2 \text{(aq)} \rightarrow \text{Ba}^{2+} \text{(aq)} + 2\text{OH}^- \text{(aq)} \\ -0.010 & +0.10 & +0.10 \end{array} \\
\text{Equilibrium: } \begin{array}{c} \text{Ba(OH)}_2 \text{(aq)} \rightarrow \text{Ba}^{2+} \text{(aq)} + 2\text{OH}^- \text{(aq)} \\ 0 & 0.10 & 0.10 \end{array}
\]

\[
p\text{OH} = -\log[\text{OH}^-] = -\log(0.10) = 1.70 \\
pH = 14.00 - 1.70 = 12.30
\]

Weak Bases:

They follow the equation:

Weak Base + H$_2$O $\rightleftharpoons$ conjugate acid + OH$^-$

example: NH$_3$ + H$_2$O $\rightleftharpoons$ NH$_4^+$ + OH$^-$

$K_b$ is the base-dissociation constant:

\[
K_b = \frac{[\text{conjugate acid}][\text{OH}^-]}{[\text{weak base}][\text{H}_2\text{O}]}
\]

example: $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$

$K_a \times K_b = K_w = 1.00 \times 10^{-14}$

To calculate the pH of a weak base, we must follow a very similar "Start, Change, Equilibrium" process as we did with the weak acid, however we must add a few steps.

Example Problem: Determine the pH of 0.15 M ammonia (NH$_3$) with a $K_b$=1.8x10$^{-5}$.
When dealing with weak acids and weak bases, you also might have to deal with the "common ion effect". This is when you add a salt to a weak acid or base which

Acid-Base Titrations

An acid-base titration is when you add a base to an acid until the equivalence point is reached which is where the moles of acid equals the moles of base. For the titration of a strong base and a strong acid, this equivalence point is reached when the pH of the solution is seven (7) as seen on the following titration curve:

![Titration Curve](image)

- low starting point
- gradual initial rise
- when near eq. point, a long steep rise
- eq. point is at center of rise
- mL of strong base added to strong acid
- pH of solution

When dealing with weak acids and weak bases, you also might have to deal with the "common ion effect". This is when you add a salt to a weak acid or base which
For the titration of a strong base with a weak acid, the equivalence point is reached when the pH is greater than seven (7). The half equivalence point is when half of the total amount of base needed to neutralize the acid has been added. It is at this point where the pH = pKa of the weak acid.

In an acid-base titration, the base will react with the weak acid and form a solution that contains the weak acid and its conjugate base until the acid is completely gone. To solve these types of problems, we will use the weak acid's Ka value and the molarities in a similar way as we have before. Before demonstrating this way, let us first examine a short cut, called the Henderson-Hasselbalch Equation. This can only be used when you have some acid and some conjugate base in your solution. If you only have acid, then you must do a pure Ka problem and if you only have base (like when the titration is complete) then you must do a Kb problem.

\[ pH - pK_a + \log \frac{[base]}{[acid]} \]

Where: pH is the log of the molar concentration of the hydrogen pKa is the equilibrium dissociation constant for an acid [base] is the molar concentration of a basic solution [acid] is the molar concentration of an acidic solution

Example Problem: 25.0 mL of .400 M KOH is added to 100. mL of .150 M benzoic acid, HC₇H₅O₂ (Ka=6.3x10⁻⁵). Determine the pH of the solution.
This equation is used frequently when trying to find the pH of buffer solutions.

A buffer solution is one which resists changes in pH upon the addition of small amounts of an acid or a base. They are made up of a conjugate acid-base pair such as HC₂H₃O₂/C₂H₃O₂⁻ (acetic/acetate) - or NH₄⁺/NH₃ (ammonium/ammonia).

They work because the acidic species neutralize the OH⁻ ions while the basic species neutralize the H⁺ ions. The buffer capacity is the amount of acid or base the buffer can neutralize before the pH begins to change to an appropriate degree. This depends on the amount of acid or base in the buffer. High buffering capacities come from solutions with high concentrations of the acid and the base and where these concentrations are similar in value.

The following figure represents the different cases of acid-base titration curves.
Problems:
Weak Base-Strong Acid Titration Curve

Titration of 40.00 mL of 0.1000 M NH₃ with 0.1000 M HCl

\[ [\text{NH}_3] = [\text{NH}_4^+] \]

\( pK_a \) of \( \text{NH}_4^+ = 9.25 \)

pH = 5.27 at equivalence point
Weak Acid-Strong Base Titration Curve

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

$pK_a$ of HPr = 4.89

$pH = 8.80$ at equivalence point

$[HPr] = [Pr^-]$
Chapter 2

OXIDATION-REDUCTION TITRATIONS

Introduction:

Oxidation - Reduction reactions (Redox rxns) involve the transfer of electrons from one species of the reactants to another. This results in an increase in oxidation number (O.N.) of a specific species and a complementary decrease in oxidation number of another species. Example:

\[ \text{Ce}^{4+} + \text{Fe}^{2+} = \text{Ce}^{3+} + \text{Fe}^{3+} \]

The O.N. of cerium was decreased while that of iron was increased. Cerium is reduced while iron is oxidized. A process that involves an increase in O.N. is an oxidation process and vice versa. Usually, a Redox reaction can be separated into two halves.

\[ \text{Ce}^{4+} + e = \text{Ce}^{3+} \quad \text{Reduction} \]
\[ \text{Fe}^{2+} = \text{Fe}^{3+} + e \quad \text{Oxidation} \]

Electrons appear in each half reaction while they do not show up in the overall equations.
Identification of a Redox Reaction

It is a good practice to indicate the O.N. of each species in a chemical reaction in order to check if it is a Redox reaction or not. If the O.N. of any species changes, then it is a definite indication of a Redox reaction. Example,

\[ 2 \text{KMnO}_4 + 5 \text{H}_2\text{C}_2\text{O}_4 + 6 \text{HCl} = 2 \text{MnCl}_2 + 2\text{KCl} + 10 \text{CO}_2 + 8 \text{H}_2\text{O} \]

It is observed that in the left-hand part of the equation, manganese has an O.N. equals 7 and carbon has an O.N. equals 3. In the right-hand part, the O.N. of manganese is 2 and that of carbon is 4. Therefore, permanganate is reduced while oxalic acid is oxidized. An example of a non-Redox reaction can be written where no change in O.N. occurs,

\[ \text{Na}_2\text{CO}_3 + 2 \text{HCl} = 2 \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \]

\[ +1 +4 -2 +1 -1 +1 -1 +4 -2 +1 -2 \]

There is no change in O.N. of any species involved in the reaction, which indicates that this is not a Redox reaction.
Balancing Redox Reactions

Balanced chemical equations are the basis of any reasonable quantitative calculations. Therefore, it is very important to learn balancing chemical equations, especially Redox equations that can be manipulated through definite steps. For example, dichromate reacts with iron yielding $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$

$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} = \text{Cr}^{3+} + \text{Fe}^{3+}$$

To balance this equation, the following steps should be followed.

1. Split the equation into two half reactions

$$\text{Fe}^{2+} = \text{Fe}^{3+}$$
$$\text{Cr}_2\text{O}_7^{2-} = \text{Cr}^{3+}$$

2. Proceed with each half reaction separately starting with mass balance. Let us start with first half reaction

$$\text{Fe}^{2+} = \text{Fe}^{3+}$$

One mole of Fe$^{2+}$ yields one mole of Fe$^{3+}$ which is balanced.

3. Balance the charges on both sides.

$$\text{Fe}^{2+} = \text{Fe}^{3+}$$

It is clear that an electron (e) should be added to the right side in order for the charges to be equal

$$\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}$$

This is a straightforward process but now consider the second half reaction, which contains species that are not mass balanced.
\[
\text{Cr}_2\text{O}_7^{2-} = \text{Cr}^{3+}
\]

1. Adjust the number of moles of chromium on both sides. This gives

\[
\text{Cr}_2\text{O}_7^{2-} = 2 \text{Cr}^{3+}
\]

2. For each oxygen atom place an H2O on the other side

\[
\text{Cr}_2\text{O}_7^{2-} = 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
\]

3. Adjust the number of hydrogen atoms on both sides of the equation by adding H+

\[
14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} = 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
\]

4. The charges on both sides should be balanced at this point. This can be done by addition of 6 electrons to the left side of the equation

\[
6 \text{e} + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

5. This is the case if the reaction is carried out in acidic solution. The combination of the two half reactions necessitates the multiplication of the half reaction involving the iron by a factor of 6 in order to cancel the electrons involved
$6 \text{Fe}^{2+} = 6 \text{Fe}^{3+} + 6 \text{e}$

$6 \text{e} + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} = 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$

$6 \text{Fe}^{2+} + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} = 6 \text{Fe}^{3+} + 2\text{Cr}^{3+} + 7 \text{H}_2\text{O}$

This is the balanced equation assuming acidic conditions.

