Chapter 5: Introduction to Reactions in Aqueous Solutions

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5-1 The Nature of Aqueous Solutions
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Focus on Water Treatment
5.1 The Nature of Aqueous Solutions
• Some solutes can *dissociate* into ions.
• Electric charge can be carried.
Types of Electrolytes

- **Strong electrolyte** dissociates completely.
  - Good electrical conduction.

- **Weak electrolyte** partially dissociates.
  - Fair conductor of electricity.

- **Non-electrolyte** does not dissociate.
  - Poor conductor of electricity.
A strong electrolyte:

\[ \text{MgCl}_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2 \text{Cl}^-(aq) \]

A weak electrolyte:

\[ \text{CH}_3\text{CO}_2\text{H}(aq) \rightarrow \text{CH}_3\text{CO}_2^-(aq) + \text{H}^+(aq) \]

A non-electrolyte:

\[ \text{CH}_3\text{OH}(aq) \]
Notation for Concentration

\[ \text{MgCl}_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2 \text{Cl}^{-}(aq) \]

In 0.0050 M MgCl\textsubscript{2}:

Stoichiometry is important.

\[ [\text{Mg}^{2+}] = 0.0050 \text{ M} \quad [\text{Cl}^{-}] = 0.0100 \text{ M} \quad [\text{MgCl}_2] = 0 \text{ M} \]
Example 5-1

Calculating Ion concentrations in a Solution of a Strong Electolyte.

What are the aluminum and sulfate ion concentrations in 0.0165 M Al₂(SO₄)₃?

Balanced Chemical Equation:

\[
\text{Al}_2(\text{SO}_4)_3 (s) \rightarrow 2 \text{Al}^{3+}(aq) + 3 \text{SO}_4^{2-}(aq)
\]
Example 5-1

**Aluminum Concentration:**

\[
[\text{Al}] = \frac{0.0165 \text{ mol Al}_2(\text{SO}_4)_3}{1 \text{ L}} \times \frac{2 \text{ mol Al}^{3+}}{1 \text{ mol Al}_2(\text{SO}_4)_3} = 0.0330 \text{ M Al}^{3+}
\]

**Sulfate Concentration:**

\[
[\text{SO}_4^{2-}] = \frac{0.0165 \text{ mol Al}_2(\text{SO}_4)_3}{1 \text{ L}} \times \frac{3 \text{ mol SO}_4^{2-}}{1 \text{ mol Al}_2(\text{SO}_4)_3} = 0.0495 \text{ M SO}_4^{2-}
\]
5-2 Precipitation Reactions

- Soluble ions can combine to form an **insoluble** compound.
- Precipitation occurs.

\[
Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)
\]
Overall Precipitation Reaction:

\[ \text{AgNO}_3(aq) + \text{NaI}(aq) \rightarrow \text{AgI}(s) + \text{NaNO}_3(aq) \]

Complete ionic equation:

\[ \text{Ag}^+(aq) + \text{NO}_3^-(aq) + \text{Na}^+(aq) + I^-(aq) \rightarrow \text{AgI}(s) + \text{Na}^+(aq) + \text{NO}_3^-(aq) \]

Net ionic equation:

\[ \text{Ag}^+(aq) + I^-(aq) \rightarrow \text{AgI}(s) \]
Solubility Rules

- Compounds that are *soluble*:
  - Alkali metal ion and ammonium ion salts
    \[ \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+ \]
  - Nitrates, perchlorates and acetates
    \[ \text{NO}_3^-, \text{ClO}_4^-, \text{CH}_3\text{CO}_2^- \]
Solubility Rules

• Compounds that are *mostly soluble*:
  
  – Chlorides, bromides and iodides \( \text{Cl}^-, \text{Br}^-, \text{I}^- \)
    
    • Except those of \( \text{Pb}^{2+}, \text{Ag}^+, \) and \( \text{Hg}_2^{2+} \).
  
  – Sulfates \( \text{SO}_4^{2-} \)
    
    • Except those of \( \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+} \) and \( \text{Hg}_2^{2+} \).
    
