Chapter 5: Introduction to Reactions in Aqueous Solutions

5-4 Oxidation-Reduction: Some General Principles

- Hematite is converted to iron in a blast furnace.

$$Fe_2O_3(s) + 3\ CO(g) \xrightarrow{\Delta} 2\ Fe(l) + 3\ CO_2(g)$$

- Oxidation and reduction always occur together.

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

$CO(g)$ is oxidized to carbon dioxide.

Oxidation State Changes

- Oxidation state is related to the number of electrons that an atom loses, gains, or otherwise appears to use in joining with other atoms in compounds.

- Assign oxidation states:

$$\overset{3+}{Fe_2}\overset{2-}{O_3}(s) + 3\,\overset{2+}{C}\overset{2-}{O}(g) \xrightarrow{\Delta} 2\,\overset{0}{Fe}(l) + 3\,\overset{4+}{C}\overset{2-}{O_2}(g)$$

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

CO(g) is oxidized to carbon dioxide.

- In an oxidation process, the O.S. of some element increases; in a reduction process, the O.S. of some element decreases.

Rules for Oxidation States

1. *The oxidation state (O.S.) of an individual atom in a free element (uncombined with other elements) is 0.*

   [*Examples:* The O.S. of an isolated Cl atom is 0; the two Cl atoms in the molecule Cl_2 both have an O.S. of 0.]

2. *The total of the O.S. of all the atoms in*

   (a) *neutral species, such as isolated atoms, molecules, and formula units, is 0;*

   [*Examples:* The sum of the O.S. of all the atoms in CH_3OH and of all the ions in $MgCl_2$ is 0.]

   (b) *an ion is equal to the charge on the ion.*

   [*Examples:* The O.S. of Fe in Fe^{3+} is +3. The sum of the O.S. of all atoms in MnO_4^- is −1.]

3. *In their compounds, the group 1 metals have an O.S. of +1 and the group 2 metals have an O.S. of +2.*

   [*Examples:* The O.S. of K is +1 in KCl and K_2CO_3; the O.S. of Mg is +2 in $MgBr_2$ and $Mg(NO_3)_2$.]

Rules for Oxidation States

4. *In its compounds, the O.S. of fuorine is −1.*

[*Examples:* The O.S. of F is −1 in HF, ClF_3, and SF_6.]

5. *In its compounds, hydrogen usually has an O.S. of +1.*

[*Examples:* The O.S. of H is +1 in HI, H_2S, NH_3, and CH_4.]

6. *In its compounds, oxygen usually has an O.S. of −2.*

[*Examples:* The O.S. of O is −2 in H_2O, CO_2 and $KMnO_4$.]

7. *In binary (two-element) compounds with metals, group 17 elements have an O.S. of −1; group 16 elements, −2; and group 15 elements, −3.*

[*Examples:* The O.S. of Br is −1 in $MgBr_2$; the O.S. of S is −2 in Li_2S; and the O.S. of N is −3 in Li_3N.]

EXAMPLE

Assigning Oxidation States What is the oxidation state of the underlined element in each of the following? a) P_4; b) Al_2O_3; c) MnO_4^-; d) NaH.

a) P_4 is an element. P OS = 0

b) Al_2O_3: O is –2. O_3 is –6. Since (+6)/2=(+3), Al OS = +3.

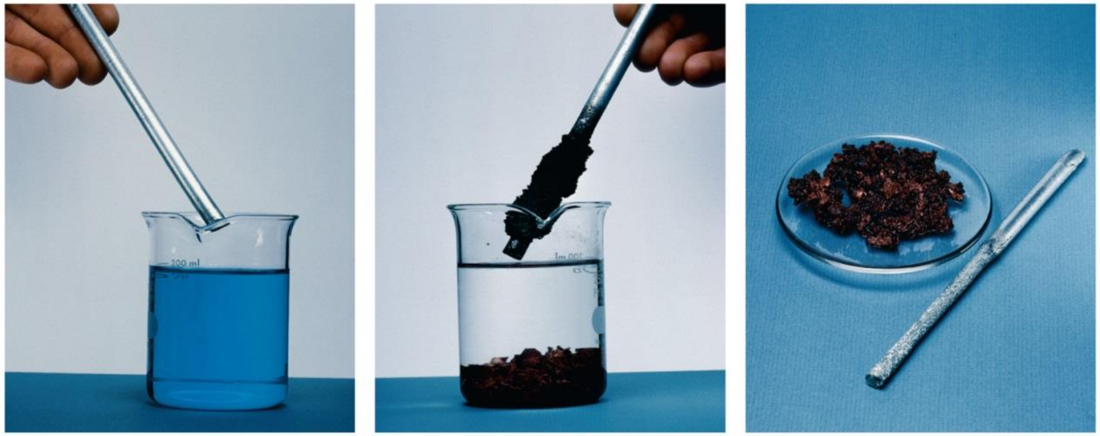
c) MnO_4^-: net OS = -1, O_4 is –8. Mn OS = +7.

