

Chapter 4

Aqueous Reactions and Solution Stoichiometry

- Many reactions do not occur until the solid reactants are dissolved to make a solution.
- A solution is a homogeneous mixture.
- Solute is the substance in lesser amount; solvent is the substance in greater amount

Electrolyte Solutions

- Most ionic solids dissolve to form ions.
- Covalent solids may or may not form ions -- difficult to predict.
- SOLIDS
  - soluble
  - insoluble
  - ionize
  - don’t ionize
  - (electrolyte)
  - (non-electrolyte)
  - NaCl
  - CH₃OH

Electrolytes

- Non-electrolyte: doesn’t ionize in solution
  (These are covalent substances.)
- Strong electrolyte: ionizes completely in solution
  (These are generally ionic substances.)
- Weak electrolyte: ionizes partially in solution
  (These are covalent substances with some ionic character, such as acetic acid, CH₃CO₂H.)

Ionic Equations

- Molecular equations used to represent chemical reactions are not the best representation if some of the dissolved substances are electrolytes. In this case, it is more accurate to write the separate ions that compose the substance.
- We should write Ag⁺(aq) + NO₃⁻(aq) instead of AgNO₃ (aq).
- Molecular Equation:
  AgNO₃ (aq) + KCl (aq) → AgCl(s) + KNO₃ (aq)
- Complete Ionic Equation (write separate ions for soluble electrolytes):
  Ag⁺(aq) + NO₃⁻(aq) + K⁺(aq) + Cl⁻(aq) → AgCl(s) + K⁺(aq) + NO₃⁻(aq)
- Net Ionic Equation (cancel any ion on both sides of the equation, called spectator ions):
  Ag⁺(aq) + Cl⁻(aq) → AgCl(s)

Net Ionic Equation

- Write a net ionic equation for
  CrCl₃(aq) + FeCl₃(aq) → CrCl₃(aq) + FeCl₂(aq)
- Write a net ionic equation for
  AgCl(s) + KI(aq) → AgI(s) + KCl(aq)
**Reaction Classes**

**Double-Displacement Reactions**
- compound 1 + compound 2 → compound 3 + compound 4
  Also called metathesis
- exchange of ionic partners
  \[ \text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB} \]
- \( \text{Pb(NO}_3\text{)}_2(\text{aq}) + \text{K}_2\text{CrO}_4(\text{aq}) \rightarrow \text{PbCrO}_4(\text{s}) + 2\text{KNO}_3(\text{aq}) \)

**4.2 Precipitation Reactions**
- Formation of an insoluble solid
- \( \text{Pb(NO}_3\text{)}_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2\text{KNO}_3(\text{aq}) \)

**4.3 Acid-Base Reactions**

**Reaction Classes**

**Acid-Base Neutralization Reactions**
- acid + base → salt + water
- \( 2\text{HCl}(\text{aq}) + \text{Mg(OH)}_2(\text{s}) \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \)
- Net ionic equation:
  \[ 2\text{H}^+(\text{aq}) + \text{Mg(OH)}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \]
- Draw a molecular diagram of this type of reaction
- Reactions of strong acids and bases:
  \( \text{NaOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \)
  \( \text{KOH}(\text{aq}) + \text{HClO}_3(\text{aq}) \rightarrow \text{KClO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \)
- Group Work: What is the net ionic equation for each of these reactions?

**Reaction Classes**

**Gas Formation Reactions**
- Acids release \( \text{H}_2\text{S}, \text{CO}_2, \text{SO}_2 \) from salts of the oxoanions \( \text{S}^{2-}, \text{CO}_3^{2-}, \text{HCO}_3^-, \text{SO}_3^{2-} \)
- \( \text{FeS}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2\text{S}(\text{g}) \)
- \( \text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \)
- \( \text{Na}_2\text{SO}_3(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) \)
- Draw a molecular diagram of this type of reaction
- Complete and balance these reaction equations:
  - \( \text{CaCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \)
  - \( \text{NaOH}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow \)
  - \( \text{Mg(OH)}_2(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \rightarrow \)

**4.4 Oxidation-Reduction Reactions**
- When a metal undergoes corrosion it loses electrons to form cations:
  \( \text{Ca(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \)
- Oxidized: atom, molecule, or ion becomes more positively charged.
- Oxidation is the loss of electrons.
- Reduced: atom, molecule, or ion becomes less positively charged.
- Reduction is the gain of electrons.
Oxidation Numbers

- What is the difference between an ionic charge and an oxidation number?
- How do maximum and minimum values of the oxidation number correlate with the position in the periodic table?