    • \( \text{Ca(SO}_4 \) is slightly soluble.
Solubility Rules

- Compounds that are *insoluble*:
  - Hydroxides and sulfides $\text{HO}^-$, $\text{S}^{2-}$
    - Except alkali metal and ammonium salts
    - Sulfides of alkaline earths are soluble
    - Hydroxides of $\text{Sr}^{2+}$ and $\text{Ca}^{2+}$ are slightly soluble.
  - Carbonates and phosphates $\text{CO}_3^{2-}$, $\text{PO}_4^{3-}$
    - Except alkali metal and ammonium salts
5-3 Acid-Base Reactions

• Latin *acidus* (sour)
  – Sour taste

• Arabic *al-qali* (ashes of certain plants)
  – Bitter taste

• Svante Arrhenius 1884 Acid-Base theory.
Acids

• Acids provide $\text{H}^+$ in aqueous solution.

• Strong acids:

$$\text{HCl}(aq) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$$

• Weak acids:

$$\text{CH}_3\text{CO}_2\text{H}(aq) \rightarrow \text{H}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)$$
Bases

• Bases provide OH\(^-\) in aqueous solution.

• Strong bases:

\[ \text{NaOH(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) \]

• Weak bases:

\[ \text{NH}_3(aq) + \text{H}_2\text{O(l)} \rightarrow \text{OH}^-(aq) + \text{NH}_4^+(aq) \]
Recognizing Acids and Bases.

- Acids have ionizable hydrogen ions.
  - $\text{CH}_3\text{CO}_2\text{H}$ or $\text{HC}_2\text{H}_3\text{O}_2$

- Bases have $\text{OH}^-$ combined with a metal ion.
  - KOH

or are identified by chemical equations

$$\text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) \rightarrow \text{HCO}_3^-(aq) + 2 \text{Na}^+(aq) + \text{OH}^-(aq)$$
More Acid-Base Reactions

- Milk of magnesia \( \text{Mg(OH)}_2 \)

\[
\text{Mg(OH)}_2(s) + 2 \text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + 2 \text{H}_2\text{O}(l)
\]

\[
\text{Mg(OH)}_2(s) + 2 \text{CH}_3\text{CO}_2\text{H}(aq) \rightarrow \text{Mg}^{2+}(aq) + 2 \text{CH}_3\text{CO}_2^-\text{(aq)} + 2 \text{H}_2\text{O}(l)
\]
More Acid-Base Reactions

- Limestone and marble.

\[
\text{CaCO}_3(s) + 2 \text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2\text{CO}_3(aq)
\]

But:

\[
\text{H}_2\text{CO}_3(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

\[
\text{CaCO}_3(s) + 2 \text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]
Limestone and Marble
## Gas Forming Reactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO$_3^-$</td>
<td>HSO$_3^-$ + H$^+$ $\rightarrow$ SO$_2$(g) + H$_2$O(l)</td>
</tr>
<tr>
<td>SO$_3^{2-}$</td>
<td>SO$_3^{2-}$ + 2 H$^+$ $\rightarrow$ SO$_2$(g) + H$_2$O(l)</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>HCO$_3^-$ + H$^+$ $\rightarrow$ CO$_2$(g) + H$_2$O(l)</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>CO$_3^{2-}$ + 2 H$^+$ $\rightarrow$ CO$_2$(g) + H$_2$O(l)</td>
</tr>
<tr>
<td>S$^{2-}$</td>
<td>S$^{2-}$ + 2 H$^+$ $\rightarrow$ H$_2$S(g)</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>NH$_4^+$ + OH$^-$ $\rightarrow$ NH$_3$(g) + H$_2$O(l)</td>
</tr>
</tbody>
</table>
5-4 Oxidation-Reduction: Some General Principles

• Hematite is converted to iron in a blast furnace.

\[ \text{Fe}_2\text{O}_3(s) + 3 \text{CO}(g) \xrightarrow{\Delta} 2 \text{Fe}(l) + 3 \text{CO}_2(g) \]

• Oxidation and reduction always occur together.

Fe\(^{3+}\) is reduced to metallic iron.

CO(g) is oxidized to carbon dioxide.
• Assign oxidation states:

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + 3 \text{CO(g)} & \xrightarrow{\Delta} 2 \text{Fe(l)} + 3 \text{CO}_2(g) \\
3^+ & \quad 2^- & \quad 2^+ & \quad 2^- & \quad 0 & \quad 4^+ & \quad 2^- \\
\end{align*}
\]

Fe\textsuperscript{3+} is reduced to metallic iron.