In basic solutions, balancing Redox equations requires extra effort where all previous steps are needed in addition to other steps.

Example:

$\text{C}_2\text{O}_4^{2-} + \text{MnO}_4^- = \text{Mn}^{4+} + \text{CO}_2$

First, proceed as in case of acidic solution.

1. Split the equation into two half reactions

   $\text{C}_2\text{O}_4^{2-} = \text{CO}_2$

   $\text{MnO}_4^- = \text{Mn}^{4+}$

2. Balance the first half reaction by adjusting the number of atoms on both sides (mass balance)

   $\text{C}_2\text{O}_4^{2-} = 2 \text{CO}_2$

3. Adjust the charges on both sides (charge balance)

   $\text{C}_2\text{O}_4^{2-} = 2 \text{CO}_2 + 2 \text{e}$
The first half reaction is completely balanced.

Now, turn to balance the second half reaction

\[ \text{MnO}_4^- = \text{Mn}^{4+} \]

1. Mass balance shows 1 mole of Mn on both sides, therefore Mn is adjusted.

2. Adjust the oxygen's on both sides by placing an H2O for each oxygen present.

\[ \text{MnO}_4^- = \text{Mn}^{4+} + 4 \text{H}_2\text{O} \]

3. Adjust the number of hydrogen atoms on both sides by addition of H+

\[ 8 \text{H}^+ + \text{MnO}_4^- = \text{Mn}^{4+} + 4 \text{H}_2\text{O} \]

4. Adjusting the charges on both sides gives

\[ 3 \text{e} + 8 \text{H}^+ + \text{MnO}_4^- = \text{Mn}^{4+} + 4 \text{H}_2\text{O} \]

Now, watch carefully.

5. Add an OH- on both sides for each H+ present

\[ 8 \text{OH}^- + 3 \text{e} + 8 \text{H}^+ + \text{MnO}_4^- = \text{Mn}^{4+} + 4 \text{H}_2\text{O} + 8 \text{OH}^- \]

6. Combine the OH- and H+ to form H2O
3 e + 8 H₂O + MnO₄⁻ = Mn⁴⁺ + 4 H₂O + 8 OH⁻

7. Adjust the number of H₂O molecules on both sides

3 e + 8 H₂O + MnO₄⁻ = Mn⁴⁺ + 8 OH⁻

8. Combine the two half reactions

\[
3 \left( C_2O_4^{2-} = 2 \text{CO}_2 + 2 \text{e} \right)
\]
\[
2 \left( 3 \text{e} + 8 \text{H}_2\text{O} + \text{MnO}_4^- = \text{Mn}^{4+} + 8 \text{OH}^- \right)
\]

\[
3 C_2O_4^{2-} + 8 \text{H}_2\text{O} + 2 \text{MnO}_4^- = 6 \text{CO}_2 + 2 \text{Mn}^{4+} + 16 \text{OH}^-
\]

The first half reaction was multiplied by 3 and the second was multiplied by 2 in order to cancel the electrons on both sides.

The previous steps will become straightforward with some training and should be followed in the same order as described.

The most important Redox reactions that will be encountered in this text are the dichromate and permanganate reactions. Permanganate ion is a good oxidizing agent and a self-indicator as well. The dark violet color of the permanganate ion turns colorless when completely reduced. This gives a very sharp end point if the reaction is carried out under recommended conditions. In case of dichromate, a Redox indicator (like diphenylamine) should be used. This
gives a distinct color when the very first excess of dichromate ion is added. However, dichromate has a major advantage besides being a very effective oxidant, where it can be obtained in an extra pure state and a primary standard dichromate solution is easily prepared.

**Preparation of Permanganate Solutions**

Usually, a stock permanganate solution is prepared first by weighing a precalculated amount of the material which is dissolved in an appropriate volume of distilled water. The solution is then heated to boiling for about an hour and then filtered through a sintered-glass Goosh of small porosity. The solution is kept away from light in dark brown glass bottles.

**Standardization of Permanganate Solutions**

Two very important methods are routinely used. The first utilizes a primary standard sodium oxalate in sulfuric acid solution at temperatures exceeding 70 oC. The equilibrium that takes place can be represented by the equation

$$2 \text{MnO}_4^- + 5 \text{C}_2\text{O}_4^{2-} + 16 \text{H}^+ = 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$$

You should be able to derive the two half reactions and find out the reason for the stoichiometry involved.
The second method involves the use of primary standard arsenic(III) oxide. The compound is soluble in alkali yielding the arsinate.

\[
\text{As}_2\text{O}_3 + 4 \text{OH}^- = 2 \text{HAsO}_3^{2-} + \text{H}_2\text{O}
\]

The arsinate then reduces the permanganate in acidic solution (as above) yeilding AsO$_4^{3-}$ and Mn$^{2+}$. Usually, potassium iodide or iodate is used as a catalyst that accelerates the reaction, which proceeds at room temperature.

\[
\text{As O}_3^{3-} = \text{As O}_4^{3-}
\]

\[
5 \text{(H}_2\text{O} + \text{AsO}_3^{3-} = \text{AsO}_4^{3-} + 2 \text{H}^+ + 2 \text{e})
\]
\[
2(\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e} = \text{Mn}^{2+} + 4 \text{H}_2\text{O})
\]

\[
5 \text{AsO}_3^{3-} + 2 \text{MnO}_4^- + 6 \text{H}^+ = 5 \text{AsO}_4^{3-} + 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}
\]

This is the net Redox equation, which describes the reaction.

**Calculations Involving Redox Systems:**

Historically, equivalents were the primary tools used in Redox calculations. The equivalent weight of a substance involved in Redox reactions can be defined as

Equivalent weight = \text{Molecular weight} / \text{number of e involved}
Equivalents were used for the definition of a concentration term called normality, \( N \), where

\[
N = \frac{\text{No of equivalents}}{L}
\]

However, the use of these terms has greatly diminished in recent literature and trends for using molarity rather than normality is widely accepted. Molarity will be the only unit to be used in our calculations.

Example: Permanganate reacts with hydrogen peroxide according to the equation

\[
2 \text{MnO}_4^- + 5 \text{H}_2\text{O}_2 + 6 \text{H}^+ = 2 \text{Mn}^{2+} + 5 \text{O}_2 + 8 \text{H}_2\text{O}
\]

Calculate the molarity of \( \text{H}_2\text{O}_2 \) if 25 mL of \( \text{H}_2\text{O}_2 \) required 12.0 mL of 0.1 M \( \text{KMnO}_4 \).

\[
\frac{\text{mol H}_2\text{O}_2}{L} = \frac{0.1 \text{ mol KMnO}_4}{1000 \text{ mL KMnO}_4} \times \frac{12 \text{ mL KMnO}_4}{5 \text{ mol H}_2\text{O}_2} \times \frac{1000 \text{ mL}}{2 \text{ mol KMnO}_4} = 0.24 \text{ M}
\]

Example: In the previous example, how many mL of 0.1M \( \text{KMnO}_4 \) are required to react with 30 mL of 0.05 M \( \text{H}_2\text{O}_2 \)?
\[ ? \text{ mL KMnO}_4 = \frac{1000 \text{ mL KMnO}_4}{0.1 \text{ mol KMnO}_4} \times X \times 2 \text{ mol KMnO}_4 \times \frac{5 \text{ mol H}_2\text{O}_2}{0.05 \text{ mol H}_2\text{O}_2} \times \frac{30 \text{ mL H}_2\text{O}_2}{1000 \text{ mL H}_2\text{O}_2} = 3 \text{ mL} \]

In case of other units being given in any problem, change to Molarity units and perform your calculations using molarity.

Redox Reactions Involving Iodine:

Iodine is an oxidizing agent and can be used in conjunction with reducing agents to determine either of them. Two methods are available that involve iodine:

The first is a direct method in which standard iodine is used for the oxidation of a reducing agent (analyte), this method is called iodimetry. The second method is an indirect method, which involves the determination of liberated iodine (from oxidation of I-) in a Redox reaction and is called iodometry.

Iodine is very slightly soluble in water but is readily soluble in water containing iodide ion due to the following equilibrium

\[ I_2 + I^- = I_3^- \]

The triiodide is the oxidizing agent involved in iodometric and iodimetric titrations. It is a mild oxidizing agent that can be efficiently used in Redox titrations, provided enough precautions are considered.
Two points that would be remembered are the volatility of iodine where some iodine is usually lost on standing and exposure to atmosphere. The second point is that the medium in which iodine is prepared should not be very acidic since some iodide is converted to iodine under very acidic conditions

$$4 \Gamma^- + O_2 + 4 H^+ = 2 I_2 + 2 H_2O$$

This results in a change in the concentration of iodine which necessitates the use of glass stoppered flasks and performing the analysis as shortly as possible. Some metal ions, like Cu$^{2+}$, nitrite as well as direct sun light catalyze the conversion of I$^-$ into I$_2$. Therefore, dark brown glass bottles are preferred for storage of solutions containing I$^-$. 

