The Major Classes of Chemical Reactions

4.1 The Role of Water as a Solvent

Water participates actively in the dissolution process.

The dissolution process

- **Hydration** (solvation) of the solute particles in solution
  - The solute particles (ions, molecules, ...) are surrounded by water (solvent) molecules
  - The solute particles are evenly spread throughout the solution

- **Electrolytes** — produce ions in solution (resulting solution conducts electricity)
  - **Strong electrolytes** — completely ionize in solution (soluble salts, strong acids and bases such as NaCl, HCl, KOH, ...)
  - **Weak electrolytes** — partially ionize in solution (weak acids and bases such as H₂S, NH₃, ...)

- **Nonelectrolytes** — do not ionize in solution (resulting solution does not conduct electricity)
  - Molecular compounds (except acids and bases) such as H₂O, sugar, acetone, methanol, ...

The molecule of water is **polar**

- The O atom pulls the shared electrons stronger
- The O is partially negative and the Hs are partially positive
- The molecule is bent

⇒ The molecule has a positive and a negative pole → **dipole**

The water dipoles surround the ions on the surface of an **ionic** compound and pull them away from the crystal → hydration → electrolyte solution

The water dipoles surround the molecules on the surface of a **covalent** compound and interact with the polar bonds in it → hydration →

- If the molecules do not dissociate (most covalent compounds) → non-electrolytes
- If the molecules dissociate to ions (for example in acids which contain polar X–H bonds) → electrolytes

The **solubility** of a compound depends in large part on the relative strengths of the attractive forces between its ions or molecules and the forces of hydration
Example:
How many Na⁺ ions are present in 8.2 mL of a 0.15 M Na₂SO₄(aq) solution?

Na₂SO₄ → strong electrolyte
⇒ Na₂SO₄(s) → 2Na⁺(aq) + SO₄²⁻(aq)

\[
0.0082 \text{ L} \left( \frac{0.15 \text{ mol Na}_2\text{SO}_4}{1 \text{ L}} \right) \left( \frac{2 \text{ mol Na}^+}{1 \text{ mol Na}_2\text{SO}_4} \right) = 1.5 \times 10^{21} \text{ Na}^+ \text{ ions}
\]

4.2 Equations for Reactions in Aqueous Solution

- Overall molecular equation (all reactants and products in their undissociated form)

AgNO₃(aq) + NaCl(aq) → AgCl(s) + NaNO₃(aq)

- Complete (total) ionic equation (all strong electrolytes are completely dissociated to ions (ionized) in aqueous solutions)

[NaCl(aq) → Na⁺(aq), Cl⁻(aq)]

Ag⁺(aq) + NO₃⁻(aq) + Na⁺(aq) + Cl⁻(aq) → AgCl(s) + Na⁺(aq) + NO₃⁻(aq)

- Spectator ions – present on both sides of the equation (can be canceled)

Ag⁺(aq) + NO₃⁻(aq) + Na⁺(aq) + Cl⁻(aq) → AgCl(s) + Na⁺(aq) + NO₃⁻(aq)

- Net ionic equation – no spectator ions

Ag⁺(aq) + Cl⁻(aq) → AgCl(s)

For simplicity, we can omit (aq) after the symbols of all ions in aqueous solutions (assume all ions in solution as aqueous)

Ag⁺ + Cl⁻ → AgCl(s)

Example:
Write the net ionic equation corresponding to the following molecular equation:

Na₂CO₃(aq) + H₂SO₄(aq) →
⇒ Na₂SO₄(aq) + H₂O(l) + CO₂(g)

⇒ Complete ionic eq:

\[
2\text{Na}^+ + \text{CO}_3^{2-} + 2\text{H}^+ + \text{SO}_4^{2-} \rightarrow 2\text{Na}^+ + \text{SO}_4^{2-} + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

⇒ Net ionic eq:

\[
\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

4.3 Precipitation Reactions

- Formation of an insoluble product (precipitate) after mixing of two electrolyte solutions

- The driving force of precipitation reactions is the elimination of ions from the solution by formation of an insoluble product
Example:
When mercury(I) nitrate and potassium phosphate solutions are mixed, mercury(I) phosphate precipitates. Write the net ionic equation.

mercury(I) → Hg$_2^{2+}$ → Hg$_2$(NO$_3$)$_2$

⇒Skeletal eq:
Hg$_2$(NO$_3$)$_2$(aq) + K$_3$PO$_4$(aq) →
⇒ (Hg$_2$)$_3$(PO$_4$)$_2$(s) + KNO$_3$(aq)