d) NaH: net OS = 0, rule 3 beats rule 5, Na OS = +1 and H OS = -1.

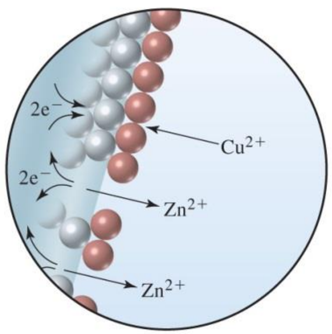
Oxidation and Reduction

- 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.

An Oxidation Reduction Reaction



(a) (b) (c)



$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Oxidation and Reduction Half-Reactions

- A reaction represented by two half-reactions.

Oxidation:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$
Reduction:	$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$
Overall:	$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

- **Oxidation** is a process in which the O.S. of some element *increases* as electrons are lost. Electrons appear on the *right* side of a half-equation.
- **Reduction** is a process in which the O.S. of some element *decreases* as electrons are gained. Electrons appear on the *left* side of a half-equation.

Balancing Oxidation-Reduction Equations

In balancing the chemical equation for a redox reaction, we focus equally on three factors:

(1) the number of atoms of each type,

(2) the number of electrons transferred,

(3) the total charges on reactants and products.

Balancing in Acid

- Write the equations for the half-reactions.
  - Balance all atoms except H and O.
  - Balance oxygen using H_2O.
  - Balance hydrogen using H^+.
  - Balance charge using e^-.
- Equalize the number of electrons.
- Add the half reactions.
- Check the balance.

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.

$$SO_3^{2-}(aq) + MnO_4^{-}(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)$$

EXAMPLE 5-6

Determine the oxidation states:

$$\overset{4+}{SO_3^{2-}}(aq) + \overset{7+}{MnO_4^{-}}(aq) \rightarrow \overset{6+}{SO_4^{2-}}(aq) + \overset{2+}{Mn^{2+}}(aq)$$

Write the half-reactions:

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

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

Balance atoms other than H and O:

Already balanced for elements.

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^-:

$$\cancel{5\ H_2O(l)} + 5\ SO_3^{2-}(aq) \rightarrow 5\ SO_4^{2-}(aq) + \cancel{10\ e^-(aq)} + \cancel{10\ H^+(aq)}$$

$$\overset{}{\underset{6}{\cancel{1}6}}\ H^+(aq) + \cancel{10\ e^-(aq)} + 2\ MnO_4^-(aq) \rightarrow 2\ Mn^{2+}(aq) + \underset{3}{\cancel{8}}\ H_2O(l)$$

Add both equations and simplify:

$$5\ SO_3^{2-}(aq) + 2\ MnO_4^-(aq) + 6H^+(aq) \rightarrow$$

$$5\ SO_4^{2-}(aq) + 2\ Mn^{2+}(aq) + 3\ H_2O(l)$$

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_2O appearing on both sides of equation.
- Check the balance.

Disproportionation Reactions

- The same substance is both oxidized and reduced.
- Some have practical significance
  - Hydrogen peroxide

$$2\ H_2O_2(aq) \rightarrow H_2O(l) + O_2(g)$$

  - Sodium thiosulphate

$$2\ S_2O_3(aq) + H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$

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.

Oxidation States of Nitrogen

Compound or ion	Oxidation state
NO_3^-	+5
N_2O_4	+4
NO_2^-	+3
NO	+2
N_2O	+1
N_2	0
NH_2OH	−1
N_2H_4	−2
NH_3	−3

This species cannot be oxidized further (NO_3^-)

This species cannot be reduced further (NH_3)