5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #25

Oxidation/Reduction Lecture 2

Topics:Electrochemical Cells, Faraday's Law, and the Relationship between Gibbs Free Energy and Cell Potential

Chapter 12

OXIDATION/REDUCTION REACTIONS

Guidelines for assigning oxidation numbers

1) In free elements, each atom has an oxidation number of zero. Example H_2

2) For ions composed of only one atom the oxidation number is equal to the charge on the ion. Thus 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 H_2O_2 and 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 LiH, NaH, CaH_2. In these cases, its oxidation number is -1.

5) 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. For example NH_4^+

H is **+1** N is **-3** Sum is **+1**

7) Oxidation numbers do not have to be integers. For example, the oxidation number of oxygen in superoxide O_2^{-1} is **-½**

Examples

Li_2O PCl_5

HNO_3 N_2O

Definitions

Oxidation -
Reduction -
Oxidizing agent -
Reducing agent –

Disproportionation Reaction

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

$NaClO \Rightarrow NaClO_3 + NaCl$ in basic solution

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

$ClO^- \Rightarrow ClO_3^-$

$ClO^- \Rightarrow Cl^-$

Balancing Redox Reactions (Ch12.2)

A. BALANCE IN **ACIDIC** SOLUTION

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

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

$Cr_2O_7^{2-} \Rightarrow Cr^{3+}$

$Fe^{2+} \Rightarrow Fe^{3+}$

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

$Cr_2O_7^{2-} \Rightarrow Cr^{3+}$

$Fe^{2+} \Rightarrow Fe^{3+}$

(3) Add H_2O to balance oxygen

$Cr_2O_7^{2-} \Rightarrow 2Cr^{3+}$

$Fe^{2+} \Rightarrow Fe^{3+}$

(4) Balance hydrogen with H^+

$Cr_2O_7^{2-} \Rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \Rightarrow Fe^{3+}$

(5) Balance the charge by inserting electrons

$$14H^+ + Cr_2O_7^{2-} \Rightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{2+} \Rightarrow Fe^{3+}$$

(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.

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

B. BALANCE IN **BASIC** SOLUTION (Book has a different approach. You can use either.)

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

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

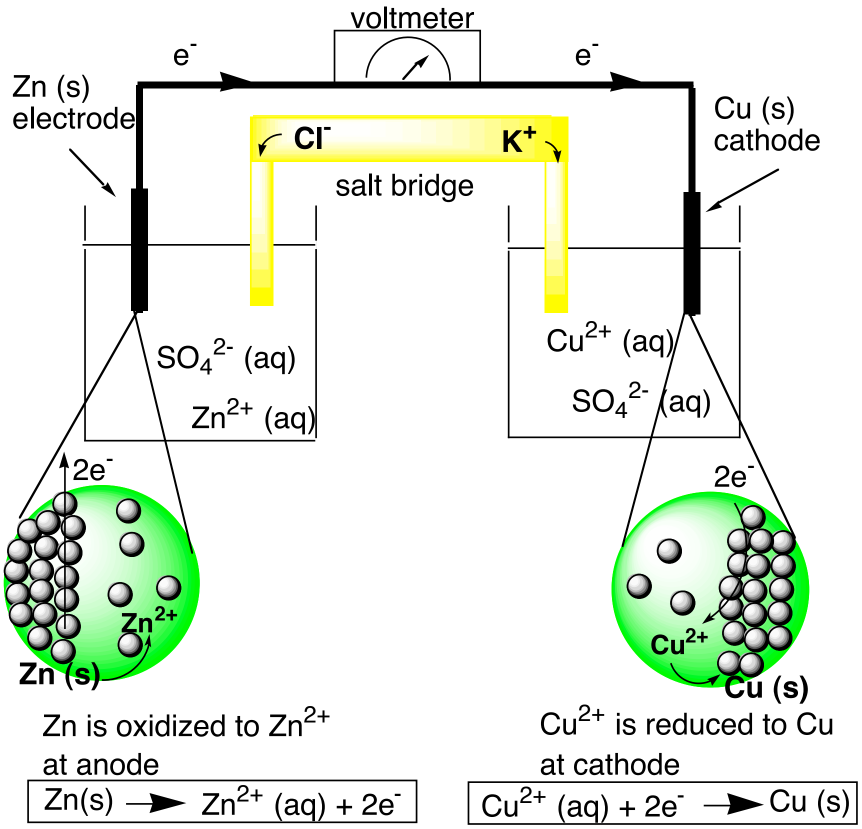
$$\overset{7}{\cancel{14H_2O}} + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + \cancel{7H_2O} + 6Fe^{3+} + 14OH^-$$

Thus: $7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^-$

Today's material

An Electrochemical Cell is a device in which an electric current (a flow of electrons through a circuit) is either produced by a spontaneous chemical reaction or used to bring about a nonspontaneous reaction. Battery - technically, a battery is a collection of cells joined in a series, so the voltage they produce is the sum of the voltages of each cell.

