Chapter 4. Balancing Oxidation Reduction Reactions

Simple Conventions to Assign Oxidation States:
1) The oxidation numbers of the atoms in a neutral molecule must add up to zero, and those in an ion must add up to the charge on the ion. All elements have oxidation states of zero (e.g. Na(s), O₂(g), H₂(g), Cl₂(g), etc.)
2) Alkali metal atoms (Group I) have oxidation number +1 in their compounds, and alkaline earth atoms (Group II) have oxidation number +2 in their compounds.
3) Fluorine always has an oxidation number of –1 in its compounds, and other halogens have an oxidation number –1 in their compounds except in compounds with oxygen and with other halogens, where they can have positive oxidation numbers. ClO₄⁻ → NaCl → SF₆ (Each fluorine in SF₆ is assigned an oxidation state of –1.)
4) Hydrogen is assigned an oxidation number of +1 in its compounds, except metal hydrides such as LiH where convention 2 takes precedence and hydrogen has an oxidation number –1.
5) Oxygen is assigned an oxidation number of –2 in compounds, except in compounds with fluorine where convention 3 takes precedence and in compounds that contain O–O bonds where convention 2 and 4 take precedence.

Balancing Redox Reactions Occurring in Acidic or Basic Solution by the Half-Reaction Method
1) Assign oxidation numbers to those species that change their oxidation states.
2) For each half-reaction, one for the species that is oxidized and one for the species that is reduced:
   a. Balance atoms of all the elements except hydrogen and oxygen.
   b. Include enough electrons to account for the total number of atoms for which the change in oxidation state occurs.
   c. Balance the charge by adding H⁺ (for acidic solution) or OH⁻ (for basic solution) to one side of each equation as required.
   d. Balance oxygen by adding H₂O to one side of each half-reaction.
3) If needed, multiply one or both balanced half-reactions by integers to make the number of electrons lost in the oxidation reaction equal to the number of electrons gained in the reduction reaction.
4) Add the half-reactions, canceling the electrons. If H⁺, OH⁻, or H₂O appear on both sides of the final equation, cancel out the duplications.

Example: Balance the reaction for the dissolution of copper(II)sulfide in aqueous nitric acid:
CuS(s) + NO₃⁻(aq) → Cu²⁺(aq) + SO₄²⁻(aq) + NO(g)

Step 1: CuS + NO₃⁻ → Cu²⁺ + SO₄²⁻ + NO
   Sulfur: +2 → +6 + 8 e⁻\[Sulfur lost 8 electrons \Rightarrow sulfur is oxidized in the reaction.\]
   CuS(s) is the substance oxidized \Rightarrow CuS(s) is the reducing agent.
   Nitrogen: +5 + 3 e⁻ → +2 \[Nitrogen gained 3 electrons \Rightarrow nitrogen is reduced in the reaction.\]
   NO₃⁻ is the oxidizing agent.

Step 2: Oxidation half-reaction: CuS → Cu²⁺ + SO₄²⁻ + 8 e⁻
   Reduction half-reaction: NO₃⁻ + 3 e⁻ → NO

Step 3: Balance electrons gained and lost by multiplying half-reactions by appropriate integers.
   \[8 \times 3 = 24 \text{ electrons lost} \quad \text{balances} \quad 3 \times 8 = 24 \text{ electrons gained} \]
   \[12 \text{H}_2\text{O} + 3 \text{CuS} \rightarrow 3 \text{Cu}^{2+} + 3 \text{SO}_4^{2-} + 24 \text{e}^- + 24 \text{H}^+ \]
   \[32 \text{H}^+ + 8 \text{NO}_3^- + 24 \text{e}^- \rightarrow 8 \text{NO} + 16 \text{H}_2\text{O} \]

Step 4: 3 CuS + 8 H⁺ + 8 NO₃⁻ → 3 Cu²⁺ + 3 SO₄²⁻ + 8 NO + 4 H₂O

Note: The procedure is exactly the same for balancing an oxidation-reduction reaction in basic solution except for step 2c where the charge is balanced by adding OH⁻ instead of H⁺.