Oxidation-Reduction Reactions

Academic Resource Center

Introduction

- Oxidation-reduction reactions are also known as redox reactions
- Def: Redox reactions describe all chemical reactions in which there is a net change in atomic charge
- It is a class of reactions that include:
  - formation of a compound from its elements
  - all combustion reactions
  - reactions that generate electricity
  - reactions that produce cellular energy

Terminology

- The key idea is the net movement of electrons from one reactant to the other
- *Oxidation* is the loss of electrons
- *Reduction* is the gain of electrons
- *Oxidizing agent* is the species doing the oxidizing
- *Reducing agent* is the species doing the reducing

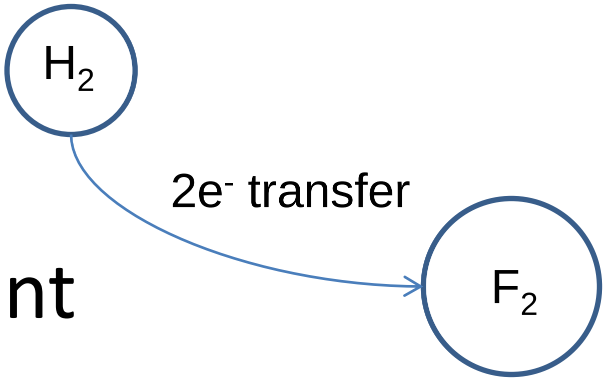
Redox Illustration

- $H_2 + F_2 \longrightarrow 2HF$
- Oxidation (electron loss by H_2)
  - $H_2 \longrightarrow 2H^+ + 2e^-$
- Reduction (electron gain by F_2)
  - $F_2 + 2e^- \longrightarrow 2F^-$

H_2

- Oxidized

- Reducing agent



H_2

$2e^-$ transfer

F_2

F_2

- Reduced

- Oxidizing agent

Oxidation Number

- Oxidation number (O.N.) is also known as oxidation state
- It is defined as the charge the atom would have if electrons were not shared but were transferred completely
- For a binary ionic compound, the O.N. is equivalent to the ionic charge
- For covalent compounds or polyatomic ions, the O.N. is less obvious and can be determined by a given set of rules

Rules for Assigning an Oxidation Number

General Rules

1. For an atom in its elemental form (Na, O_2): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals to zero. (equals to the ion's charge if it is a polyatomic ion)

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1): O.N. = +1 in all compounds
2. For Group 2A(2): O.N. = +2 in all compounds
3. For hydrogen: O.N. = +1 in combination with nonmetals
   O.N. = -1 in combination with metals and boron
4. For fluorine: O.N. = -1 in all compounds
5. For oxygen: O.N. = -1 in peroxides
   O.N. = -2 in all other compounds (except with F)
6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Example 1

- Determine the oxidation number (O.N.) of each element in these compounds:
  a) CaO (s)
  b) KNO_3 (s)
  c) $NaHSO_4$ (aq)
  d) $CaCO_3$ (s)
  e) N_2 (g)
  f) H_2O (l)

Solution to Example 1

Simply apply the rules for assigning an oxidation number as described earlier

a) $\overset{+2}{Ca}\overset{-2}{O}$ (s)

b) $\overset{+1}{K}\overset{+5}{N}\overset{-2}{O}_3$ (s)

$N = 0-(+1)-3(-2) = +5$

c) $\overset{+1}{Na}\overset{+1}{H}\overset{+6}{S}\overset{-2}{O}_4$ (aq)

$S = 0-(+1)-(+1)-4(-2) = +5$

d) $\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O}_3$ (s)

$C = 0-(+2)-3(-2) = +4$

e) $\overset{0}{N}_2$ (g)

f) $\overset{+1}{H}_2\overset{-2}{O}$ (l)

Example 2

- Identify the oxidizing agent and reducing agent in each of the following:

a) $2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$

b) $Cu\ (s) + 4HNO_3\ (aq) \longrightarrow Cu(NO_3)_2\ (aq) + 2NO_2\ (g) + 2H_2O\ (l)$

Solution to Example 2

Assign oxidation numbers and compare.