ELECTROCHEMICAL CELL



Anode (Oxidation) Electrons produced from oxidation flow out of compartment through a wire. Positive charge increases in the compartment due to the production of Zn^{2+} from Zn^0. To maintain neutrality, Cl^- flows in through the salt bridge.

Cathode (Reduction) Elections entering the compartment are consumed in the reduction of Cu^{2+} to Cu^0. Positive charge decreases and K^+ ions migrate through the salt bridge and enter the cathodic compartment to maintain the charge.

Overall, the electrochemical cell may be represented by:

$\mathrm{Zn\ (s)} \mid \mathrm{Zn^{2+}\ (aq)} \parallel \mathrm{Cu^{2+}\ (aq)} \mid \mathrm{Cu\ (s)}$

Phase boundaries are represented by "|"

The salt bridge is represented by "||"

In the above electrochemical cell, Zn is consumed and Cu is deposited in a quantity proportional to the charge passed (<u>Faraday's Law</u>).

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

Step1. Find how much charge passed though the circuit.

Q	$=$	I	$\bullet$	t
magnitude of charge in Coulombs (C)		current in amperes (A) (amperes = coulombs/second)		time in seconds

$Q = 1.0\ \mathrm{A} \bullet 3600\ \mathrm{sec} = 3600\ \mathrm{C}$

Step 2. Find how many moles of electrons this charge is equivalent to.

Use Faraday's constant 96,485 C/mol = 1 Faraday ($\mathfrak{I}$)

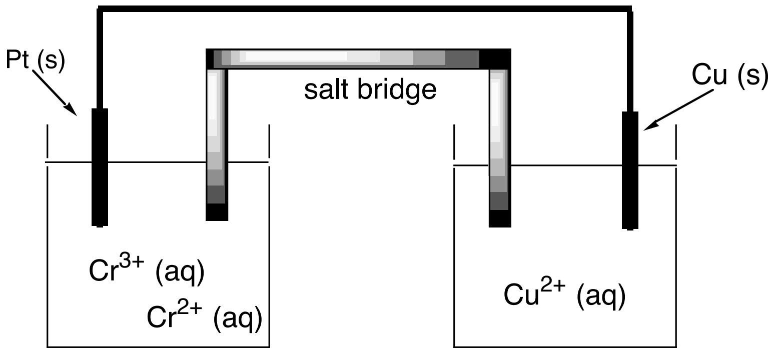
$$3600\ \mathrm{C} \quad \times \quad \frac{1\ \mathrm{mol}}{96{,}485\ \mathrm{C}} \quad = \quad 0.0373 \text{ moles of electrons}$$

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

$$0.0373 \text{ moles of } e^- \text{ passed} \quad \times \quad \frac{1 \text{ mol Zn consumed}}{2 \text{ moles of } e^- \text{ passed}} \quad \times \quad \frac{65.39\ \mathrm{g}}{\mathrm{mol}} \quad = \quad 1.2\ \mathrm{g}$$

$$0.0373 \text{ moles of } e^- \text{ passed} \quad \times \quad \frac{1 \text{ mol Cu deposited}}{2 \text{ moles of } e^- \text{ passed}} \quad \times \quad \frac{63.55\ \mathrm{g}}{\mathrm{mol}} \quad = \quad 1.2\ \mathrm{g}$$

Electrodes (anodes, cathodes) are not always consumed or produced during electrochemical experiments. A Pt electrode, which is inert, can be used.



Notation for this type of cell is:

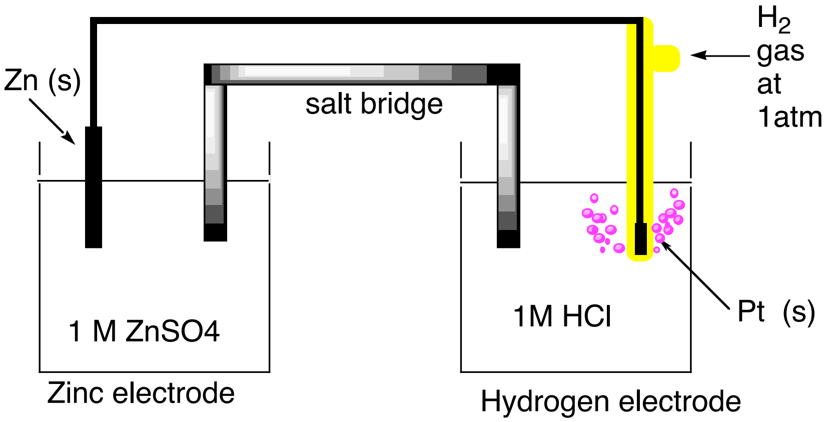
Pt (s) | Cr^{2+} (aq) , Cr^{3+} (aq) || Cu^{2+} (aq) | Cu (s)

anode	Cr^{2+} (aq) $\Rightarrow$ Cr^{3+} (aq) + e^-
cathode	Cu^{2+} (aq) + $2e^-$ $\Rightarrow$ 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:

H^+ (aq) | H_2 (g) | Pt (s)	when it acts as a cathode (H^+ is reduced) and
Pt (s) | H_2 (g) | H^+ (aq)	when it acts as an anode (H_2 is oxidized).