**Reducing Agents Used in Titrations Involving Iodine:**

Sodium thiosulfate is the most widely used reducing agent and is historically associated with titrations involving iodine. The reaction between iodine and thiosulfate can be represented by the equation,

$$I_2 + 2 S_2O_3^{2-} = 2 \Gamma^- + S_4O_6^{2-}$$
This is the easier way to describe the reaction but what actually takes place is the following equilibrium,

\[ I_3^- + 2 \text{S}_2\text{O}_3^{2-} = 3 \text{I}^- + \text{S}_4\text{O}_6^{2-} \]

since I\(_2\) is present as the triiodide in aqueous solutions containing iodide.

Sodium thiosulfate can not be used as a primary standard due to the ambiguity of its content of water of hydration. In case of iodate,

\[ \text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ = 3 \text{I}_2 + 3 \text{H}_2\text{O} \]

It is obvious from this equation that the reaction should be conducted in acidic solution and in presence of excess iodide. However, great care should be observed in weighing the iodate in order to obtain good results.

Another method for thiosulfate standardization uses potassium dichromate, also in acidic solution, and in presence of excess iodide according to the equation:

\[ \text{Cr}_2\text{O}_7^{2-} + 6 \text{I}^- + 14 \text{H}^+ = 2 \text{Cr}^{3+} + 3 \text{I}_2 + 7 \text{H}_2\text{O} \]

Again, the liberated iodine oxidizes the thiosulfate. The reaction takes place in acidic solution and in presence of excess I\(^-\).
If thiosulfate solutions are to be stored for prolonged periods, it should be emphasized that carbon dioxide present in water will result in the decomposition of thiosulfate giving elemental sulfur as the result. This behavior can also be observed when some bacteria is present in solution,

$$S_2O_3^{2-} + H^+ = HSO_3^- + S$$

The elemental sulfur can easily be observed as the solution turns yellowish. Therefore, solutions of thiosulfate should be prepared from recently boiled and recooled distilled water with the addition of 3-5 drops of chloroform or about 10 mg/L of HgCl₂ which improves the storage capacity of thiosulfate.

It is also a good practice to store thiosulfate solutions in dark brown bottles with the addition of about 0.1 g/L of sodium carbonate to decrease the bacterial activity.

**Indicators Involved in Iodine Methods:**

The most widely accepted indicator in iodine titrations is starch. Starch forms a complex with iodine leading to a deep blue color. This complex is insoluble in water, which necessitates the addition of starch just before the end point which can be determined when the yellow color of iodine fades.
significantly. Ethanol and strong acid conditions should be avoided when starch is used as indicator. This is because ethanol diminishes the color of the complex while strong acidic solutions will hydrolyze the starch. It is advised that the starch should be freshly prepared for sensitive appearance of the blue color.

A starch derivative, sodium starch glycollate, is soluble in hot water and can be prepared in 1% solutions by gradually adding 1g of the starch glycollate to 100 mL of water and boiling for few minutes. About 0.1 - 0.2 mL of this solution is sufficient as an indicator.

Calculations Involved in Iodine Methods:

It is very important to relate all species to each other by correct stoichiometric relationships for successful calculations. For example; Calculate the Molarity of thiosulfate solution if 0.200 g of KIO₃ required 50.0 mL of the thiosulfate solution. Provided that excess KI and HCl were added.

\[
\begin{align*}
\text{IO}_3^- &= 3 \text{I}_2 \\
\text{I}_2 &= 2 \text{S}_2\text{O}_3^{2-} \\
\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ &= 3 \text{I}_2 + 3 \text{H}_2\text{O} \\
\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} &= 2 \text{I}^- + \text{S}_4\text{O}_6^{2-} \\
\text{IO}_3^- &= 6 \text{S}_2\text{O}_3^{2-}.
\end{align*}
\]

\[
\frac{\text{mol S}_2\text{O}_3^{2-}}{\text{L}} = \frac{0.200 \text{ g KIO}_3 \times \text{ mol KIO}_3}{214 \text{ g KIO}_3} \times \text{ X}
\]
Therefore, always find the relationships involved and follow each till you obtain a direct relation between titrant and the material being titrated. Then, straightforward calculations are performed.

**Applications**

Experiment 1. Standardization of Potassium Permanganate Using Sodium Oxalate

**Background**

Potassium permanganate stock solution can be standardized against primary standard sodium oxalate. The reaction takes place in acidic medium at about 80 °C. As mentioned in the text, permanganate is reduced to Mn2+ while oxalate is oxidized to CO2. It should be clear that this takes place in acid solution and temperature should not be allowed to drop below 60 °C through the whole titration.
Reactions

\[ 2 \text{MnO}_4^- + 5 \text{C}_2\text{O}_4^{2-} + 16 \text{H}^+ = 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O} \]

Reagents and Chemicals

a. Provided

1. Stock KMnO4 solution (about 0.02 M).
2. H_2SO_4 solution, 3 M.
3. Predried and desiccated sodium oxalate.

b. Need Preparation

250 mL of 0.05 M solution. Prepare by dissolving an appropriate weight of the oxalate in 250 mL of distilled water.

Procedure

1. Transfer exactly 25 mL of NaC_2O_4 into a 250 mL conical flask (keep the rest of the oxalate for next experiment).
2. Add 25 mL of the 3 M H_2SO_4 and heat the solution to about 80 °C (below boiling).
3. Titrate against KMnO4 solution until the very first appearance of pink color which persists for at least 30 seconds.
4. Repeat steps 1-3 twice and always record the volume of KMnO$_4$ consumed to two significant figures after the decimal point.

5. Calculate the molarity of KMnO$_4$ stock solution according to the reaction given above.

Report of Results

Wt of Na$_2$C$_2$O$_4$ =
Molarity of Na$_2$C$_2$O$_4$ =

<table>
<thead>
<tr>
<th>Vol of C$_2$O$_4$</th>
<th>Vol of KMnO$_4$</th>
<th>Molarity of KMnO$_4$</th>
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$\bar{x} = \frac{\sum \text{Vol of C}_2\text{O}_4 \times \text{Vol of KMnO}_4}{\text{Molarity of KMnO}_4}$

$\sigma =$

Calculations

Assume that 25.0 mL of 0.050 M Na$_2$C$_2$O$_4$ required 30.00 mL of KMnO$_4$ for complete reaction. Calculate the Molarity of KMnO$_4$:

\[
\frac{\text{mol KMnO}_4}{L} = \frac{0.050 \text{ mol Na}_2\text{C}_2\text{O}_4}{1000 \text{ mL Na}_2\text{C}_2\text{O}_4} \times \frac{2 \text{ mol KMnO}_4}{5 \text{ mol Na}_2\text{C}_2\text{O}_4}
\]

\[
\frac{25 \text{ mL Na}_2\text{C}_2\text{O}_4}{30 \text{ mL K MnO}_4} \times \frac{1000 \text{ mL}}{L} = 0.017 \text{ M}
\]
Experiment 2. Determination of Hydrogen Peroxide by Titration with Potassium Permanganate

Background

Hydrogen peroxide can act as either an oxidizing agent or a reducing agent. From the analytical point of view, it is a very important species because many enzymatic reactions yield hydrogen peroxide and a method for quantitation of this compound is of special value. Depending on the volume of oxygen released by 1 mL of hydrogen peroxide, the solution of the compound is usually denoted as 3, 6, 12, or 30 percent.

Reactions

\[ 2 \text{MnO}_4^- + 5 \text{H}_2\text{O}_2 + 6 \text{H}^+ = 2 \text{Mn}^{2+} + 5 \text{O}_2 + 8 \text{H}_2\text{O} \]

Reagents and Chemicals

a. Provided

1. Stock KMnO\(_4\) solution.
2. H\(_2\)SO\(_4\) solution, 3M.
3. H\(_2\)O\(_2\) solution of unknown concentration.

b. Need Preparation

1. Standard oxalate solution (about 0.05 M), You should have enough from previous experiment.

Procedure

1. Follow steps in experiment 9 to standardize the KMnO\(_4\) stock solution.
2. Transfer exactly 25.00 mL of the H₂O₂ unknown sample into a 250 mL conical flask followed by 50 mL of distilled water.
3. Add 25 mL of H₂SO₄ to the solution in step 2.
4. Titrate the solution against standardized KMnO₄ and record the volume to two significant figures after the decimal point.
5. Repeat steps 2 - 4 two more times.
6. Calculate the molarity of H₂O₂ in the sample.

Report of Results

Molarity of KMnO₄ =

<table>
<thead>
<tr>
<th>Vol of H₂O₂</th>
<th>Vol of KMnO₄</th>
<th>g H₂O₂ / L</th>
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\[ X = \]
\[ \sigma = \]

Experiment 3. Determination of Iron by Redox Titrations

Background

Iron (II) is oxidized by potassium dichromate to iron (III) after full reduction of iron present.