⇒Overall balanced eq:
3Hg$_2$(NO$_3$)$_2$(aq) + 2K$_3$PO$_4$(aq) →
⇒ (Hg$_2$)$_3$(PO$_4$)$_2$(s) + 6KNO$_3$(aq)

⇒Complete ionic eq:
3Hg$_2^{2+}$ + 6NO$_3^-$ + 6K$^+$ + 2PO$_4^{3-}$ →
⇒ (Hg$_2$)$_3$(PO$_4$)$_2$(s) + 6K$^+$ + 6NO$_3^-$

⇒Net ionic eq:
3Hg$_2^{2+}$ + 2PO$_4^{3-}$ → (Hg$_2$)$_3$(PO$_4$)$_2$(s)

Predicting the outcome of precipitation
– Precipitation reactions are classified as double replacement (metathesis) reactions – exchange of ions leads to an insoluble combination of ions

Example:
Predict the outcome of the mixing of silver nitrate and potassium carbonate solutions.
⇒Ions present in the solution:
Ag$^+$, NO$_3^-$, K$^+$, CO$_3^{2-}$
⇒consider all possible combinations of ions to find if an insoluble product can form:
Ag$^+$ and CO$_3^{2-}$ form insoluble Ag$_2$CO$_3$
⇒Net ionic eq: 2Ag$^+$ + CO$_3^{2-}$ → Ag$_2$CO$_3$(s)
Note: The net ionic equation can be predicted directly from the formula of the precipitate.

4.4 Acid-Base Reactions
– Acids - sharp, sour taste; Bases - soapy, bitter taste
• Arrhenius acids – release hydrogen ions, H$^+(aq)$ [or H$_3$O$^+(aq)$], in water solutions
• Acidic hydrogen atoms in molecules
– can be released as H$^+$ ions
– formulas normally begin with the acidic Hs
Examples:
⇒ HCl, H$_2$SO$_4$, HCN, ....

HCl(g) $\xrightarrow{H_2O}$ H$^+$ + Cl$^-$
HCl(g) + H$_2$O(l) $\rightarrow$ H$_3$O$^+$ + Cl$^-$

• Arrhenius bases – release hydroxide ions, OH$^-$, in water solutions
Examples:
⇒NaOH dissolves in water and dissociates to Na$^+$ and OH$^-$:
NaOH(s) $\xrightarrow{H_2O}$ Na$^+$ + OH$^-$
⇒Ammonia gas, NH$_3$, dissolves in water and produces NH$_4^+$ and OH$^-$:
NH$_3$(g) + H$_2$O(l) $\rightarrow$ NH$_4^+$ + OH$^-$
• **Strong acids** – almost completely ionized in aqueous solutions
  ⇒ \( HBr(g) + H_2O(l) \rightarrow H_3O^+ + Br^- \) (~100% ionized)

• The strong acids in aqueous solution are:
  HCl(aq), HBr(aq), HI(aq), HNO\(_3\), H\(_2\)SO\(_4\), HClO\(_4\), and HClO\(_3\)

• **Weak acids** – only partially ionized in aqueous solutions (HF, H\(_2\)S, organic acids ... )
  ⇒ \( CH_3COOH(aq) + H_2O(l) \rightarrow H_3O^+ + CH_3COO^- \) (~1% ionized)

• **Strong bases** – almost completely ionized in aqueous solutions (oxides and hydroxides of alkali and alkaline earth metals)
  ⇒ \( KOH(s) \rightarrow K^+ + OH^- \) (~100% ionized)

• The strong bases in aqueous solution are:
  Group I hydroxides, Ca(OH)\(_2\), Sr(OH)\(_2\), and Ba(OH)\(_2\)

• **Weak bases** – only partially ionized in aqueous solutions (ammonia, amines, ...)
  ⇒ \( NH_3(aq) + H_2O(l) \rightarrow NH_4^+ + OH^- \) (~1% ionized)

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**Neutralization**

\[ \text{acid} + \text{base} \rightarrow \text{salt} + \text{water} \] (or other products)

• **Salt** – an ionic compound with a cation from the base and an anion from the acid
  \( H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l) \)

• Neutralization reactions are also viewed as **double replacement** (metathesis) reactions – exchange of ions leads to a salt and water