CO(g) is oxidized to carbon dioxide.
Zinc in Copper Sulfate

\[ \text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \]
• Represent a reaction by two half-reactions.

\[ \text{Oxidation:} \quad \text{Zn}(s) \quad \text{Zn}^{2+}(aq) + 2 \, e^- \]

\[ \text{Reduction:} \quad \text{Cu}^{2+}(aq) + 2 \, e^- \quad \text{Cu}(s) \]

\[ \text{Overall:} \quad \text{Cu}^{2+}(aq) + \text{Zn}(s) \quad \text{Cu}(s) + \text{Zn}^{2+}(aq) \]
Oxidation and Reduction

• Oxidation
  – O.S. of some element *increases* in the reaction.
  – Electrons are on the right of the equation

• Reduction
  – O.S. of some element *decreases* in the reaction.
  – Electrons are on the left of the equation.
Balancing Oxidation-Reduction Equations

- Few can be balanced by inspection.
- Systematic approach required.

- The Half-Reaction (Ion-Electron) Method
Example 5-6

Balancing the Equation for a Redox Reaction in Acidic Solution.

The reaction described below is used to determine the sulfite ion concentration present in wastewater from a papermaking plant. Write the balanced equation for this reaction in acidic solution.

\[
\text{SO}_3^{2-}(\text{aq}) + \text{MnO}_4^{-}(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + \text{Mn}^{2+}(\text{aq})
\]
Example 5-6

Determine the oxidation states:

\[
\begin{align*}
\text{SO}_3^{2-}(aq) + \text{MnO}_4^{-}(aq) & \quad \text{SO}_4^{2-}(aq) + \text{Mn}^{2+}(aq) \\
4^+ & \quad 7^+ & \quad 6^+ & \quad 2^+
\end{align*}
\]

Write the half-reactions:

\[
\begin{align*}
\text{SO}_3^{2-}(aq) & \quad \text{SO}_4^{2-}(aq) + 2\, e^{-}(aq) \\
5\, e^{-}(aq) + \text{MnO}_4^{-}(aq) & \quad \text{Mn}^{2+}(aq)
\end{align*}
\]

Balance atoms other than H and O:
Example 5-6

Balance O by adding $H_2O$:

$$H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2 e^- (aq)$$

$$5 e^- (aq) + MnO_4^{-}(aq) \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$$

Balance hydrogen by adding $H^+$:

$$H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2 e^- (aq) + 2 H^+ (aq)$$

$$8 H^+ (aq) + 5 e^- (aq) + MnO_4^{-}(aq) \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$$

Check that the charges are balanced: Add $e^-$ if necessary.
Example 5-6

Multiply the half-reactions to balance all e−:

\[ 5 \text{H}_2\text{O(l)} + 5 \text{SO}_3^{2-}(\text{aq}) \quad 5 \text{SO}_4^{2-}(\text{aq}) + 10 e^-(\text{aq}) + 10 \text{H}^+(\text{aq}) \]

\[ 16 \text{H}^+(\text{aq}) + 10 e^-(\text{aq}) + 2 \text{MnO}_4^-(\text{aq}) \quad 2 \text{Mn}^{2+}(\text{aq}) + 8 \text{H}_2\text{O(l)} \]

Add both equations and simplify:

\[ 5 \text{SO}_3^{2-}(\text{aq}) + 2 \text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq}) \]

\[ 5 \text{SO}_4^{2-}(\text{aq}) + 2 \text{Mn}^{2+}(\text{aq}) + 3 \text{H}_2\text{O(l)} \]

Check the balance!
Balancing in Acid

• Write the equations for the half-reactions.
  – Balance all atoms except H and O.
  – Balance oxygen using $\text{H}_2\text{O}$.
  – Balance hydrogen using $\text{H}^+$.
  – Balance charge using $e^-$.

• Equalize the number of electrons.

• Add the half reactions.

• Check the balance.
Balancing in Basic Solution

• OH\(^-\) appears instead of H\(^+\).

• Treat the equation as if it were in acid.
  – Then add OH\(^-\) to each side to neutralize H\(^+\).
  – Remove H\(_2\)O appearing on both sides of equation.

• Check the balance.
5-6 Oxidizing and Reducing Agents.