The method is good for the determination of iron in ores or in different types of salts. Usually, the sample is treated with a reducing agent like Sn²⁺ and excess Sn²⁺ is oxidized by addition of HgCl₂. The result of the reaction is a white precipitate of Hg₂Cl₂. Excess HgCl₂ does not affect the reaction of iron (II) with dichromate. If a too large amount of Sn²⁺ is added, heavy precipitate with some blackish particles (of Hg metal) appear.

Reactions

Pretreatment Steps
\[
2 \text{Fe}^{3+} + \text{Sn}^{2+} = 2 \text{Fe}^{2+} + \text{Sn}^{4+} \\
\text{Sn}^{2+} + 2 \text{Hg}^{2+} = \text{Hg}_2^{2+} + \text{Sn}^{4+}
\]

**Redox Reaction**

\[
6 \text{Fe}^{2+} + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} = 6 \text{Fe}^{3+} + 2\text{Cr}^{3+} + 7 \text{H}_2\text{O}
\]

**Reagents and Chemicals**

**a. Provided**

1. Predried and desiccated iron sample.
2. Predried and desiccated K\(_2\)Cr\(_2\)O\(_7\) .
3. 0.1 M SnCl\(_2\) in 4 M HCl .
4. 0.1 M HgCl\(_2\) .
5. 1 : 1 HCl solution.
6. 1 : 1 H\(_2\)SO\(_4\) solution.
7. 1 : 1 H\(_3\)PO\(_4\) solution.
8. Sodium diphenylamine sulfonate indicator solution.

**b. Need Preparation**

1. Standard K\(_2\)Cr\(_2\)O\(_7\) solution. Weigh accurately about 1.25 g of K\(_2\)Cr\(_2\)O\(_7\) that was dried and desiccated. Dissolve in about 100 mL of distilled water and transfer to a 250 mL measuring flask and adjust the volume to the mark using distilled water.

**Procedure:**

1. Weigh out accurately three samples of the iron unknown. Check with your instructor on the range allowed. The following steps should be applied to each sample separately.
2. Add 10 mL of the HCl solution provided and heat the solution gently. The solution should appear yellowish.
3. Add SnCl₂ dropwise to the hot solution till the yellowish color disappears. You should be very careful in this step and confine excess SnCl₂ to 1 or 2 drops only, otherwise you will discard the solution later.

4. If the yellowish color reappears while heating carefully add some more SnCl₂ till the color disappears.

5. Stop heating at this point and wait till the solution cools down to room temperature then add about 50 mL of distilled water followed by 20 mL of HgCl₂, a white precipitate should appear.

6. If no precipitate appears, insufficient SnCl₂ was added and if a grey precipitate is formed too much of SnCl₂ was added. In both cases you have to discard the sample and start over.

7. If a white precipitate is formed, add 150 mL of distilled water, 4 mL of H₂SO₄, 12 mL of H₃PO₄ and 8-10 drops of the indicator.

8. Titrate against standard K₂Cr₂O₇ and report the results as % Fe in the sample.

**Report of Results**

<table>
<thead>
<tr>
<th>Wt of Iron Sample</th>
<th>Vol of K₂Cr₂O₇</th>
<th>% Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>

\[
\bar{x} = \text{ }
\sigma = \text{ }
\]

**Calculations**

*Molarity of K₂Cr₂O₇* assuming that 1.25 g of K₂Cr₂O₇ were dissolved in a total volume of 250 mL:
% Fe can be calculated as follows:

Assume that 20 mL of K₂Cr₂O₇ were needed for the oxidation of the iron present:

\[
\text{? g Fe} = \frac{0.0170 \text{ mol K}_2\text{Cr}_2\text{O}_7}{0.114 \text{ g}} \times \frac{6 \text{ mol Fe}}{1000 \text{ mL}} \times \frac{55.8 \text{ g Fe}}{\text{ mol K}_2\text{Cr}_2\text{O}_7} \times \text{ mol Fe} \times 20 \text{ mL} = 0.114 \text{ g}
\]

\[
\% \text{ Fe} = \frac{0.114 \text{ g}}{\text{ Wt. of sample}} \times 100 \%
\]

Experiment 4. Iodometric Titration of a Hypochlorite Sample

Background

Hypochlorite anions are good oxidizing agents that can oxidize I⁻ into I₂. The produced iodine can be titrated with standard solution of thiosulfate which can be related to hypochlorite concentration. Since the thiosulfate is not a primary standard, it is standardized against KIO₃ primary standard.

Reactions
Standardization Step

$$\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ = 3 \text{I}_2 + 3 \text{H}_2\text{O}$$

$$\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} = 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}$$

Titration Step

$$\text{ClO}^- + 2 \text{I}^- + 2 \text{H}^+ = \text{I}_2 + \text{Cl}^- + \text{H}_2\text{O}$$
The resulting iodine is titrated with standardized thiosulfate.

Reagents and Chemicals

a. Provided

1. Predried and desiccated KIO$_3$.
2. Predried and desiccated hypochlorite sample. Alternatively, the solution of hypochlorite can be provided. Hypochlorite solutions can cause severe irritation and burns when concentrated!!!
3. Predried and desiccated Na$_2$S$_2$O$_3$.
4. 1 : 4 H$_2$SO$_4$.
5. Glacial acetic acid.
6. Chloroform.
7. Starch indicator.
8. Solid KI.
b. Need Preparation

1. 0.1 M Na$_2$S$_2$O$_3$ solution. Weigh an appropriate amount that can yield 500 mL solution, add 3 drops of chloroform.
2. 0.01 M KIO$_3$ solution. Weigh accurately appropriate amount necessary for preparation of 250 mL of the compound in distilled water.

Procedure

a. Standardization of the thiosulfate solution

1. Transfer 25 mL of the KIO$_3$ solution into a conical flask, add about 2 g of KI, dissolve well and add 5 mL of the H$_2$SO$_4$ solution.
2. Rapidly titrate against the Na$_2$S$_2$O$_3$ solution till the color of the iodine becomes very faint.
3. Add 2 mL of starch indicator and continue titration till the blue color of the indicator just disappears.
4. Calculate the molarity of the Na$_2$S$_2$O$_3$ solution.

b. Determination of the ClO$^-$

1. Weigh out an appropriate amount (check with your instructor) or transfer exactly 25 mL of the ClO$^-$ solution.
2. Add about 2 g of KI, dissolve well and add about 5 mL of the H2SO4 solution provided.
3. Rapidly titrate against the standardized Na2S2O3 solution till the color of the I2 becomes very faint (pale yellow).
4. Add 2 mL of starch indicator and continue titration till the first disappearance of the blue color.
5. Report your results as % ClO⁻ or g ClO⁻/100mL.

Report of Results

Standardization step

<table>
<thead>
<tr>
<th>Vol of KIO₃</th>
<th>Vol of Na₂S₂O₃</th>
<th>Molarity of Na₂S₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

\[ \bar{X} = \] \\
\[ \sigma = \]

<table>
<thead>
<tr>
<th>Vol of ClO⁻</th>
<th>Vol of Na₂S₂O₃</th>
<th>g NaClO /100 mL</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tbody>
</table>

\[ \bar{X} = \] \\
\[ \sigma = \]

Calculations

Assume that 25.00 mL of ClO⁻ solution required 20.00 mL of the 0.1M Na₂S₂O₃ solution. Calculate the amount of NaClO in g /100 mL
Another simple method is to calculate the number of grams of NaClO reacting with 20 mL of standard thiosulfate then multiplying the answer by 4 will result in g NaClO / 100 mL. Compare results.

**Experiment 5. Iodometric Determination of Copper**

**Background**

This is one of the important methods for determination of copper in ores. Cupric ions oxidize iodide yielding quantitative amounts of iodine, which can be determined by titration against standard Na$_2$S$_2$O$_3$. The solution is buffered, at pH 3.5, using ammonium hydrogen fluoride. The pH is critical because higher pH values lead to low results due to reaction of the Cu$^{2+}$ hydrolysis products with I$^-$ incompletely. Below pH 3, As (V) is reduced by iodide. Also, the use of the NH$_4$.HF$_2$ buffer is advantageous because F$^-$ complexes the Fe (III) present. When I$^-$ is oxidized by Cu$^{2+}$, CuI (s) is formed which absorbs released
I\textsubscript{2} resulting in diffuse end point. The addition of KSCN releases I\textsubscript{2} yielding sharper end points.

**Reactions**

\[
2 \text{Cu}^{2+} + 4 \text{I}^- = 2 \text{Cu} \text{(s)} + \text{I}_2
\]

\[
\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} = 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}
\]

**Reagents and Chemicals**

**a. Provided**

1. Predried and desiccated Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and KIO\textsubscript{3}
2. Solid KI.
3. Cu\textsuperscript{2+} unknown.
4. Starch indicator.
5. Solid KSCN.
6. 1 : 4 H\textsubscript{2}SO\textsubscript{4}.
7. Solid NH\textsubscript{4}.HF\textsubscript{2}.