Oxidation is represented by an increase in oxidation number

Reduction is represented by a decrease in oxidation number

a) $$2\overset{0}{H}_2\ (g) + \overset{0}{O}_2\ (g) \longrightarrow 2\overset{+1}{H}_2\overset{-2}{O}\ (g)$$

- O_2 was reduced (O.N. of O: 0 -> -2); O_2 is the oxidizing agent
- H_2 was oxidized (O.N. of H: 0 -> +1); H_2 is the reducing agent

b) $$\overset{0}{Cu} + 4\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3 \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O}_3)_2 + 2\overset{+4}{N}\overset{-2}{O}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$$

- Cu was oxidized (O.N. of Cu: 0 -> +2); Cu is the reducing agent
- HNO_3 was reduced (O.N. of N: +5 -> +4); HNO_3 is the oxidizing agent

Balancing Redox Equations

- When balancing redox reactions, make sure that the number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent

- Two methods can be used:
  1. Oxidation number method
  2. Half-reaction method

Balancing Redox Equations

Method 1: Oxidation number method

1. Assign oxidation numbers to all elements in the reaction
2. From the changes in O.N., identify the oxidized and reduced species
3. Compute the number of electrons lost in the oxidation and gained in the reduction from the O.N. changes
4. Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients
5. Complete the balancing by inspection, adding states of matter

Example 3

- Use the oxidation number method to balance the following equations:

a) $Al(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + H_2(g)$

b) $PbS(s) + O_2(g) \longrightarrow PbO(s) + SO_2(g)$

Part a: Solution to Example 3

- Step 1. Assign oxidation numbers to all elements

$$\overset{0}{\mathrm{Al}}(s) + \overset{+1}{\mathrm{H}_2}\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}_4}(aq) \longrightarrow \overset{+3}{\mathrm{Al}_2}(\overset{+6}{\mathrm{S}}\overset{-2}{\mathrm{O}_4})_3(aq) + \overset{0}{\mathrm{H}_2}(g)$$

- Step 2. Identify oxidized and reduced species
  - Al was oxidized (O.N. of Al: 0 -> +3)
  - H_2SO_4 was reduced (O.N. of H: +1 -> 0)
- Step 3. Compute e^- lost and e^- gained
  - In the oxidation: $3e^-$ were lost from Al
  - In the reduction: $1e^-$ was gained by H

Part a: Solution to Example 3

- Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients
  - Al lost $3e^-$, so the $1e^-$ gained by H should be multiplied by 3. Put the coefficient 3 before H_2SO_4 and H_2.

$$Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

- Step 5. Complete the balancing by inspection

$$2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

Part b: Solution to Example 3

- Step 1. Assign oxidation numbers to all elements

$$\overset{+2}{\text{Pb}}\overset{-2}{\text{S}}(s) + \overset{0}{\text{O}}_2(g) \longrightarrow \overset{+2}{\text{Pb}}\overset{-2}{\text{O}}(s) + \overset{+4}{\text{S}}\overset{-2}{\text{O}}_2(g)$$

- Step 2. Identify oxidized and reduced species
  - PbS was oxidized (O.N. of S: -2 -> +4)
  - O_2 was reduced (O.N. of O: 0 -> -2)
- Step 3. Compute e^- lost and e^- gained
  - In the oxidation: $6e^-$ were lost from S
  - In the reduction: $2e^-$ were gained by each O

Part b: Solution to Example 3

- Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients
  - S lost $6e^-$, O gained $4e^-$ ($2e^-$ each O). Thus, put the coefficient 3/2 before O_2.