Rules for Assigning Oxidation Numbers

1. The oxidation number of the atoms of an uncombined element is 0.
2. The sum of the oxidation numbers of all atoms in a substance must equal the total charge on the species: 0 for molecules; the ionic charge for ions.
3. Fluorine has an oxidation number of $-1$ in its compounds.
4. Hydrogen has an oxidation number of $+1$ unless it is combined with metals, in which case it has an oxidation number of $-1$.
5. The position of the element in the periodic table may be useful:
   a. Group IA (1) elements have oxidation numbers of $+1$ in their compounds.
   b. Group IIA (2) elements have oxidation numbers of $+2$ in their compounds.
   c. Group VIIA (17) elements have oxidation numbers of $-1$ unless combined with oxygen or a halogen closer to the top of the group.
   d. In binary compounds, Group VIA (16) elements have oxidation numbers of $-2$, unless combined with oxygen or halogens.
   e. In binary compounds, Group VA (15) elements have oxidation numbers of $-3$, unless combined with elements to their right in the periodic table.
6. Oxygen usually has an oxidation number of $-2$ in its compounds. There are some exceptions:
   a. Oxygen has an oxidation number of $-1$ in peroxides, which contain the $\text{O}_2^{2-}$ ion.
   b. Oxygen has an oxidation number of $-1/2$ in superoxides, which contain the $\text{O}_2^-$ ion.
   c. When combined with fluorine, as in $\text{OF}_2$, oxygen has a positive oxidation number (+2 in $\text{OF}_2$).

Example

- $\text{H}_2\text{SO}_4$
- $\text{H}$ is $+1$
- $\text{S}$ is $-2$ unless combined with oxygen or a halogen, so leave this for last
- $\text{O}$ is $-2$
- Use summation rule for $\text{S}$:
  
  $2(+1) + 1(\text{S}) + 4(-2) = 0$

  $\text{S} = 0 - 2 + 8 = +6$

Assignment of Oxidation Numbers

- Determine values of the oxidation number of each element in these compounds or ions:
  
  \[
  \begin{align*}
  \text{H}_2\text{O} & \quad \text{SO}_2 \\
  \text{CCl}_4 & \quad \text{H}_2\text{O}_2 \\
  \text{NO}_3^- & \quad \text{MnO}_4^- \\
  \text{CN}^- & \quad \text{NaNO}_3 \\
  \text{KClO}_4 & \\
  \end{align*}
  \]
Oxidation of Elements
Single-Displacement Reactions

- element + cmpd → cmpd + element
  (The more metallic element in the compound is displaced.)
- carbon + metal oxides
- \( 3C + Fe_2O_3 \rightarrow 3CO + 2Fe \)
  C is oxidized, \( Fe^{3+} \) is reduced
- metals + water
  \( Ca(s) + 2H_2O(aq) \rightarrow Ca(OH)_2(aq) + H_2(g) \)
- Metals can also be oxidized by other salts:
  \( Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s) \)
  Notice that the Fe is oxidized to \( Fe^{2+} \) and the \( Ni^{2+} \) is reduced to Ni.
- metals + acids
  \( Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \)
  \( Fe(s) \) is oxidized
  \( 2H^+(aq) \) is reduced to \( H_2(g) \)
- metals + metal salts
  \( Zn(s) + SnCl_2(aq) \rightarrow ZnCl_2(aq) + Sn(s) \)
  \( Zn(s) \) is oxidized
  \( Sn^{2+}(aq) \) is reduced
- nonmetals + salts
  \( Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq) \)

Figure 4.8: Activity Series
Matter tends to react in such a way that more reactive substances form less reactive substances. Some metals are easily oxidized whereas others are not.
- Activity series: a list of metals arranged in decreasing ease of oxidation.
- The higher the metal on the activity series, the more active that metal.
- Any metal can be oxidized by the ions of elements below it.
- Predict whether a reaction occurs
  - \( Na + H_2O \)
  - \( Fe + HCl \)
  - \( Cr + Fe^{2+} \)
  - \( Ni + Pb^{2+} \)
  - \( Ag + Mg^{2+} \)
  - \( Zn + Co^{2+} \)

4.5 Concentrations of Solutions
- Concentration: measure of the relative amounts of substances making up a solution
- Solute: the substance being dissolved; the substance present in lesser amount
- Solvent: the substance doing the dissolving; the substance present in greater amount
- Concentration = amount of solute/amount of solvent or solution
- Variety of units
- Most commonly used is M (molarity)
• Molarity
  \[ M = \text{moles solute/Liter solution} = \text{mol/L} \]

4.6 Solution Stoichiometry and Chemical Analysis
• Molarity = moles/liter or M
• Stoichiometric Relations in Solution
  Use volume and M to calculate moles
• Titration and Dilution
  What concentrations give equivalent moles?

Example Problem
• Consider the reaction:
  \[ 3\text{CaCl}_2(\text{aq}) + 2\text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 6\ \text{NaCl(\text{aq})} \]
If we mix 25.0 mL of 0.200 M CaCl$_2$ solution with 50.0 mL of 0.250 M Na$_3$PO$_4$ solution,
what mass of Ca$_3$(PO$_4$)$_2$(s) is formed? What concentration of NaCl(aq) results?