**Example:** Predict the products of the reaction between carbonic acid and calcium hydroxide.

\( H_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + 2H_2O \)

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**Proton Transfer**

• Net ionic equations for reactions between strong acids and bases

\( HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l) \)
\( H^+ + Cl^- + K^+ + OH^- \rightarrow K^+ + Cl^- + H_2O(l) \)

⇒ \( H^+ + OH^- \rightarrow H_2O(l) \)

– H\(^+\) is present in the form of H\(_3\)O\(^+\)

\( \Rightarrow H_3O^+ + OH^- \rightarrow 2H_2O(l) \)

Net ionic equation for all strong acid/strong base reactions (transfer of a proton from H\(_3\)O\(^+\) to OH\(^-\))

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– The driving force of strong acid-base reactions is the elimination of ions (H\(^+\) and OH\(^-\)) from the solution by formation of water

• Net ionic equations for reactions between weak acids and strong bases

**Example:**

\( HF(aq) + NaOH(aq) \rightarrow NaF(aq) + H_2O(l) \)
\( HF(aq) \rightarrow \text{weak acid (only partially ionized)} \)

\( HF(aq) + Na^+ + OH^- \rightarrow Na^+ + F^- + H_2O(l) \)

⇒ \( HF(aq) + OH^- \rightarrow F^- + H_2O(l) \)

⇒ transfer of a proton from HF to OH\(^-\)

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• Net ionic equations for reactions between strong acids and weak bases

**Example:**

\( HCl(aq) + NH_3(aq) \rightarrow NH_4Cl (aq) \)

\( NH_3(aq) \rightarrow \text{weak base (only partially ionized)} \)

\( H^+ + Cl^- + NH_3(aq) \rightarrow NH_4^+ + Cl^- \)

⇒ \( H^+ + NH_3(aq) \rightarrow NH_4^+ \)

– H\(^+\) is present in the form of H\(_3\)O\(^+\)

\( \Rightarrow H_3O^+ + NH_3(aq) \rightarrow NH_4^+ + H_2O(l) \)

⇒ transfer of a proton from H\(_3\)O\(^+\) to NH\(_3\)
Gas Formation Reactions

- Reactions of salts of weak or volatile acids with strong acids

Example:

\[
\begin{align*}
ZnS(s) + 2HCl(aq) & \rightarrow ZnCl_2(aq) + H_2S(g) \\
ZnS(s) + 2H^+ + 2Cl^- & \rightarrow Zn^{2+} + 2Cl^- + H_2S(g)
\end{align*}
\]

\[\Rightarrow ZnS(s) + 2H^+ \rightarrow Zn^{2+} + H_2S(g)\]

- \(H^+\) is present in the form of \(H_3O^+\)

\[\Rightarrow ZnS(s) + 2H_3O^+ \rightarrow Zn^{2+} + H_2S(g) + 2H_2O(l)\]

\[\Rightarrow\text{transfer of a proton from } H_3O^+ \text{ to } S^{2-}\]

Acid-base titrations

- Titrations use measurements of volumes
- Based on stoichiometric acid-base reactions between the analyzed solution (analyte) and a solution with known concentration (titrant)

- **Equivalence point** – the amount of titrant added is stoichiometrically equivalent to the amount of analyte present in the sample

- **Indicators** – change color at the equivalence point (signal the end point of the titration)

Example: A 25.0 mL \(H_2SO_4\) solution is titrated with 16.4 mL 0.255 M KOH. What is the molarity of the acid solution.

\[\text{balanced equation:} \quad 2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)\]

\[\Rightarrow \text{mole ratio: } \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol KOH}}\]

\[16.4 \times 10^{-3} \text{ L} \times \left( \frac{0.255 \text{ mol KOH}}{1 \text{ L}} \right) \times \left( \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol KOH}} \right) = 2.09 \times 10^{-3} \text{ mol } H_2SO_4\]

\[2.09 \times 10^{-3} \text{ mol } H_2SO_4 = \frac{8.36 \times 10^{-2} \text{ mol } H_2SO_4}{25.0 \times 10^{-3} \text{ L}}\]

4.5 Redox Reactions

**Oxidation and reduction**

- **Transfer of electrons** from one species to another
- Driving force of redox reactions – movement of electrons from an atom with less to an atom with more attraction for electrons

\[2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)\]

NaCl is an ionic compound:

\[2Na(s) + Cl_2(g) \rightarrow 2Na^+(s) + 2Cl^-(s)\]

