IB Diploma Programme Chemistry

Reactivity 3: What are the Mechanisms of Chemical Change?

Subtopic R3.2

R3.2 - Electron Transfer Reactions (Redox and Electrochemistry)

Comprehensive Revision Notes

Both SL and AHL Content

MINDLAB

January 21, 2026

Contents

1 R3.2 - Electron Transfer Reactions (Redox and Electrochemistry)

1.1 Overview

Guiding Question: *What happens when electrons are transferred?*
Teaching Hours: SL: 10 hours — HL: 15 hours (10 SL + 5 HL)

1.2 Core Definitions

SL Core Content

Oxidation and Reduction (OIL RIG):

- **Oxidation:** Loss of electrons, increase in oxidation state
- **Reduction:** Gain of electrons, decrease in oxidation state
- **Oxidizing agent:** Causes oxidation (itself gets reduced)
- **Reducing agent:** Causes reduction (itself gets oxidized)

Mnemonic: OIL RIG (Oxidation Is Loss, Reduction Is Gain)

1.3 Oxidation States (SL)

Rules for Assigning Oxidation States:

1. Elements in pure form: 0 (e.g., O_2, Fe)
2. Monatomic ions: charge on ion (e.g., Na^+ = +1, Cl^- = -1)
3. Oxygen: usually -2 (except peroxides -1, OF_2 +2)
4. Hydrogen: usually +1 (except metal hydrides -1)
5. Fluorine: always -1
6. Group 1 metals: always +1
7. Group 2 metals: always +2
8. Sum of oxidation states = overall charge

Example: Determine oxidation state of S in H_2SO_4.
Solution: Let S = x
$2(+1) + x + 4(-2) = 0$
$2 + x - 8 = 0$
$x = +6$

1.4 Half-Equations (SL)

Balancing Half-Equations in Acidic/Neutral Solution:

1. Balance atoms other than O and H
2. Balance O by adding H_2O
3. Balance H by adding H^+
4. Balance charge by adding e^-

Example: $MnO_4^- \longrightarrow Mn^{2+}$ (acidic)

Step 1: Mn already balanced

$MnO_4^- \longrightarrow Mn^{2+}$

Step 2: Balance O with H_2O

$MnO_4^- \longrightarrow Mn^{2+} + 4\,H_2O$

Step 3: Balance H with H^+

$MnO_4^- + 8\,H^+ \longrightarrow Mn^{2+} + 4\,H_2O$

Step 4: Balance charge with e^-

$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$

1.5 Voltaic (Galvanic) Cells (SL)

SL Core Content

Components:

- **Anode:** Oxidation occurs, negative terminal (-), electron source
- **Cathode:** Reduction occurs, positive terminal (+), electron sink
- **Salt bridge:** Allows ion flow to maintain neutrality (NOT electron flow!)
- **External circuit:** Wire connecting electrodes (electrons flow anode → cathode)

Mnemonic: "An Ox" (Anode = Oxidation), "Red Cat" (Reduction = Cathode)
Example - Zn/Cu Cell:

- Anode: $Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-$ (oxidation)
- Cathode: $Cu^{2+}\,(aq) + 2\,e^- \longrightarrow Cu\,(s)$ (reduction)
- Overall: $Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$

Common Pitfall

Common Error: Electrons do NOT flow through salt bridge!

- Electrons: Flow through external wire only (anode → cathode)
- Ions: Flow through salt bridge (anions toward anode, cations toward cathode)

1.6 Electrolytic Cells (SL)

SL Core Content

Key Differences from Voltaic Cells:

- Requires external DC power source
- Drives non-spontaneous reactions
- **Anode:** Oxidation, POSITIVE terminal (connected to + of battery)
- **Cathode:** Reduction, NEGATIVE terminal (connected to - of battery)
- Polarity REVERSED compared to voltaic cell!

Electrolysis of Molten NaCl:

- Cathode: $Na^+ + e^- \longrightarrow Na$ (reduction)
- Anode: $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$ (oxidation)
- Overall: $2\,NaCl\,(l) \longrightarrow 2\,Na\,(l) + Cl_2\,(g)$

1.7 Organic Redox Reactions (SL)

SL Core Content

Oxidation of Alcohols:

- **Primary (1°):** $RCH_2OH \xrightarrow{\text{oxidize}} RCHO \xrightarrow{\text{oxidize}} RCOOH$
  - Use distillation to collect aldehyde (prevents further oxidation)
  - Use reflux to form carboxylic acid (prolonged heating)
- **Secondary (2°):** $R_2CHOH \xrightarrow{\text{oxidize}} R_2CO$ (ketone, stops here)
- **Tertiary (3°):** No oxidation under normal conditions

Reduction of Carbonyl Compounds:

- $RCHO \xrightarrow{\text{reduce}} RCH_2OH$ (aldehyde → primary alcohol)
- $R_2CO \xrightarrow{\text{reduce}} R_2CHOH$ (ketone → secondary alcohol)
- $RCOOH \xrightarrow{\text{reduce}} RCHO \xrightarrow{\text{reduce}} RCH_2OH$ (acid → aldehyde → alcohol)

Reduction of Alkenes/Alkynes:

- $C{=}C + H_2 \longrightarrow C{-}C$ (alkene → alkane)
- $C{\equiv}C + H_2 \longrightarrow C{=}C + 2\,H_2 \longrightarrow C{-}C$ (alkyne → alkene → alkane)

1.8 AHL - Standard Electrode Potentials

AHL Additional Content

Standard Electrode Potential ($E^\ominus$):