**b. Need Preparation**

1. Standard Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution, 0.1 M. You should have enough solution left from previous experiment. If not, follow procedure described in previous experiment to prepare it.
2. Standard KIO₃ solution. You should also have enough left from experiment 12. If not follow procedure described there to prepare it.

Procedure

1. Standardize the thiosulfate solution against standard KIO₃ and calculate the molarity of Na₂S₂O₃.
2. Weigh out accurately three samples of the Cu²⁺ unknown, place in a 250mL conical flask and perform the following steps on each sample separately. See your instructor for the approximate weight of each sample.
3. Dissolve the sample in 50.00 mL of distilled water, add 1g of KI, 2g of NH₄HF₂, and dissolve well.
4. Titrate against standard Na₂S₂O₃ till the color of the liberated I₂ becomes very faint.
5. Add 2 mL of starch indicator and continue titration till the blue color just disappears.
6. Add 1g of KSCN and dissolve, the blue color will reappear. Titrate with Na₂S₂O₃ till the disappearance of the blue color.
   Be careful at this stage.
7. Calculate % Cu in the sample.

Report of Results
<table>
<thead>
<tr>
<th>Wt of Cu Sample</th>
<th>Vol of Na$_2$S$_2$O$_3$</th>
<th>% Cu</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

$\bar{x} =$

$\sigma =$
Chapter 3

A-Precipitation Titrations

Titrations in which precipitates are formed are called precipitation titrations. The most frequent application of this type of titration uses silver ion to determine chloride. Therefore, these titrations are called argentometric titrations. According to the indicator used, three methods can be described. Chromate is the indicator in Mohr's method while Fajans method makes use of adsorption indicators. Both methods are direct methods. The third method is an indirect method where an excess silver is added to chloride unknown and the remaining silver is back-titrated with a standard thiocyanate solution in presence of Fe(III) as an indicator. These methods will be detailed below.

Titration Curves

A titration curve for a precipitation titration can be constructed by plotting mL Ag+ against pX (X can be Cl^-, Br^-, I^-, or SCN^-) where the sharpness of the end point and the break is directly proportional to:

1. ksp of the silver salt.
2. The concentration of reactants.

This is true when a suitable indicator concentration is used. Mixtures can also be titrated provided that enough difference in the solubilities of the two silver salts exists (at least 10^3).

Example
Find the pCl in a 20 mL of a 0.10 M Cl- solution after addition of 0, 10, 20, and 30 mL of 0.10 M AgNO3. Ksp = 1.0x10^-10.

Solution
1. After addition of 0 mL Ag+
   \([\text{Cl}^-] = 0.10 \text{ M}\)
   \(\text{pCl} = 1.00\)
2. After addition of 10 mL Ag+
   Initial mmol Cl- = 0.10 \times 20 = 2.0
   Mmol Ag+ added = 0.10 \times 10 = 1.0
   Mmol Cl- excess = 2.0 – 1.0 = 1.0
   
   \([\text{Cl}^-]_{\text{excess}} = \frac{1.0}{30} = 0.033 \text{ M}\)

   We should expect that this is the actual concentration present in solution since the solubility of AgCl is very small (as seen from the ksp) and this is especially true since we have a common ion. However, let us try to calculate the [Cl-]dissociation of AgCl.

<table>
<thead>
<tr>
<th>Before Equilibrium</th>
<th>Solid</th>
<th>0</th>
<th>1.0/30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation AgCl(s) Ag+ Cl-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At Equilibrium Solid s 1/30 + s</td>
<td></td>
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<tr>
<td>Ksp = s(1/30 + s)</td>
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</tr>
</tbody>
</table>
Assume $1/30 >> s$

$1.0 \times 10^{-10} = 1/30 * s$

$s = 3 \times 10^{-9} \text{ M}$

Therefore, $[\text{Cl}^-] = 0.033$

$p\text{Cl} = 1.48$

3. After addition of 20 mL Ag$^+$

Initial mmol Cl$^-$ = $0.10 \times 20 = 2.0$

Mmol Ag$^+$ added = $0.10 \times 20 = 2.0$

Mmol Cl$^-$ excess = $2.0 - 2.0 = ??$

This is the equivalence point

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Before Equilibrium} & \text{Solid} & 0 & 0 \\
\hline
\text{Equation} & \text{AgCl(s)} & \text{Ag}^+ & \text{Cl}^- \\
\hline
\text{At Equilibrium} & \text{Solid} & s & s \\
\hline
\end{array}
\]

Ksp = $s \times s$

$S = (1.0 \times 10^{-10})^{1/2}$

$S = 1.0 \times 10^{-5} \text{ M}$

4. After addition of 30 mL Ag$^+$

Initial mmol Cl$^-$ = $0.10 \times 20 = 2.0$

Mmol Ag$^+$ added = $0.10 \times 30 = 3.0$

Mmol Ag$^+$ excess = $3.0 - 2.0 = 1.0$

$[\text{Ag}^+]\text{excess} = 1.0/50 = 0.02 \text{ M}$

Therefore, once again we have a common ion situation. We should expect that this is the actual Ag$^+$ concentration present in solution since the
solubility of AgCl is very small (as seen from the ksp) and this is especially true since we have a common ion. However, we can calculate the Cl- concentration from dissociation of AgCl in presence of excess Ag+ since this is the only source of Cl-.

$$K_{sp} = (0.02 + s) \times s$$

Assume that $0.02 \gg s$

$1.0 \times 10^{-10} = 0.02$ S

$S = 5.0 \times 10^{-9}$ M = [Cl-]

$pCl = 8.30$

**Methods for Chloride Determination**

a. Mohr Method

This method utilizes chromate as an indicator. Chromate forms a precipitate with Ag+ but this precipitate has a greater solubility than that of AgCl, for example. Therefore, AgCl is formed first and after all Cl- is consumed, the first drop of Ag+ in excess will react with the chromate indicator giving a reddish precipitate.

$$2 \text{Ag}^+ + \text{CrO}_4^{2-} \text{(Yellow)} = \text{Ag}_2\text{CrO}_4 \text{(Red)}$$
In this method, neutral medium should be used since, in alkaline solutions, silver will react with the hydroxide ions forming AgOH. In acidic solutions, chromate will be converted to dichromate. Therefore, the pH of solution should be kept at about 7. There is always some error in this method because a dilute chromate solution is used due to the intense color of the indicator. This will require additional amount of Ag$^+$ for the Ag$_2$CrO$_4$ to form.

**Example:**

Find the concentration of chloride in a 25 mL solution to which few drops of K$_2$CrO$_4$ were added, if the end point required 20 mL of 0.10 M AgNO$_3$.

**Solution**

Ag$^+$ + Cl$^-$ = AgCl(s)

The reaction between silver ions and chloride is 1:1

Mmol Ag$^+$ = mmol Cl$^-$

0.10 x 20 = MCl$^-$ * 25

MCl$^-$ = 0.08 M

**b. Volhard Method**

This is an indirect method for chloride determination where an excess amount of standard Ag$^+$ is added to the chloride solution containing Fe$^{3+}$ as an indicator. The excess Ag$^+$ is then titrated with standard SCN$^-$ solution until a red color is obtained which results from the reaction:

Fe$^{3+}$ (Yellow) + SCN$^-$ = Fe(SCN)$_2^+$ (Red)

The indicator system is very sensitive and usually good results are obtained. The medium should be acidic to avoid the formation of Fe(OH)$_3$. However,
the use of acidic medium together with added SCN- titrant increase the solubility of the precipitate leading to significant errors.

This problem had been overcome by two main procedures:
The first method includes addition of some nitrobenzene, which surrounds the precipitate and shields it from the aqueous medium. The second procedure involves filtration of the precipitate directly after precipitation, which protects the precipitate from coming in contact with the added SCN\(^-\) solution.

**Example:**
A 10 mL of a chloride sample was treated with 15 mL of 0.1182 M AgNO\(_3\). The excess silver was titrated with 0.101 M SCN\(^-\) requiring 2.38 mL to reach the red Fe(SCN)\(^2+\) end point. Find the concentration of chloride (At Wt = 35.5) in g/L.

**Solution**

\[
\text{Mmol Ag}^+ \text{ reacted} = \text{mmol Ag}^+ \text{ taken} - \text{mmol Ag}^+ \text{ back-titrated} \\
\text{Mmol Ag}^+ \text{ reacted} = \text{mmol Cl}\text{mmolAg}^+ \\
\text{back-titrated} = \text{mmol SCN}\text{mmol} \\
\text{Cl}^- = 0.1182 \times 15 - 0.101 \times 2.38 = 1.53 \text{M Cl}^- = 1.53/10 = 0.153 \text{ M} \\
? \text{ mg Cl}^- \text{ in 10 mL} = 1.53 \times 35.5 = 54.4 \\
\text{mg/L Cl}^- = 5.44 \times 103 \\
\text{g/L Cl}^- = 5.44 \text{ g} \\
\]

**C. Fajans Method**

Fluorescein and its derivatives are adsorbed to the surface of colloidal AgCl.
Analytical Chemistry  
(Quantitative Analysis)  
Dr.Hassan A.Mohamed

After all chloride is used, the first drop of Ag+ will react with fluorescein (FI) forming a reddish color.

