Reading For Lecture #26: 13.6-13.12 in 5th (4th ed: 12.6-12.12)

Topic: I. Introduction to Oxidation-Reduction (Redox) Reactions
   II. Balancing Redox Reactions
   III. Electrochemical Cells

I. INTRODUCTION TO OXIDATION-REDUCTION (REDOX) REACTIONS
Redox reactions are a major class of chemical reactions in which there is an exchange of electrons from one species to another.

For example, \(2\text{Mg (s) + O}_2 (g) \rightarrow 2\text{MgO}\)

Definitions

Oxidation:

Reduction:

Oxidizing agent:

Reducing agent:

Guidelines for Assigning Oxidation Numbers

1) In free elements, each atom has an oxidation number of zero. Example \(\text{H}_2\)

2) For ions composed of only one atom the oxidation number is equal to the charge on the ion. Thus \(\text{Li}^{+1}\) has an oxidation number of +1. Group 1 and group 2 metals have oxidation numbers of +1 and +2, respectively. Aluminum has an oxidation number of +3 in all its compounds.

3) The oxidation number of oxygen in most compounds is -2. However, in peroxides such as \(\text{H}_2\text{O}_2\) and \(\text{O}_2^{-2}\), oxygen has an oxidation state of -1.

4) The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds, such as \(\text{LiH}, \text{NaH}, \text{CaH}_2\). In these cases, its oxidation number is -1.

5) \(\text{F}\) 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 compounds (Ex. NaCl). However, when combined with oxygen (oxoacids), they have positive oxidation numbers (Ex. ClO⁻).
6) 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.
Example $\text{NH}_4^+$

H is _______  N is _______  Sum is _______

7) Oxidation numbers do not have to be integers. For example, the oxidation number of oxygen in superoxide $\text{O}_2^-$ is ________

Examples:

$\text{Li}_2\text{O}$  \hspace{2cm} \text{PCl}_3$

$\text{HNO}_3$  \hspace{2cm} $\text{N}_2\text{O}$

**Disproportionation Reactions**

A reactant element in one oxidation state is both oxidized and reduced.

$\text{NaClO} \Rightarrow \text{NaClO}_3 + \text{NaCl}$

Write the half reactions and determine the changes in oxidation state. $\text{Na}^+$ is a spectator ion so:

$\text{ClO}^- \quad \Rightarrow \quad \text{ClO}_3^-$

$\text{ClO}^- \quad \Rightarrow \quad \text{Cl}^-$
II. BALANCING REDOX REACTIONS

A. BALANCE IN ACIDIC SOLUTION

\[ \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} \]

(1) Write two unbalanced half reactions for oxidized and reduced species.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(2) Insert coefficients to make the number of atoms of all elements except oxygen and hydrogen equal on the two sides of each equation.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(3) Add H\textsubscript{2}O to balance oxygen

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(4) Balance hydrogen with H\textsuperscript{+}

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

(5) Balance the charge by inserting electrons

\[ 14\text{H}^{+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]
(6) Multiply the half reactions so that the number of electrons given off in the oxidation equals the number of electrons accepted in the reduction.

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]
\[ Fe^{2+} \rightarrow Fe^{3+} + e^- \]

(7) Add half reaction, make appropriate cancellations.

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 6e^- \]

B. BALANCE IN BASIC SOLUTION.

\[ Fe^{2+} + Cr_2O_7^{2-} \rightarrow Cr^{3+} + Fe^{3+} \]

Follow steps (1-7) to get your answer for acidic solution:

\[ 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} \]

(8) Then "adjust pH" by adding OH\(^-\) to both sides to neutralize H\(^+\).

\[ 14OH^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^- \]

OR

\[ 14H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^- \]

CANCEL

\[ \frac{7}{14}H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow \frac{2}{7}Cr^{3+} + \frac{7}{7}H_2O + \frac{6}{7}Fe^{3+} + 14OH^- \]

Thus:

\[ 7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^- \]

Summary
Acidic: \[ 14H^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \]

Basic: \[ 7\text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 14\text{OH}^- \]

Oxidation-reduction (redox) reactions are essential for photosynthesis, fuel cells, and life! Electrochemistry is the study of redox reactions at an electrode, including:

- Obtaining electricity directly from a spontaneous (\(\Delta G < 0\)) reaction.
- Using an electric current to drive a non-spontaneous (\(\Delta G > 0\)) reaction.

III. ELECTROCHEMICAL CELLS: are devices in which an electric current (a flow of electrons through a circuit) is either

- produced by a spontaneous chemical reaction (________cell); or
- used to bring about a non-spontaneous reaction (________cell).

