Chapter 10

Redox reactions in aqueous solutions

Oxidation-Reduction Reactions

- The class of reactions called oxidation-reduction, or redox, reactions are considered electron transfer reactions.
- Consider the formation of magnesium oxide (MgO) from magnesium and oxygen.

$$2\mathrm{Mg}(s) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{MgO}(s)$$

- In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in O2). Each of these steps is called a half-reaction.

$$2\mathrm{Mg} \longrightarrow 2\mathrm{Mg}^{2+} + 4e^-$$

$$\mathrm{O_2} + 4e^- \longrightarrow 2\mathrm{O}^{2-}$$

- The sum of the half-reactions gives the overall reaction:

$$2\mathrm{Mg} + \mathrm{O_2} + 4e^- \longrightarrow 2\mathrm{Mg}^{2+} + 2\mathrm{O}^{2-} + 4e^-$$

$$2\mathrm{Mg}(s) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{MgO}(s)$$

Oxidation-Reduction Reactions

- An **oxidation reaction** is a half-reaction that involves loss of electrons. In the formation of magnesium oxide, magnesium is oxidized. It is said to act as a **reducing agent or reductant** because it donates electrons to oxygen and causes oxygen to be reduced.

$$2Mg \longrightarrow 2Mg^{2+} + 4e^-$$

- A **reduction reaction** is a half-reaction that involves gain of electrons. Oxygen is reduced and acts as an **oxidizing agent or oxidant** because it accepts electrons from magnesium, causing magnesium to be oxidized.

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

Oxidation Number

- **An atom's oxidation number, also called oxidation state**, signifies the number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely.
- **We use the following rules to assign oxidation numbers:**

1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H_2, Br_2, Na, Be, K, O_2, and P_4 has the same oxidation number: zero.

2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li^{+1} ion has an oxidation number of +1; Ba^{+2}ion, +2; Fe^{+3} ion, +3; I^{-} ion, -1; O^{-2} ion, -2; and so on.

3- All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.

4. The oxidation number of oxygen in most compounds (for example, MgO and H_2O) is -2, but in peroxide ion (O_2^{-2}) as in H_2O_2 it is -1.

5- The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH, NaH, CaH_2), its oxidation number is -1.

6. Fluorine has an oxidation number of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds (as HCl). When combined with O as (ClO_4^-) they have positive oxidation numbers.

7- In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. **In a polyatomic ion**, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.

8- Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O_2^-, is -1/2 (as in KO_2).

Give the oxidation numbers of the underlined atoms in the following molecules and ions: (a) $Mg_3\underline{N}_2$, (b) $Cs\underline{O}_2$, (c) $Ca\underline{C}_2$, (d) $\underline{C}O_3^{2-}$, (e) $\underline{C}_2O_4^{2-}$, (f) $Zn\underline{O}_2^{2-}$, (g) $Na\underline{B}H_4$, (h) $\underline{W}O_4^{2-}$.

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Balancing Redox Equations

- **There are two methods for balancing redox reactions:**

1- Oxidation number method.

2- Half reaction method.

- **We consider the balancing of equations for redox reactions that occur in two situations:**

1- When the redox equation written as molecular equation.

2- When the redox equation written as a net ionic equation.

Oxidation number method for molecular equation

- **Step 1**: assign oxidation numbers for all atoms.
- **Step 2:** note which atom appear to lose and which atom appear to gain electrons and determine how many electrons are lost or gained for each atom.
- **Step 3:** determine the total loss or gain of electrons per formula unit.
- **Step 4:** make the total gain of electrons equals the total loss of electrons by multiplying a coefficient on the left side of equation.
- **Step 5:** Balance the atoms that gain or lose electrons then balance other atoms except O and H. Then, balance O atoms then hydrogen atoms.

Balance the following equation:

$$H_2C_2O_4 + KMnO_4 \rightarrow CO_2 + MnO + K_2O + H_2O$$

Solution

Step 1:

$$\begin{array}{ccccccccccccccccc}
+2 & +6 & -8 & & +1 & +7 & -8 & & +4 & -4 & & +2 & -2 & & & & \\
H_2 & C_2 & O_4 & + & K & Mn & O_4 & \rightarrow & C & O_2 & + & Mn & O & + & K_2O & + & H_2O \\
+1 & +3 & -2 & & +1 & +7 & -2 & & +4 & -2 & & +2 & -2 & & +1\ -2 & & +1\ -2
\end{array}$$

Step 2:

$$\begin{array}{ccccccccccc}
H_2C_2O_4 & + & KMnO_4 & \rightarrow & CO_2 & + & MnO & + & K_2O & + & H_2O \\
+3 & & +7 & & +4 & & +2 & & & &
\end{array}$$

Reduction:

Each Mn gains $5e^-$

Oxidation:

Each C loses $1e^-$

Step 3:

$$\begin{array}{ccccccccccc}
H_2C_2O_4 & + & KMnO_4 & \rightarrow & CO_2 & + & MnO & + & K_2O & + & H_2O \\
+3 & & +7 & & +4 & & +2 & & & &
\end{array}$$