Ag⁺ + FI⁻ (Yellowish green) = AgF (Red)

Since fluorescein and its derivatives are weak acids, the pH of the solution should be slightly alkaline to keep the indicator in the anion form but, at the same time, is not alkaline enough to convert Ag⁺ into AgOH. Fluorescein derivatives that are stronger acids than fluorescien (like eosin) can be used at acidic pH without problems. This method is simple and results obtained are reproducible.

Calculations are the same as in Mohr's method.

2-Complexometric titrations

EDTA TITRATIONS:

Complexometric titrations have many applications, especially for determination of metal ions. Ethylenediaminetetraacetic acid (EDTA) is the most widely used complexing agent for routine analysis of water hardness and other applications. EDTA is a polydentate ligand that is represented by the formula H₄Y. Usually, EDTA titrations are conducted in alkaline conditions under which EDTA will be present in different forms including H₄Y, H₃Y⁻, H₂Y²⁻, HY³⁻, and Y⁴⁻. Therefore, controlling the pH is one major factor that affects complexation.
The total concentration of EDTA will be the sum of all equilibrium species

\[ C_T = [H_4Y] + [H_3Y^+] + [H_2Y^{2-}] + [HY^3-] + [Y^{4-}] \]

The fraction of any species can be found if desired where:

\[ \alpha_0 = \frac{[H_4Y]}{C_T} \]
\[ \alpha_1 = \frac{[H_3Y^+]}{C_T} \]
\[ \alpha_2 = \frac{[H_2Y^{2-}]}{C_T} \]
\[ \alpha_3 = \frac{[HY^3-]}{C_T} \]
\[ \alpha_4 = \frac{[Y^{4-}]}{C_T} \]

Now, assume a divalent metal reacts with EDTA, \( Y^{4-} \), the following equilibrium will be observed in alkaline medium:

\[ M^{2+} + Y^{4-} \rightarrow MY^{2-} \]

\[ K_f = \frac{[MY^{2-}]}{[M^{2+}][Y^{4-}]} \]

\( Y^{4-} \) concentration is dependent on pH and, therefore, should be calculated as follows:

\[ \alpha_4 = \frac{K_1K_2K_3K_4}{[H_3O^+]^4 + K_1[H_2O^+]^3 + K_1K_2[H_3O^+]^2 + K_1K_2K_3[H_3O^+] + K_1K_2K_3K_4} \]

\[ [Y^{4-}] = \alpha_4 \frac{C_T}{M_1V_1 \text{ (EDTA)} = M_2 V_2 \text{ (metal ion)} \]
can be used for calculation of the metal ion concentration.

It is a common practice to express the concentration of the metal ion in ppm units where

\[ 1 \text{ ppm} = \frac{1 \text{ mg}}{L} \]

The number of mgs of the metal ion present in 1 L of the solution gives the ppm value.

**Indicators for EDTA Titrations**

**Metal ion indicators form complexes with the metal ions**

\[ M^{n+} + In^{n-} = M-In \]

When EDTA is added, the weak M-In complex is destroyed and the free In is released giving color at the end point.

Among the very important indicators that are routinely used, you will encounter two indicators namely Muroxide and Eriochrome Black T (solochrome Black). However, there are many other indicators some of them are very important because of their high selectivity towards specific metal ions.

**Preparation of an EDTA Standard Solution:**

Primary standards of EDTA cannot be prepared. EDTA solutions should be standardized against ZnSO4 or MgSO4 of very high purity. Water used in EDTA solution preparations should be free from polyvalent metal ions and preferably distilled through all Pyrex glass. Calmagite is a suitable
indicator. The titration is conducted at a buffered solution at about pH 10.

**Sharpness of the End Point**

The end point is affected by two major factors, the stability constant of the metal ion-EDTA complex and the concentrations of the metal ion and EDTA. As the value of both factors is increased, sharper end points are achieved. If either of the two factors has a low value, end points of less sharpness result. For very low stability constants diffuse end points are observed and large errors should be expected.

**Masking and Demasking Agents**

Some metal ions that interfere in EDTA titrations can be masked by addition of a suitable masking agent. The titration is performed then, if desired, a demasking agent can be added to free the previously masked metal ions so that they can be determined.

Usually, cadmium and zinc ions can be masked by the addition of cyanide. If desired, Cd and Zn ions can be demasked by addition of chloral hydrate or a 3:1 formaldehyde : acetic acid solution.

**Back Titration Using EDTA**
This is very important because, in some cases, there may not be a suitable indicator or the MY\textsuperscript{2-} complex is very weak. An excess of standard EDTA is added and the extra EDTA is back titrated with standard Mg\textsuperscript{2+} using a suitable indicator like Arsenazo I.

Calculations Involved in EDTA Titrations

As mentioned previously, this type of calculation is very simple. For example:

In an experiment for the determination of Ca\textsuperscript{2+} in tap water, it was observed that 75.0 mL of tap water required 15.0 mL of 0.05 M EDTA solution. Calculate the concentration of Ca\textsuperscript{2+} expressed as ppm CaCO\textsubscript{3}.

\[
\text{mg CaCO}_3 \times \frac{0.05 \text{ mol Y}^4\text{-}}{1000 \text{ mL Y}^4\text{-}} \times \frac{15.0 \text{ mL Y}^4\text{-}}{75.0 \text{ mL CaCO}_3} \times \frac{\text{mol CaCO}_3}{\text{mol Y}^4\text{-}} = \frac{100.0 \text{ g CaCO}_3}{\text{mol CaCO}_3} \times \frac{1000 \text{ mg CaCO}_3}{\text{g CaCO}_3} \times \frac{1000 \text{ mL}}{\text{L}} = 1 \times 10^3 \text{ ppm}
\]

This is because Ca\textsuperscript{2+} forms a 1:1 complex with EDTA. In fact, EDTA forms a 1:1 complex with all known divalent metal ions unless otherwise indicated.
Applications

Experiment 5. Complexometric Determination of Total Hardness of Water

Background

Water hardness is attributed to the presence of Ca$^{2+}$ and Mg$^{2+}$ and usually their total concentration is a measure of water hardness. EDTA forms complexes with both ions and the end point can be detected using Eriochrome Black T or calmagite indicator. Results are reported as ppm CaCO$_3$.

Reactions

\[
\begin{align*}
\text{Ca}^{2+} + \text{H}_2\text{Y}^{2-} & = \text{CaY}^{2-} + 2 \text{H}^+ \\
\text{Mg}^{2+} + \text{H}_2\text{Y}^{2-} & = \text{MgY}^{2-} + 2 \text{H}^+
\end{align*}
\]

The titration is conducted at about pH 10, which can be achieved by addition of ammonium buffer to the titration flask.

Reagents and Chemicals

a. Provided

1. Approximately 0.01 M EDTA solution containing about 0.1% NaOH and 0.01% MgCl$_2$·6H$_2$O.
2. Eriochrome Black T indicator that is 0.5% (W/V) in ethanol.
3. Ammonium buffer at pH 10.
4. Primary standard CaCO$_3$ (solid, Predried and desiccated).
5. 1:1 HCl solution.

b. Need Preparation

1. Standard Ca$^{2+}$ solution, 0.01 M.
   This can be prepared by weighing out about 0.1 - 0.15 g of CaCO$_3$, transfer to conical flask and add about 15 mL of HCl provided. Dilute with 50 mL of distilled water and heat the solution to boiling in order to remove CO$_2$. Transfer to 500 mL measuring flask and dilute to volume.

Procedure

a. Standardization of EDTA Solution

1. Transfer exactly 25.00 mL of the Ca$^{2+}$ standard solution into a 250 mL conical flask.
2. Add about 10 mL of the ammonium buffer, followed by 5 drops of the Eriochrome Black T indicator.
3. Titrate against the EDTA solution and record the volume to two significant figures after the decimal point.
4. Repeat steps 1-3 two more times.
5. Calculate the molarity of EDTA.
b. Determination of Water Hardness

1. Pipet exactly 50 mL of tap water into a 250 mL conical flask.
2. Add 10 mL of the ammonium buffer and 5 drops of the Eriochrome Black T indicator.
3. Titrate against standard EDTA solution and record the volume.
4. Repeat steps 1-3 two more times.
5. Calculate the total hardness of water and report your results as ppm CaCO$_3$.