- Voltage of half-cell relative to standard hydrogen electrode (SHE)
- Standard conditions: 298 K, 1 bar, 1 mol dm^{-3}
- All data booklet values written as REDUCTION potentials
- More positive $E^\ominus$ = stronger oxidizing agent (easier to reduce)
- More negative $E^\ominus$ = stronger reducing agent (easier to oxidize)

Standard Hydrogen Electrode (SHE):

$$2\,H^+\,(aq) + 2\,e^- \longrightarrow H_2\,(g) \quad E^\ominus = 0.00\text{ V (by convention)} \tag{1}$$

1.9 AHL - Standard Cell Potential

AHL Additional Content

Key Formula

Standard Cell Potential:

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \tag{2}$$

Spontaneity Criterion:

- If $E^\ominus_{\text{cell}} > 0$: Spontaneous (forward reaction favored)
- If $E^\ominus_{\text{cell}} < 0$: Non-spontaneous (reverse reaction favored)
- If $E^\ominus_{\text{cell}} = 0$: At equilibrium

Example (HL): Calculate $E^\ominus_{\text{cell}}$ for $Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$
Given: $E^\ominus(Cu^{2+}/Cu) = +0.34$ V, $E^\ominus(Zn^{2+}/Zn) = -0.76$ V
Solution:

- More positive $E^\ominus$ = cathode: Cu^{2+}/Cu = +0.34 V
- More negative $E^\ominus$ = anode: Zn^{2+}/Zn = -0.76 V

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \\ &= (+0.34) - (-0.76) \\ &= +1.10\text{ V} \end{aligned}$$

Since $E^\ominus_{\text{cell}} > 0$, reaction is spontaneous.

1.10 AHL - Gibbs Energy and Electrochemistry

AHL Additional Content

Key Formula

Relationship Between $\Delta G^\ominus$ and $E^\ominus_{\text{cell}}$:

$$\Delta G^\ominus = -nFE^\ominus_{\text{cell}} \tag{3}$$

Where:

- n = moles of electrons transferred
- F = Faraday constant = 96,500 C mol^{-1}
- $E^\ominus_{\text{cell}}$ in volts (V)
- $\Delta G^\ominus$ in joules (J) [convert to kJ: divide by 1000]

Example (HL): Calculate $\Delta G^\ominus$ for the Zn/Cu cell ($E^\ominus_{\text{cell}} = +1.10$ V, $n = 2$).
Solution:

$$\begin{aligned}\Delta G^\ominus &= -nFE^\ominus_{\text{cell}}\\ &= -2 \times 96500 \times 1.10\\ &= -212300 \text{ J}\\ &= -212 \text{ kJ mol}^{-1}\end{aligned}$$

Negative $\Delta G^\ominus$ confirms spontaneous reaction.

1.11 AHL - Electrolysis of Aqueous Solutions

AHL Additional Content

Competing Reactions:
At cathode (reduction):

- Metal ion reduction: $\mathrm{M}^{n+} + \mathrm{ne}^- \longrightarrow \mathrm{M}$
- Water reduction: $2\,\mathrm{H_2O} + 2\,\mathrm{e}^- \longrightarrow \mathrm{H_2} + 2\,\mathrm{OH}^-$ ($E^\ominus = -0.83$ V)

At anode (oxidation):

- Halide oxidation: $2\,\mathrm{X}^- \longrightarrow \mathrm{X_2} + 2\,\mathrm{e}^-$
- Water oxidation: $2\,\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\,\mathrm{H}^+ + 4\,\mathrm{e}^-$ ($E^\ominus = +1.23$ V)

Prediction: Species with more positive $E^\ominus$ is preferentially reduced (cathode); species with more negative $E^\ominus$ is preferentially oxidized (anode)
Example - Electrolysis of $\mathrm{CuSO_4}$(aq):

- Cathode: $\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Cu}$ ($E^\ominus = +0.34$ V) preferred over water reduction
- Anode: $2\,\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\,\mathrm{H}^+ + 4\,\mathrm{e}^-$ ($\mathrm{SO_4^{2-}}$ cannot be oxidized)

1.12 AHL - Electroplating

AHL Additional Content

Electroplating Setup:

- Object to be plated = cathode (reduction deposits metal)
- Metal source = anode (oxidation supplies metal ions)
- Electrolyte contains metal ions

Example - Copper Plating:

- Cathode (object): $Cu^{2+} + 2\,e^- \longrightarrow Cu$ (metal deposited)
- Anode (Cu electrode): $Cu \longrightarrow Cu^{2+} + 2\,e^-$ (replenishes Cu^{2+})
- Electrolyte: $CuSO_4(aq)$

1.13 Topic Linkages

- **R1.4 (Gibbs Energy):** $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$ connects electrochemistry to thermodynamics (HL)
- **S3.1 (Periodic Trends):** Reactivity series follows ionization energy trends
- **R2.3 (Equilibrium):** Secondary cells involve reversible reactions

Key Points to Remember

Key Tips

- Activity series follows periodic trends:: Group 1 and 2 metals: Very reactive (lose electrons easily)
- Transformed Structure:: CH2OH -¿ -CHO -¿ -COOH, carbon oxidation state -1 -¿ +1 -¿ +3
- Sum of oxidation states = overall charge: Core principle for all calculations

2 Diagram Practice

Use these spaces to practice drawing essential diagrams for this topic.

▷ Draw: Oxidation state determination flowchart

▷ Draw: Half-equation balancing steps

▷ Draw: Oxidation and reduction memory aid (OIL RIG)

▷ Draw: Electron transfer in a redox reaction