- \(Na(s) \rightarrow Na^+(s)\) \(\Rightarrow\) loss of \(1e^-\) by \(Na\)
- \(Cl_2(g) \rightarrow 2Cl^-(s)\) \(\Rightarrow\) gain of \(2e^-\) by \(Cl_2\)

Result \(\rightarrow\) transfer of electrons from \(Na\) to \(Cl_2\)

- **Oxidation** - loss of electrons (\(Na\) is oxidized)
  - term originates from reactions of substances with oxygen

- **Reduction** - gain of electrons (\(Cl_2\) is reduced)
  - term originates from reactions of metal oxides with C, CO, H2, etc. to extract (reduce) the pure metal

- Oxidation and reduction can not occur independently
  - electrons gained by one species must be lost by another (\(e^-\) gained by \(Cl_2\) are lost by \(Na\))
  - \(Cl_2\) oxidizes \(Na\) and \(Na\) reduces \(Cl_2\)
• The transfer of electrons during redox reactions is not always complete

\[ 2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \]

H₂O is a covalent compound with polar bonds in which the electrons are not shared equally

\[ H^{\delta+} - O^{\delta-} - H^{\delta+} \]

⇒ Electrons are shifted from H to O

\[ H \rightarrow H^{\delta+} \Rightarrow \text{loss of } e^- \text{ density by H} \]

\[ O \rightarrow O^{\delta-} \Rightarrow \text{gain of } e^- \text{ density by O} \]

Result → incomplete transfer of electrons from H to O

Oxidation Numbers (Ox#)
• Oxidation number (oxidation state) – the charge an atom would have if the e⁻'s in polar bonds are not shared but are transferred completely to the atom with more attraction for e⁻'s
  – Assigned to each element in a substance

• Oxidation numbers can help determine whether substances are oxidized or reduced
  – Oxidation – increase in Ox#
  – Reduction – decrease in Ox#

\[ \text{Na}(s) \rightarrow \text{Na}^+(s) \Rightarrow \text{Ox# increases } (0 \rightarrow +1) \]

\[ \text{Cl}_2(g) \rightarrow 2\text{Cl}^-(s) \Rightarrow \text{Ox# decreases } (0 \rightarrow -1) \]

• Rules for assigning Ox#
  – Monoatomic ions → Ox# = charge of ion
  – Free elements → Ox# = 0
  – F → Ox# = -1
  – O → Ox# = -2 (except in combination with F and in peroxides)
  – H → Ox# = +1 (in combination with nonmetals)
  → Ox# = -1 (in combination with metals)
  – Halogens → Ox# = -1 (except in comb. with O or other halogen higher in the group)
  – The sum of Ox# of all elements in a species equals the charge of the species

Example:
Assign the oxidation numbers of all elements in NO₃⁻ and HClO₃.

\[ \text{NO}_3^- \Rightarrow \text{O} (-2) \text{ by rule} \]

\[ 3x(-2) + 1x(X) = -1 \Rightarrow X = +5 \Rightarrow \text{N} (+5) \]

\[ \text{HClO}_3 \Rightarrow \text{O} (-2) \text{ by rule} \]

\[ \Rightarrow \text{H} (+1) \text{ by rule} \]

\[ 3x(-2) + 1x(+1) + 1x(X) = 0 \]

\[ \Rightarrow X = +5 \Rightarrow \text{Cl} (+5) \]

• The highest and lowest Ox# for main group elements can be predicted from the periodic table (with some exceptions)

Oxidizing agent – causes oxidation
  – removes electrons from the species being oxidized
  – is the species being reduced
  – contains an element which undergoes a decrease in Ox# (reduction)

Reducing agent – causes reduction
  – supplies electrons to the species being reduced
  – is the species being oxidized
  – contains an element which undergoes an increase in Ox# (oxidation)
Identification of Ox/Red agents – need to examine the Ox# of all elements in the reaction

**Example:**
Identify the Ox. and Red. agents in the reaction of Cu with hot, concentrated H₂SO₄.

\[
\text{Cu(s) + 2H}_2\text{SO}_4(\text{aq, conc.}) \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})
\]

Cu
\[
\begin{array}{c}
\text{Cu} \\
\text{0 (in Cu)} \\
\text{+2 (in Cu}^{2+})
\end{array}
\]