Report of Results

a. Standardization of EDTA Solution

<table>
<thead>
<tr>
<th>Vol of EDTA</th>
<th>Vol of Ca$^{2+}$</th>
<th>Molarity of EDTA</th>
</tr>
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</table>

$\bar{X} =$ \\
$\sigma =$

b. Determination of Total Hardness of Water

<table>
<thead>
<tr>
<th>Vol of Water Sample</th>
<th>Vol of EDTA</th>
<th>ppm CaCO$_3$</th>
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</table>

$\bar{X} =$ \\
$\sigma =$

It should be observed that this method gives the total Mg$^{2+}$ and Ca$^{2+}$ present in the solution. However, results should be
reported as ppm CaCO$_3$ since this is the unit, which is used by analytical laboratories for comparative purposes.

Another important note concerns storage of standardized EDTA solutions where these solutions should never be stored in soda based glass. Preferably, polyethylene bottles should always be used.

Experiment 6. Indirect Complexometric Determination of Cobalt

Background

$\text{Co}^{2+}$ reacts with EDTA to form a complex at low pH. If an alkaline pH is used, $\text{Co}^{2+}$ precipitates as $\text{Co(OH)}_2$. However, Eriochrome Black T indicator is not suitable at low pH values. Therefore, $\text{Co}^{2+}$ is allowed to form a complex with excess EDTA at low pH. The pH is then increased to alkaline pH where the excess EDTA can be back-titrated with standard $\text{Mg}^{2+}$.

Reactions

$$\text{Co}^{2+} + \text{H}_2\text{Y}^{2- (excess)} = \text{CoY}^{2-} + 2 \text{H}^+$$

$$(\text{excess}) \text{H}_2\text{Y}^{2-} + \text{Mg}^{2+} = \text{MgY}^{2-} + 2 \text{H}^+$$

Reagents and Chemicals

a. Provided
1. Approximately 0.01 M EDTA solution.
2. Predried and desiccated MgCl₂ 6H₂O
3. Eriochrome Black T indicator 0.5% (w/v) in ethanol.
5. Co²⁺ solution of unknown concentration.

b. Need Preparation

1. Standard EDTA solution, 0.01 M.
The standardization of EDTA can be achieved simply by titration against MgCl₂ 6H₂O standard solution at pH 10 as follows:
Exactly 25.00 mL of Mg²⁺ (0.01 M) are transferred into a conical flask (250 mL) and 10 mL of ammonium buffer are added, followed by 5 drops of the indicator. The solution is titrated against standard Mg²⁺ and the experiment is repeated so that precise results are obtained.

2. Standard Mg²⁺ solution.
This solution can be prepared by weighing an appropriate amount of the magnesium salt provided, transferring to a 250 mL measuring flask and dissolution of the sample followed by adjustment of the volume to the mark. The required concentration is approximately 0.01 M, which should be exactly determined.

Procedure
1. Transfer exactly 25.00 mL of the Co\(^{2+}\) solution into a 250 mL conical flask.
2. Add 10 mL of the ammonium buffer, pH 10.
3. Add 5 drops of the Eriochrome Black T indicator.
4. Titrate against standard Mg\(^{2+}\) and record the volume to two significant figures after the decimal point.
5. Repeat steps 1-4 two more times.
6. Calculate the concentration of Co\(^{2+}\) in the solution and report your results as ppm Co\(^{2+}\).

Report of Results

1. Standardization of EDTA Solution

<table>
<thead>
<tr>
<th>Vol of Mg(^{2+})</th>
<th>Vol of EDTA</th>
<th>Molarity of EDTA</th>
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<tr>
<td>(\bar{X} = )</td>
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<td>(\sigma = )</td>
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2. Determination of Co\(^{2+}\)

<table>
<thead>
<tr>
<th>Vol of EDTA</th>
<th>Vol of Mg(^{2+})</th>
<th>Molarity of Co(^{2+})</th>
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<tr>
<td>(\bar{X} = )</td>
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<tr>
<td>(\sigma = )</td>
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Calculations

Assume that 50 mL of 0.01 M EDTA solution were added to 25 mL of Co\(^{2+}\) solution and the excess EDTA required 20 mL of 0.005 M Mg\(^{2+}\) solution. Calculate ppm Co\(^{2+}\) present.

First, find the Volume of EDTA present in excess, which reacted with the Mg\(^{2+}\) added.

\[
? \text{ mL EDTA} = \frac{1000 \text{ mL EDTA}}{0.01 \text{ mol EDTA}} \times \frac{\text{mol EDTA}}{\text{mol Mg}^{2+}} \times \frac{0.005 \text{ mol Mg}^{2+}}{1000 \text{ mL Mg}^{2+}} \times 20 \text{ mL Mg}^{2+} = 10 \text{ mL}
\]

Vol of EDTA which reacted with Co\(^{2+}\) = 50 - 10 = 40 mL

\[
\frac{? \text{ mg Co}^{2+}}{L} = \frac{0.01 \text{ mmol EDTA}}{\text{mL EDTA}} \times \frac{40 \text{ mL EDTA}}{25 \text{ mL Co}^{2+}} \times \frac{\text{mmol Co}^{2+}}{\text{mmol EDTA}}
\]

\[
\frac{58.9 \text{ mg Co}^{2+}}{\text{mmol Co}^{2+}} \times \frac{1000 \text{ mL}}{L} = 942 \text{ ppm}
\]
Chapter 4

Gravimetric analysis

Introduction

Gravimetric analysis, by definition, includes all methods of analysis in which the final stage of the analysis involves weighing. In the most basic case, this could involve simply heating a sample to dryness and weighing to determine the amount of volatile components. In this account, however, I shall limit myself to gravimetric methods which rely on the use of precipitation reactions.

The quantitative determination of a substance by precipitation followed by isolation and weighing of the precipitate is called gravimetric analysis.

The basic method of gravimetric analysis is fairly straightforward. A weighed sample is dissolved after which an excess of a precipitating agent is added. The precipitate which forms is filtered, dried or ignited and weighed. From the mass and known composition of the precipitate, the amount of the original ion can be determined.

For successful determinations the following criteria must be met:

1. The desired substance must be completely precipitated. In most determinations the precipitate is of such low solubility that losses from dissolution are negligible. An additional factor is the "common ion" effect, this further reduces the solubility of the precipitate. When Ag⁺ is precipitated out by addition of Cl⁻
Ag$^+ + $Cl$^- \rightleftharpoons AgCl(s)$

the (low) solubility of AgCl is reduced still further by the excess of Cl$^-$ which is added, pushing the equilibrium to the right.

2. The weighed form of the product should be of known composition.
3. The product should be "pure" and easily filtered. It is usually difficult to obtain a product which is "pure", i.e. one which is free from impurities but careful precipitation and sufficient washing helps reduce the level of impurity.

Properties of precipitates and precipitating agents:

1. The ideal precipitating agents is one that reacts with one and only one analyte to produce as solid that is...
   
   a. Sparingly soluble (i.e., not lost during filtration and washing).
   b. Readily filterable and washes free of contaminates (i.e., not a gelatinous mess).
   c. Unreactive to the atmosphere.
   d. Of known composition (or can be converted to something of known composition).

2. Precipitates with large particles size work best for filtration and washing.

3. Colloidal suspensions (precipitates with particles sizes of 1-100 nanometers) are undesirable.
   
   a. The particles do not settle out.
b. Filtration is difficult due to plugging of pores in the filter, or passing through the filter.

4. Precipitate size can be controlled (to some extent) by the conditions used to cause precipitation.

**Mechanism of Precipitation:**

After the addition of the precipitating agent to the solution of the ion under analysis there is an initial induction period before nucleation occurs. This induction period may range from a very short time period to one which is relatively long, ranging from the almost instantaneous to several minutes (for dilute solutions of barium sulphate). After induction, nucleation occurs, here small aggregates or nuclei of atoms form and it is from these "clumps" of atoms that the crystals which form the filtrate will grow. These nuclei may be composed of just a few atoms each so there may be up to 10^10 of these per mole of precipitating product. As these nuclei form so ions from solution (which at this point are in excess) congregate around them. For example if silver nitrate were added very slowly to a solution of sodium chloride, silver chloride nuclei would form and chloride ions (which would be in excess relative to Ag^+ ions) would congregate around them.

In addition to the primary adsorbed chloride ion, there are some sodium ions aggregating further from the AgCl nucleus. These are counter ions and tend to aggregate around the [AgCl:Cl]^− centre because these centers have a net negative charge (excess Cl−) and additional positive charge is required to maintain electrical neutrality. The counter ions are less tightly held than the primary adsorbed ions and the counter ion layer is somewhat diffuse and contains ions other than those of the counter ions.
After nucleation growth occurs, large nuclei grow at the expense of smaller nuclei which dissolve. This process helps produce more easily filtered crystals (since it produces larger crystals) and is encouraged by the analyst.

Growth of larger nuclei or crystallites can be encouraged by digestion, a process which involves heating the solid and mother liquor for a certain period of time. During digestion, small particles dissolve and larger ones grow. Digestion of the product is an important practical process and you will find that most if not all gravimetric analysis involve a digestion period.