- An oxidizing agent (oxidant):
  - Contains an element whose oxidation state decreases in a redox reaction

- A reducing agent (reductant):
  - Contains an element whose oxidation state increases in a redox reaction.
Redox

<table>
<thead>
<tr>
<th>Compound or ion</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>+5</td>
</tr>
<tr>
<td>N$_2$O$_4$</td>
<td>+4</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>+3</td>
</tr>
<tr>
<td>NO</td>
<td>+2</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>+1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
</tr>
<tr>
<td>NH$_2$OH</td>
<td>-1</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>-2</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-3</td>
</tr>
</tbody>
</table>

This species cannot be oxidized further.

This species cannot be reduced further.

Oxidation half-reaction (reducing agent)

Reduction half-reaction (oxidizing agent)
Example 5-8

Identifying Oxidizing and Reducing Agents.

Hydrogen peroxide, $\text{H}_2\text{O}_2$, is a versatile chemical. Its uses include bleaching wood pulp and fabrics and substituting for chlorine in water purification. One reason for its versatility is that it can be either an oxidizing or a reducing agent. For the following reactions, identify whether hydrogen peroxide is an oxidizing or reducing agent.

\[
5 \text{H}_2\text{O}_2(\text{aq}) + 2 \text{MnO}_4^- (\text{aq}) + 6\text{H}^+ \rightarrow 8 \text{H}_2\text{O(l)} + 2 \text{Mn}^{2+}(\text{aq}) + 5 \text{O}_2(\text{g})
\]
Example 5-8

\[ \text{H}_2\text{O}_2(\text{aq}) + 2 \text{Fe}^{2+}(\text{aq}) + 2 \text{H}^+ \rightarrow 2 \text{H}_2\text{O}(l) + 2 \text{Fe}^{3+}(\text{aq}) \]

Iron is oxidized and peroxide is reduced.

\[ 5 \text{H}_2\text{O}_2(\text{aq}) + 2 \text{MnO}_4^-\text{(aq)} + 6 \text{H}^+ \rightarrow 8 \text{H}_2\text{O}(l) + 2 \text{Mn}^{2+}(\text{aq}) + 5 \text{O}_2(g) \]

Manganese is reduced and peroxide is oxidized.
5-7 Stoichiometry of Reactions in Aqueous Solutions: Titrations.

- **Titration**
  - Carefully controlled addition of one solution to another.

- **Equivalence Point**
  - Both reactants have reacted completely.

- **Indicators**
  - Substances which change colour near an equivalence point.
Indicators

(a) 

(b) 

(c)
Example 5-10

Standardizing a Solution for Use in Redox Titrations.

A piece of iron wire weighing 0.1568 g is converted to Fe\(^{2+}\)(aq) and requires 26.42 mL of a KMnO\(_4\)(aq) solution for its titration. What is the molarity of the KMnO\(_4\)(aq)?

\[
5 \text{ Fe}^{2+}(aq) + \text{MnO}_4^- (aq) + 8 \text{ H}^+(aq)
\]
\[
\quad 4 \text{ H}_2\text{O}(l) + 5 \text{ Fe}^{3+}(aq) + \text{Mn}^{2+}(aq)
\]
Example 5-6

\[ 5 \text{Fe}^{2+}(aq) + \text{MnO}_4^-(aq) + 8 \text{H}^+(aq) \rightarrow 4 \text{H}_2\text{O}(l) + 5 \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) \]

Determine \( \text{KMnO}_4 \) consumed in the reaction:

\[ n_{\text{H}_2\text{O}} = 0.1568 \text{g Fe} \times \frac{1 \text{mol Fe}}{55.847 \text{g Fe}} \times \frac{1 \text{mol Fe}^{2+}}{1 \text{mol Fe}} \times \]

\[ \frac{1 \text{mol MnO}_4^-}{5 \text{mol Fe}^{2+}} \times \frac{1 \text{mol KMnO}_4}{1 \text{mol MnO}_4^-} = 5.615 \times 10^4 \text{ mol KMnO}_4 \]

Determine the concentration:

\[ [\text{KMnO}_4] = \frac{5.615 \times 10^4 \text{ mol KMnO}_4}{0.2624 \text{ L}} = 0.2140 \text{ M KMnO}_4 \]
Chapter 5 Questions

1, 2, 3, 5, 6, 8, 14, 17, 19, 24, 27, 33, 37, 41, 43, 51, 53, 59, 68, 71, 82, 96.