Chemistry 2000 Slide Set 14: Redox reactions

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Review: Oxidation states

The oxidation state of an atom in a molecule is a charge calculated assuming that bonds are purely ionic.

Calculation of oxidation states:

1. The sum of the oxidation states in a molecule is equal to the charge.
2. In a bond between two identical atoms, the electrons are equally shared.
3. In any other bond, we "give" all the shared electrons to the more electronegative atom.
4. $$\left\{\begin{matrix}\text{oxidation}\\ \text{state}\end{matrix}\right\} = \left\{\begin{matrix}\text{valence electrons}\\ \text{of neutral atom}\end{matrix}\right\} - \left\{\begin{matrix}\text{electrons in}\\ \text{ionized structure}\end{matrix}\right\}$$

Example: Determine the oxidation states of all atoms in the sulfate ion.

Answer: Oxidation state of S $= 6$

Oxidation state of O $= -2$

Redox reactions

Reduction is a gain of electrons by an atom or set of atoms during a chemical reaction.

Oxidation is a loss of electrons by an atom or set of atoms.

A redox (reduction-oxidation) reaction involves oxidation of some atoms and reduction of others.

- During a redox reaction, the oxidation states of some atoms increase, while the oxidation states of others decrease.

Redox reactions

Oxidizing and reducing agents

- If the oxidation state of an atom has increased, it has lost electrons and therefore been oxidized.
  A species containing an atom that has been oxidized has caused something else to be reduced and so is a
  reducing agent.
- If the oxidation state of an atom has decreased, it has gained electrons and therefore been reduced.
  A species containing an atom that has been reduced has caused something else to be oxidized and so is an
  oxidizing agent.

Is the following a redox reaction?

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Oxidation states of reactants:

C in CH_4	H in CH_4	O in O_2
-4	$+1$	0

Oxidation states of products:

C in CO_2	O in CO_2	H in H_2O	O in H_2O
$+4$	-2	$+1$	-2

O has been reduced.

C has been oxidized.

Conclusion: Yes, this is a redox reaction.

Is the following a redox reaction?

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Oxidation states of reactants:

C in CO_2	O in CO_2	H in H_2O	O in H_2O
$+4$	-2	$+1$	-2

Oxidation states of atoms in product H_2CO_3:

H	C	O
$+1$	$+4$	-2

Conclusion: No change in oxidation states, therefore not a redox reaction.

Half-reactions

- A redox reaction can generally be separated into reduction and oxidation half-reactions.

Example: For the reaction

$$\mathrm{Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}}$$

the half-reactions are

$$\text{Reduction:} \quad \mathrm{Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}}$$

$$\text{Oxidation:} \quad \mathrm{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}$$

Balancing aqueous redox reactions

1. Separate the half-reactions and balance them for all atoms except O and H.
2. Balance each half-reaction for O by adding $H_2O_{(l)}$.
3. Balance each half-reaction for H by adding $H^+_{(aq)}$.
4. Balance each half-reaction for charge by adding electrons.
5. Multiply the half-reactions so that each has the same number of electrons, then add them together.
   The reaction is balanced for acidic conditions.
6. If the reaction occurs in neutral medium, it is OK to have H^+ as a product, but not as a reactant. If the reaction occurs in basic medium, there shouldn't be any H^+ in the overall reaction. In either of these cases, add OH^- to "neutralize" excess H^+.

Example

When $Na_2Cr_2O_7$ reacts with KBr in acidic medium, the products are Br_2 and Cr^{3+}. Balance the reaction.

Answer:

$$Cr_2O^{2-}_{7(aq)} + 14H^{+}_{(aq)} + 6Br^{-}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3Br_{2(aq)}$$

Example: Reaction in neutral medium

- If the reaction of the last example had occurred in a neutral (or basic) environment, there would not have been many protons available, so they could not have appeared as reactants.
- To fix this, add equal numbers of hydroxides to both sides to neutralize the protons.
- Reaction balanced in neutral (or basic) medium:

$$Cr_2O^{2-}_{7(aq)} + 7H_2O_{(l)} + 6Br^-_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Br_{2(aq)} + 14OH^-_{(aq)}$$

Example: Fuel cells

- In a fuel cell, a fuel is oxidized in a controlled manner to produce electricity.
- Common fuel cells use a basic electrolyte.
- Find the half-reactions for the methane fuel cell.

Answer:

$$\begin{aligned} \mathrm{CH_{4(g)}} + 8\mathrm{OH^-_{(aq)}} &\rightarrow \mathrm{CO_{2(g)}} + 6\mathrm{H_2O_{(l)}} + 8\mathrm{e^-} \\ 2\mathrm{O_{2(g)}} + 4\mathrm{H_2O_{(l)}} + 8\mathrm{e^-} &\rightarrow 8\mathrm{OH^-_{(aq)}} \end{aligned}$$