Battery: a collection of galvanic cells joined in a series, so the voltage they produce is the sum of the voltages of each cell.

Electrodes: Conductors through which electrons can travel. Anodes and cathodes are two types of electrodes.

Anode: Electrons produced from __________flow out of compartment through a wire.

\[ \text{Zn} (s) \rightarrow \text{Zn}^{2+} (aq) \text{ at the anode} \]

Cathode: Electrons entering the compartment are consumed in a __________reaction.

\[ \text{Cu}^{2+} (aq) \rightarrow \text{Cu} (s) \text{ at the cathode} \]

The voltmeter measures the flow of electrons (the electric current).

Neutrality is maintained by the flow of ions through the salt bridge.

Overall, the electrochemical cell may be represented by:

Where phase boundaries are represented by "| | ", and the salt bridge is represented by "| | ".

\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} (aq) + 2e^- \quad \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \]
Another cell has utilizes the following redox reactions:

\[ \text{Zn (s)} \rightarrow \text{Zn}^{2+} (aq) + 2e^- \text{ and } \text{Sn}^{4+} (aq) + 2e^- \rightarrow \text{Sn}^{2+} (aq) \]

The reaction at the anode is:

The reaction at the cathode is:

The electrochemical cell may be represented by:

**Faraday’s Law**

In the electrochemical cell on page 1, Zn is consumed and Cu is deposited. Faraday’s Law states that Zn is consumed and Cu is deposited in a quantity \( \frac{\text{charge passed}}{\text{Faraday's constant}} \) to the charge passed.

**Example:** How much Zn is consumed and how much Cu is deposited if a current of 1.0 A flows for 1.0 hours?

Step 1. Determine the amount of charge that passed though the circuit.

\[
Q = I \times t
\]

magnitude of charge in Coulombs (C)

\[
= 1.0 \text{ A} \times 3600 \text{ sec} = 3600 \text{ C}
\]

Step 2. Determine the number of moles of electrons to which this charge is equivalent.

Use Faraday’s constant 96,485 C/ mol = 1 Faraday (F)

\[
\frac{3600 \text{ C}}{96,485 \text{ C/mol}} = 0.0373 \text{ moles of electrons}
\]

Step 3. Calculate the number of moles of Zn consumed and Cu deposited and convert to grams.

\[
0.0373 \text{ moles of e}^- \text{ passed} \times \frac{1 \text{ mol Zn consumed}}{?? \text{ moles of e}^- \text{ passed}} \times \frac{65.39 \text{ g}}{1 \text{ mol}} = 1.2 \text{ g}
\]
0.0373 moles of e\textsuperscript{-} passed × \frac{1\ mol\ Cu\ deposited}{??\ moles\ of\ e\textsuperscript{-}\ passed} × \frac{63.55\ g}{mol} = 1.2\ g
Electrodes (anodes, cathodes) are not always consumed or deposited upon during electrochemical experiments. A Pt electrode, which is ____________, can be used.

\[
\begin{align*}
\text{Pt (s)} & \quad \text{salt bridge} \\
\text{Cr}^{2+} (aq) & \quad \text{Cu}^{2+} (aq)
\end{align*}
\]

Anode (oxidation)
\[
\text{Cr}^{2+} (aq) \Rightarrow \text{Cr}^{3+} (aq) + e^{-}
\]

Cathode (reduction)
\[
\text{Cu}^{2+} (aq) + 2e^{-} \Rightarrow \text{Cu} (s)
\]

Notation for this type of cell is:

\[\text{Pt (s)} \mid \text{Cr}^{2+} (aq), \text{Cr}^{3+} (aq) \mid \mid \text{Cu}^{2+} (aq) \mid \text{Cu (s)}\]

A Hydrogen Electrode constructed with Pt is commonly used. Many reduction potentials are measured against a Standard Hydrogen Electrode (S.H.E). The hydrogen electrode is denoted:

\[\begin{align*}
\text{H}^+ (aq) & \mid \text{H}_2 (g) \mid \text{Pt (s)} & \text{when it acts as a cathode (H}^+ \text{ is reduced)} \\
\text{Pt (s)} & \mid \text{H}_2 (g) \mid \text{H}^+ (aq) & \text{when it acts as an anode (\text{______________})}
\end{align*}\]

Example of cell using hydrogen electrode.
5.111 Principles of Chemical Science
Fall 2014

For information about citing these materials or our Terms of Use, visit: https://ocw.mit.edu/terms.