To summarize the mechanism of precipitate formation.

1. Two steps are involved in precipitation:
   b. Particle Growth: Deposition of ions/molecules on the surface of the solid, nucleated particles.

2. In general, particle size is governed by the number of nuclei formed:
   a. Large supersaturation leads to more nuclei (and smaller particle size) and often produce colloids.
   b. Dilute solutions lead to fewer nuclei, more deposition on the fewer nuclei and larger crystals.

3. Spontaneous nucleation is rare. Usually, you must induce nucleation to provide a site to attract and hold ions/molecules by...
a. Scratching the side of the container.

b. Adding seed crystals.

4. Other experimental factors controlling precipitate size include...

a. Diffusion of ions/molecules to the surface of the growing crystal. This is affected by stirring, temperature, the nature of the ions/molecules, and concentration (low concentration is usually best).
b. Deposition on the surface of the crystal. This is affected by concentration, impurities on the surface of the crystal, growth characteristics of the crystal and pH (if pH-dependent)

**Practical Aspects:**

You will be shown in the laboratory sessions the important practical aspects of gravimetric analysis (e.g. handling of sinters, transfer of solid etc.). One aspect that should be emphasised is weighing. All weighings must be done at room temperature, you must not weigh your sinters straight from the oven - they must first be cooled in a desiccator. You must also weigh to constant mass. This means drying your product, cooling to room temperature, weighing and returning the product to the oven. The process of heating, cooling and weighing should be repeated until a constant mass is obtained. Generally, you can reduce the drying times by about a third each time, so if you dried the product for two hours the first time, you can cut this to one and a half hours the second time and so on. You must report all weighings.
**Conditions for analytical precipitation**

In an ideal world, an analytical precipitate for gravimetric analysis should consist of perfect crystals large enough to be easily washed and filtered. The perfect crystal would be free from impurities and be large enough so that it presented a minimum surface area onto which foreign ions could be adsorbed. The precipitate should also be "insoluble" (i.e. be of such slight solubility that loses from dissolution would be minimal).

Without going into detail, it has been shown (Von Weimarn) that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during precipitation; relative supersaturation = \((Q-S)/S\)

Where Q is the molar concentration of the mixed reagents before any precipitation occurs and S is the molar solubility of the product (precipitate) when the system has reached equilibrium. For the best possible results, conditions need to be adjusted such that Q will be as low as possible and S will be relatively large.

The following methods are used to approach these criteria:

**Precipitation from dilute solution.** This keeps Q low. Slow addition of precipitating reagent with effective stirring. This also keeps Q low, stirring prevents local high concentrations of the precipitating agent.

Precipitation at a pH near the acidic end of the pH range in which the precipitate is quantitative. Many precipitates are more soluble at the lower (more acidic) pH values and so the rate of precipitation is slower.
Precipitation from hot solution. The solubility $S$ of precipitates increases with temperature and so an increase in $S$ decreases the supersaturation.

Digestion of the precipitate. See earlier. (Also the digestion period results in some improvement in the internal perfection of the crystal structure [sometimes called ripening], here some internal foreign atoms may be expelled).

Precipitation from homogenous solution:

In this method, the precipitating ion is not added to the solution but is generated throughout the solution by a homogenous chemical reaction. This is the ultimate in precipitation technique. (!) Since the precipitating agent is generated evenly throughout the solution, local excess of the precipitating agent are avoided. In precipitation from homogenous solution the supersaturation ($Q - S$) is kept extremely low at all times resulting in a very pure, dense precipitate. Often substances which form only as amorphous (if you don’t know what that means - look it up!) solids will precipitate as well formed crystalline solids using this technique.

The major techniques of homogenous precipitation may be classified as follows;

- **1. Increase in pH.**

Usually the pH is made more alkaline by hydrolysis of urea ($\text{NH}_2\text{CONH}_2$) in boiling aqueous solution. The ammonia slowly liberated raises the pH of the solution homogeneously, causing metal ions that form insoluble hydroxides or hydrous oxides to precipitate. In the precipitation of aluminium from homogenous solution, urea is added to an acidic solution of aluminium.
containing some sulphuric or succinic acid. No precipitation occurs until the solution has been boiled long enough for the ammonia to raise the pH to the necessary value (about one hour or so). In this procedure aluminium precipitates as the basic sulphate or the basic succinate, not as aluminium hydroxide. The precipitate obtained in the way is much denser and freer from impurities than are aluminium precipitates formed by the conventional addition of ammonia to aluminium solutions.

Another example is the precipitation from homogeneous solution of barium chromate. Chromate is added to barium in solution which is acidic enough to prevent precipitation. Urea is added and the solution boiled. The ammonia released raises the solution pH and barium chromate slowly precipitates out.

2. Anion release
3. Cation release
4. Precipitation from mixed solvents
5. Valency change

These last four, although useful, are less common and so we shall not consider other than to note their existence. (Further information available in the set book).

Impurities in Precipitates:

No discussion of gravimetric analysis would be complete without some discussion of the impurities which may be present in the precipitates.
Coprecipitation:

This is anything unwanted which precipitates with the thing you do want. Coprecipitation occurs to some degree in every gravimetric analysis (especially barium sulphate and those involving hydrous oxides). You cannot avoid it - all you can do is minimise it by careful precipitation and thorough washing.

There are several mechanisms of co-precipitation. These include...

1. Surface adsorption.

2. Mechanical entrapment. Two crystals grow together and trap a species in the space between them.

3. Occlusion. An ion and its counter ion are trapped in a pocket of a rapidly growing crystal (i.e., the crystal grows around them).

4. Post precipitation. The precipitate causes a localized high concentration of unwanted species.

Co-precipitation is reduced by...

1. Using dilute solutions.

2. Rapid filtration.

3. Removing undesired ions before precipitation.
Surface adsorption:

Here unwanted material is adsorbed onto the surface of the precipitate. Digestion of a precipitate reduces the amount of surface area and hence the area available for surface adsorption. Washing can also remove surface material.

Occlusion:

This is a type of coprecipitation in which impurities are trapped within the growing crystal.

Postprecipitation:

Sometimes a precipitate standing in contact with the mother liquor becomes contaminated by the precipitation of an impurity on top of the desired precipitate.

Washing and Filtering:

Problems with coprecipitation and surface adsorption may be reduced by careful washing of the precipitate. With many precipitates, peptization occurs during washing. Here part of the precipitate reverts to the colloidal form e.g.

\[ \text{AgCl(colloidal)} \rightleftharpoons \text{AgCl(s)} \]

This results in the loss of part of the precipitate because the colloidal form may pass through on filtration.
Drying the solid:

Generally the solids are dried at about 120°C but conditions for drying can vary considerably. To determine the correct drying regime, a thermogravimetric balance may be used.

Drying removes the solvent(s) of the mother liquid from which the precipitate was formed.

Ignition converts the precipitate to a known composition called the weighing form.

Calculations:

You may find reference to the gravimetric factor in some texts - this is the ratio of RMM of substance sought to that of substance weighed.

Worked Examples and Problems

Worked Example

A certain barium halide exists as the hydrated salt BaX2.2H2O, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 cm3) and excess sulphamic acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulphate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.
Answer:

The precipitate is barium sulphate. The first stage is to determine the number of moles of barium sulphate produced, this will, in turn give us the number of moles of barium in the original sample.

Relative Molecular Mass of barium sulphate = 137.34 (Ba) + 32.06 (S) + (4 x 16.00) (4 x O)
= 233.40

Number of moles = mass / RMM
= 0.2533 / 233.40
= 1.09 x 10^-3

This is the number of moles of barium present in the precipitate and, therefore, the number of moles of barium in the original sample. Given the formula of the halide, (i.e. it contains one barium per formula unit), this must also be the number of moles of the halide. From this information we can deduce the relative molecular mass of the original halide salt:

RMM = mass / number of moles
= 0.2650 / 1.09 x 10^-3
= 244.18

The relative atomic mass of 2 X will be given by the RMM of the whole salt - that of the remaining components; So RAM of 2 X = 244.18 - 173.37 = 70.81

2 X = 70.81, so X = 35.41.
The RAM of chlorine is 35.45 which is in good agreement with the result obtained and hence the halide salt is hydrated barium chloride and X = Chlorine

Problems:

1. A sample (0.203 g) of hydrated magnesium chloride (MgCl$_m$·nH$_2$O) was dissolved in water and titrated with silver nitrate solution (0.100 moldm$^{-3}$), 20.0 cm$^3$ being required. Another sample of the hydrated chloride lost 53.2 % of its mass when heated in a stream of hydrogen chloride, leaving a residue of anhydrous magnesium chloride. Calculate the values of m and n

(Answer: m = 2, n = 6)

2. When a sample of impure potassium chloride (0.4500g) was dissolved in water and treated with an excess of silver nitrate, 0.8402 g of silver chloride was precipitated. Calculate the percentage KCl in the original sample.

(Answer: 97.12 %)