$$PbS(s) + 3/2O_2(g) \longrightarrow PbO(s) + SO_2(g)$$

- Step 5. Complete the balancing by inspection

$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

Balancing Redox Equations

Method 2: Half-reaction method

1. Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species
2. Balance the atoms and charges in each half-reaction
   - Atoms are balanced in order: atoms other than O and H, then O, then H
   - Charge is balanced by adding electrons
     - To the left in reduction half-reactions
     - To the right in oxidation half-reactions
3. If necessary, multiply one or both half-reactions by an integer to make the number of e^- gained equal to the number of e^- lost
4. Add the balanced half-reactions, and include states of matter
5. Check that the atoms and charges are balanced

Example 4

- Use the half-reaction method to balance the following equations:

a) $ClO_3^-(aq) + I^-(aq) \longrightarrow I_2(s) + Cl^-(aq)$ [acidic]

b) $Fe(OH)_2(s) + Pb(OH)_3^-(aq) \longrightarrow Fe(OH)_3(s) + Pb(s)$ [basic]

Part a: Solution to Example 4

- Step 1. Divide the reaction into half-reactions

$ClO_3^-(aq) \longrightarrow Cl^-(aq)$ $I^-(aq) \longrightarrow I_2(s)$

- Step 2. Balance atoms and charges in each half-reaction
  - Atoms other than O and H

$ClO_3^-(aq) \text{ -> } Cl^-(aq)$	Cl is balanced
$2I^-(aq) \text{ -> } I_2(s)$	I now balanced

  - Balance O atoms by adding H_2O molecules

$ClO_3^-(aq) \text{ -> } Cl^-(aq) + 3H_2O(l)$	Add $3H_2O$
$2I^-(aq) \text{ -> } I_2(s)$	No change

Part a: Solution to Example 4

- Balance H atoms by adding H^+ ions

$ClO_3^-(aq) + 6H^+ \text{->} Cl^-(aq) + 3H_2O(l)$	Add $6H^+$
$2I^-(aq) \text{->} I_2(s)$	No change

- Balance charge by adding electrons

$ClO_3^-(aq) + 6H^+ + 6e^- \text{->} Cl^-(aq) + 3H_2O(l)$	Add $6e^-$
$2I^-(aq) \text{->} I_2(s) + 2e^-$	Add $2e^-$

- Step 3. Multiply each half-reaction by an integer to equalize number of electrons

$ClO_3^-(aq) + 6H^+ + 6e^- \text{->} Cl^-(aq) + 3H_2O(l)$	x 1
$3[2I^-(aq) \text{->} I_2(s) + 2e^-]$	x 3

Part a: Solution to Example 4

- Step 4. Add the half-reactions together

$ClO_3^-(aq) + 6H^+ + 6e^- \text{->} Cl^-(aq) + 3H_2O(l)$

$6I^-(aq) \text{->} 3I_2(s) + 6e^-$

$ClO_3^-(aq) + 6H^+(aq) + 6I^-(aq) \longrightarrow Cl^-(aq) + 3H_2O(l) + 3I_2(s)$

- Step 5. Check that atoms and charges balance
  - Reactants (Cl, 3O, 6H, 6I, -1) -> products (Cl, 3O, 6H, 6I, -1)

- ClO_3^- is the oxidizing agent
- I^- is the reducing agent

Part b: Solution to Example 4

- The only difference in balancing a redox equation that takes place in basic solution is in Step 4.
- At this point, we add one OH^- ion to both sides of the equation for every H^+ ion present
- The H^+ ions on one side are combined with the added OH^- ions to form H_2O, and OH^- ions appear on the other side of the equation

Part b: Solution to Example 4

- Step 1. Divide the reaction into half-reactions

  $Pb(OH)_3^-(aq) \rightarrow Pb(s)$ $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$

- Step 2. Balance atoms and charges in each half-reaction
  - Atoms other than O and H