Each $KMnO_4$ gains $5e^-$

Each $H_2C_2O_4$ loses 2×1, or $2e^-$

Step 3:

$$\underset{+3}{H_2C_2O_4} + \underset{+7}{KMnO_4} \rightarrow \underset{+4}{CO_2} + \underset{+2}{MnO} + K_2O + H_2O$$

Each $KMnO_4$ gains $5e^-$

Each $H_2C_2O_4$ loses 2×1, or $2e^-$

Step 4:

$$5H_2C_2O_4 + 2KMnO_4 \rightarrow CO_2 + MnO + K_2O + H_2O$$

Step 5:

$$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO + K_2O + 5H_2O$$

Oxidation number method for net ionic equation

- **Steps 1-4: as former**
- **Step 5 :** Balance the atoms that gain or lose electrons.
- **Step 6:** Balance other atoms except O and H.
- **Step 7: Balance the charges:**
  - A- If the reaction takes place in **acidic** medium, balance the hydrogen atoms by add H^+ in the site deficient in positive charge.
  - B- If the reaction takes place in **basic** medium, balance the charge by adding OH^- in the site deficient in negative charge.
  - **Step 8:** add water molecules to balance oxygen atoms. So, if your balance is correct, hydrogen atom would be already balanced.

Oxidation number method for net ionic equation in acidic medium

Complete and balance the following equation for a reaction which takes in acidic solution:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+} \qquad \text{(acidic solution)}$$

Solution

Step 1:

$$\underset{+6}{\overset{+12}{Cr_2}}\,\underset{-2}{\overset{-14}{O_7}}{}^{2-} + \underset{+2}{Fe^{2+}} \rightarrow \underset{+3}{Cr^{3+}} + \underset{+3}{Fe^{3+}}$$

Step 2:

$$\underset{+6}{Cr_2}O_7^{2-} \quad + \quad \underset{+2}{Fe^{2+}} \quad \rightarrow \quad \underset{+3}{Cr^{3+}} \quad + \quad \underset{+3}{Fe^{3+}}$$

Oxidation: Loss of $1e^-$ per Fe^{2+} ion

Reduction: Gain of $3e^-$ per Cr atom

Step 3:

$$\underset{+6}{Cr_2O_7^{2-}} + \underset{+2}{Fe^{2+}} \longrightarrow \underset{+3}{Cr^{3+}} + \underset{+3}{Fe^{3+}}$$

Loss of 1e⁻ per Fe^{2+} ion

Total Gain of 2 × 3,
or 6e^- per $Cr_2O_7^{2-}$ ion

Step 4:

$$Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$$

Step 5:

$$Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+}$$

Step 6: Done!

Step 7:

Total charge on left $= -2 + 6(+2) = +10$

Total charge on right $= 2(+3) + 6(+3) = +24$

Additional (positive) charge needed *on left* $= +14$

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+}$$

Step 8:

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Oxidation number method for net ionic equation in basic medium

Complete and balance the following equation for a reaction in basic solution:

+6 8- 2+ -2 +3 -4 +3 3-

$$CrO_4^{2-} + Fe(OH)_2 \rightarrow CrO_2^- + Fe(OH)_3 \qquad \text{(basic solution)}$$

Solution

Step 1:

$$\underset{+6\,-2}{CrO_4^{2-}} + \underset{+2\,-2\,+1}{Fe(OH)_2} \rightarrow \underset{+3\,-2}{CrO_2^-} + \underset{+3\,-2\,+1}{Fe(OH)_3}$$

Step 2:

$$\underset{+6}{CrO_4^{2-}} + \underset{+2}{Fe(OH)_2} \rightarrow \underset{+3}{CrO_2^-} + \underset{+3}{Fe(OH)_3}$$

Oxidation: Loss of $1e^-$ per Fe atom

Reduction: Gain of $3e^-$ per Cr atom

Step 3:

$$\underset{+6}{CrO_4^{2-}} + \underset{+2}{Fe(OH)_2} \rightarrow \underset{+3}{CrO_2^{-}} + \underset{+3}{Fe(OH)_3}$$

Loss of 1e per $Fe(OH)_2$ formula unit

Gain of $3e^-$ per CrO_4^{2-} ion

Step 4:

$$CrO_4^{2-} + 3Fe(OH)_2 \rightarrow CrO_2^{-} + Fe(OH)_3$$

Step 5:

$$CrO_4^{2-} + 3Fe(OH)_2 \rightarrow CrO_2^{-} + 3Fe(OH)_3$$

Step 6: Done!

Step 7:

Total charge on left $= -2 + 3(0) = -2$

Total charge on right $= -1 + 3(0) = -1$

Additional (negative) charge needed *on right* $= -1$

$$CrO_4^{2-} + 3Fe(OH)_2 \rightarrow CrO_2^{-} + 3Fe(OH)_3 + OH^-$$

Step 8:

$$2H_2O + CrO_4^{2-} + 3Fe(OH)_2 \rightarrow CrO_2^{-} + 3Fe(OH)_3 + OH^-$$