Example of cell using hydrogen electrode.



Cell Potential (ΔE cell)/Cell Voltage/Electromotive Force (emf) and Gibbs Free Energy

The flow of electrons arises from a potential difference, ΔE, between the electrodes in the circuit.

The overall free energy of the cell is related to the cell potential by

$\Delta G_{cell} = -n\Im\Delta E_{cell}$

n = number of electrons
$\Im$ = Faraday's constant

Standard States and Cell Potentials

$\Delta G^\circ_{cell} = -n\Im\Delta E^\circ_{cell}$

ΔE°_{cell} = cell potential (cell voltage) in which products and reactants are in their standard states
Units for ΔE is volts.

Example - Calculate ΔE°_{cell} for

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

anode

cathode

ΔE°(cell) = standard reduction potential for the couple at cathode minus standard reduction potential for the couple at anode

$\Delta E^\circ(\text{cell}) = E^\circ(\text{cathode}) - E^\circ\ (\text{anode})$

Look up Standard **REDUCTION** Potentials (E°) in back of book (measured against S.H.E)

$Zn^{2+}\ (aq) + 2e^- \Rightarrow Zn\ (s) \quad E^\circ = -0.7628$ volts
$Cu^{2+}\ (aq) + 2e^- \Rightarrow Cu\ (s) \quad E^\circ = +0.3402$ volts

$$\begin{aligned}\Delta E^\circ(\text{cell}) &= E^\circ(\text{cathode}) - E^\circ\ (\text{anode})\\ &E^\circ\ (Cu^{2+}/Cu(s)) - E^\circ(Zn^{2+}/Zn(s))\\ &= 0.3402 - (-0.7628\ ) = 1.103 \text{ volts}\end{aligned}$$

Is the flow of electrons spontaneous?

$\Delta G^\circ_{cell} = -n\Im\Delta E^\circ_{cell}$

So, if ΔE°_{cell} is positive, ΔG°_{cell} will be negative.

Is a reaction spontaneous when ΔG° is negative?

Galvanic Cell is an electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current.

Electrolytic Cell uses electrical energy provided by an external circuit to carry out nonspontaneous reactions.

Summary

Whether the cell operates spontaneously can be determined by ΔE_{cell}. ((+) = spontaneous)

ΔE_{cell} can be calculated from the Standard Reduction Potentials ($E°$) of half-cell reactions.

Meaning of standard reduction potential $E°$

A large positive $E°$ means the element or compound is easy to reduce

ex. F_2 (g) + $2e^- \Rightarrow 2F^-$ $E°$=+2.87 volts (easy to add electrons to F_2)
positive $E°$, negative $\Delta G°$, favorable

Is F_2 a good oxidizing agent?

A large positive $E°$ means the oxidized species of the couple is very oxidizing.

A large negative $E°$ means the element or compound is hard to reduce

ex. $Li^{+1} + e^- \Rightarrow$ Li (s) $E°$=-3.045 volts (hard to add electrons to Li^{+1})
negative $E°$, positive $\Delta G°$, not favorable

Is Li^{+1} a good oxidizing agent?

A large negative $E°$ means the reduced species of the couple is very reducing.

<u>Example:</u> What is $\Delta E°$ for the cell reaction: $2Fe^{3+}$ (aq) + $2I^{-}$ (aq) $\Rightarrow$ $2Fe^{2+}$ (aq) + I_2 (s)?

balanced reaction at the cathode:

balanced reaction at the anode:

Standard Reduction Potentials are:
$E°(Fe^{3+}/Fe^{2+}) = +0.770$ V
$E° (I_2/I^-) = +0.535$ V

$\Delta E°(\text{cell}) = E°(\text{cathode}) - E°(\text{anode})$

=

Is the reaction spontaneous?

Which is the better oxidizing agent: Fe^{3+}, I_2?

Which is the better reducing agent: I^-, Fe^{2+}?

<u>Question</u>: Vitamin B_{12} has a large negative reduction potential, so how is it reduced in the body? Vitamin B_{12} needs to be reduced to be active. Proper functioning of an enzyme that requires vitamin B_{12} and folic acid is thought to be necessary for preventing heart disease and birth defects.

Where do you get vitamin B_{12} and folic acid in your diet? and how is the vitamin B_{12} reduced?