S
\[
\begin{array}{c}
\text{S} \\
\text{+6 (in H}_2\text{SO}_4) \\
\text{+4 (in SO}_2)
\end{array}
\]

⇒ Cu is oxidized ⇒ Cu is the reducing agent
⇒ S in H₂SO₄ is reduced ⇒ H₂SO₄ is the oxidizing agent
⇒ H₂SO₄ oxidizes Cu; Cu reduces H₂SO₄

**Redox titrations**
- Use redox reactions

**Example:**
A 0.202 g sample of iron ore is dissolved in HCl and all of its Fe content is converted to Fe²⁺. The resulting solution is titrated with 16.7 mL 0.0108 M KMnO₄ solution. Determine the mass% of Fe in the sample, if the equation of the redox reaction is:

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

⇒ mole ratio: \([5 \text{ mol Fe}^{2+} / 1 \text{ mol MnO}_4^-]\)

**4.6 Free Elements in Redox Reactions**
- If a reaction involves a free element as either reactant or product, it is a redox reaction
- **Combining two elements**
  - Metal + Nonmetal → Ionic compound
    \[
    2\text{K(s) + F}_2(\text{g}) \rightarrow 2\text{KF(s)}
    \]
    \[
    \begin{array}{c}
    \text{0} \\
    \text{0} \\
    \text{+1} \\
    \text{-1}
    \end{array}
    \]
  - Nonmetal + Nonmetal → Covalent compound
    \[
    \text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF(g)}
    \]
    \[
    \begin{array}{c}
    \text{0} \\
    \text{0} \\
    \text{+1} \\
    \text{-1}
    \end{array}
    \]
• Combining compounds and elements
  \[2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)\]
  \(+4 -2 0 +6 -2\)

• Decomposing compounds into elements
  – Thermal decomposition
    \[2HgO(s) \xrightarrow{\triangle} 2Hg(l) + O_2(g)\]
    \(+2 -2 0 0\)
  – Electrolytic decomposition
    \[2H_2O(l) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)\]
    \(+1 -2 0 0\)

• Displacing one element by another
  \(A + BC \rightarrow AB + C\) (single displacement)

• The activity series of the metals – orders the metals by their ability to displace H or each other from compounds
  – Metals displacing hydrogen from acids or H_2O
    \[Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)\]
    \(+1 -1 0 +2 -1 0\)
  – Metals displacing each other
    \[Zn(s) + 2AgNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + 2Ag(s)\]
    \(+0 +1 +2 0\)

• Activity series – metals higher in the list are stronger reducing agents and can displace (reduce) metals lower in the list from their aqueous solutions

• The most active metals are unstable in water

• The activity series of the halogens
  – Reactivity decreases down the group (halogens higher in the group are stronger oxidizing agents and can displace (oxidize) halogens lower in the group)
    \[2KI(aq) + Cl_2(g) \rightarrow 2KCl(g) + I_2(aq)\]
    \(+1 -1 0 +1 -1 0\)

• Combustion reactions – combination of elements or compounds with oxygen
    \[CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)\]
    \(-4 +1 0 +4 -2 +1 -2\)

Example:
Classify the following reactions:

a) \[2H_3PO_4(aq) + 3Ba(OH)_2(aq) \rightarrow \]
   \[\rightarrow Ba_3(PO_4)_2(s) + 6H_2O(l)\]

  \(H_3PO_4\) is a weak acid; \(Ba(OH)_2\) is a strong base
  Products are salt and water
  \(\Rightarrow\) Neutralization reaction
  \(\Rightarrow\) The salt is insoluble \(\Rightarrow\) precipitate
  \(\Rightarrow\) Precipitation reaction
  \(\Rightarrow\) Double displacement reaction

b) \[2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)\]
  \(\Rightarrow\) Free elements involved in the reaction
  \(\Rightarrow\) Change in Ox# of K and H
  \(\Rightarrow\) Redox reaction
  \(\Rightarrow\) K displaces H from water
  \(\Rightarrow\) Single displacement reaction

c) \[2HBr(aq) + Na_2CO_3(aq) \rightarrow \]
   \[\rightarrow 2NaBr(aq) + CO_2(g) + H_2O(l)\]

  \(\Rightarrow\) No change in Ox# of elements
  \(\Rightarrow\) HBr is a strong acid, \(Na_2CO_3\) is a salt of a weak acid
  \(\Rightarrow\) Gas formation reaction
  \(\Rightarrow\) Neutralization reaction