    $Pb(OH)_3^-(aq) \rightarrow Pb(s)$ Pb is balanced

    $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$ Fe is balanced

  - Balance O atoms by adding H_2O molecules

    $Pb(OH)_3^-(aq) \rightarrow Pb(s) + 3H_2O$ Add $3H_2O$

    $Fe(OH)_2(s) + H_2O \rightarrow Fe(OH)_3(s)$ Add H_2O

Part b: Solution to Example 4

- Balance H atoms by adding H^+ ions

  $Pb(OH)_3^-(aq) + 3H^+ \text{->} Pb(s) + 3H_2O$ Add $3H^+$

  $Fe(OH)_2(s) + H_2O \text{->} Fe(OH)_3(s) + H^+$ Add H^+

- Balance charge by adding electrons

  $Pb(OH)_3^-(aq) + 3H^+ + 2e^- \text{->} Pb(s) + 3H_2O$ Add $2e^-$

  $Fe(OH)_2(s) + H_2O \text{->} Fe(OH)_3(s) + H^+ + e^-$ Add e^-

- Step 3. Multiply each half-reaction by an integer to equalize number of electrons

  $Pb(OH)_3^-(aq) + 3H^+ + 2e^- \text{->} Pb(s) + 3H_2O$ x 1

  $2[Fe(OH)_2(s) + H_2O \text{->} Fe(OH)_3(s) + H^+ + e^-]$ x 2

Part b: Solution to Example 4

- Step 4. Add the half-reactions together

$$Pb(OH)_3^-(aq) + 3H^+ + 2e^- \text{->} Pb(s) + 3H_2O$$

$$2Fe(OH)_2(s) + 2H_2O \text{->} 2Fe(OH)_3(s) + 2H^+ + 2e$$

$$Pb(OH)_3^-(aq) + H^+(aq) + 2Fe(OH)_2(s) \longrightarrow Pb(s) + H_2O(l) + 2Fe(OH)_3(s)$$

- Step 4(basic). Add OH^-
  - Here, we add 1 OH^-

$Pb(OH)_3^-(aq) + H^+(aq) + OH^- + 2Fe(OH)_2(s) \text{->} Pb(s) + H_2O(l) + 2Fe(OH)_3(s) + OH^-$

$$Pb(OH)_3^-(aq) + 2Fe(OH)_2(s) \longrightarrow Pb(s) + 2Fe(OH)_3(s) + OH^-(aq)$$

- Step 5. Check
  - Reactants (Pb, 7O, 7H, 2Fe, -1) -> products (Pb, 7O, 7H, 2Fe, -1)
- $Pb(OH)_3^-$ is the oxidizing agent
- $Fe(OH)_2$ is the reducing agent

Practice Problem

1. Identify the oxidizing and reducing agents in the following:

a) $8H^+(aq) + 6Cl^-(aq) + Sn(s) + 4NO_3^-(aq) \longrightarrow SnCl_6^{2-}(aq) + 4NO_2(g) + 4H_2O(l)$

b) $2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \longrightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Practice Problem

2. Use the oxidation number method to balance the following equations and then identify the oxidizing and reducing agents:

a) $HNO_3(aq) + C_2H_6O(l) + K_2Cr_2O_7(aq) \longrightarrow KNO_3(aq) + C_2H_4O(l) + H_2O(l) + Cr(NO_3)_3(aq)$

b) $KClO_3(aq) + HBr(aq) \longrightarrow Br_2(l) + H_2O(l) + KCl(aq)$

Practice Problem

3. Use the half-reaction method to balance the following equations and then identify the oxidizing and reducing agents:

   a) $Mn^{2+}(aq) + BiO_3^{-}(aq) \longrightarrow MnO_4^{-}(aq) + Bi^{3+}(aq)$ [acidic]

   b) $Fe(CN)_6^{3-}(aq) + Re(s) \longrightarrow Fe(CN)_6^{4-}(aq) + ReO_4^{-}(aq)$ [basic]

References

- Silberberg, Martin. Chemistry The Molecular Nature of Matter and Change. New York: McGraw-Hill Science/Engineering/Math, 2008.