CHEM 116

Electrochemistry in Non-Standard Conditions and Introduction to Thermochemistry

December 5 and 7, 2006
Prof. Sevian

Electrochemistry overview

- What you need to know (mostly boils down to vocabulary)
  - How to recognize an electron transfer (redox) reaction
  - Oxidation vs. reduction
    - Loss of electrons is oxidation, gain of electrons is reduction (LEO the lion says GER)
    - Reduction is moving (oxidation number) down on a number line, oxidation is up
  - Agent means "that which causes"
- What you need to be able to do
  - Assign oxidation numbers to elements to figure out which **species** contain elements that are changing
  - Balance redox rxns in neutral, acid, and base solutions
  - Diagram an electrochemical cell and indicate direction of flow of negative charge through the system
  - Read and write electrochemical cell notation
  - Use reduction potentials to predict cell voltage under standard conditions
  - Use the Nernst equation to predict cell voltage at non-standard conditions

Agenda

- Oxidation states
- Balancing redox reactions
  - Inspection method
  - SOHe method
- Redox reactions that occur spontaneously
  - Predicting whether a reaction will be spontaneous
  - How to separate the halves of a reaction to generate electricity
  - How much electricity?
- Non-standard conditions
  - When solutions are not 1.0 M (or gases are not at 1.0 atm)
  - When temperature is not 25 ºC
- Thermodynamics (an introduction)

The **final exam** is scheduled for Monday, December 18, 11:30AM-2:30PM. Location TBA.

Redox Reactions and Electrochemistry

Part I: Foundational
- Assigning oxidation numbers
- Balancing redox equations

Part II: Applied
- Diagramming electrochemical cells
- Facility with cell notation

Part III: Making mathematical predictions of properties
- Calculating cell potential at standard conditions
- Calculating cell potential at non-standard conditions
- Relating the amount of a substance oxidized or reduced to the electrical current and the time during which current is allowed to flow

Key ideas so far about electrochem (what we did as of last Thursday)

- You need to know ions and ionic charges
- You must be able to assign oxidation numbers to elements in a compound or ion
- Redox reactions are when oxidation numbers change during a reaction
  - One element (part or all of a "species") has its oxidation number increase (this is oxidation)
  - Another element (part or all of a "species") has its oxidation number decrease (this is reduction)
  - Both processes must occur, because redox is electron transfer
- Study the vocabulary

Electrochemical Cells

Parts of an electrochemical cell
- Anode = oxidation half-cell
- Cathode = reduction half-cell
- Wire
- Salt bridge

Predicting voltage under standard conditions
- Voltage = cell potential (E^o_{cell}) = related to ΔG, which is related to ΔH, T, and ΔS
- Table of reference voltages, all referenced to the hydrogen half-cell
- All reference voltages are reduction potentials, so if you need an oxidation potential you just take the opposite
- See table of standard reduction potentials
- Examples

Non-standard conditions: Nernst equation

- Concentrations of solutions not at standard 1.0 M

$$E_{cell} = E^o_{cell} - \frac{0.0257}{n}\ln Q$$

$$= E^o_{cell} - \frac{0.0592}{n}\log Q$$

Reaction quotient

Least common multiple of electrons exchanged in the redox reaction

- Temperature not at standard 25 ºC

$$E_{cell} = E^o_{cell} - \frac{RT}{n\mathfrak{F}}\ln Q$$

where $\mathfrak{F}$ is the Faraday constant: $\mathfrak{F}$ = 96,500 C/mol

Electrolysis: electrochemical cell forced to run backwards (against its will)

- Note: sections 20.7 and 20.8 in the text book are fascinating reading, but they are not required reading, we will get back to section 20.5 after we cover chapter 19
- Electroplating: The longer you run the cell, the more metal electroplate builds up
- Current means how many electrons pass by per second
- If you know how much metal electroplate you want to make, then stoichiometry tells you how many electrons are required
  - $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$
  - $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$
  - $Ag^{+}(aq) + 1\,e^- \rightarrow Ag(s)$
- If you know what current is being applied (e.g., 0.800 amperes = 0.800 Coulombs/second), then you can figure out how much time you must run the cell for in order to build the amount of electroplated metal that you want

Electrolysis example

Similar to Sample Exercise 20.14, pp. 885-886

Calculate the mass of O_2 produced in the electrolysis of water, using a current of 0.445 A for a period of 45 minutes.

Three laws of thermodynamics

1. The total energy of the universe is constant.
   - Energy is conserved in all processes
   - If a system gains/loses heat energy, then the surroundings must do the opposite
2. In processes that occur spontaneously, disorder in the universe increases.
   - Disorder (called “entropy”) is a measure of how spread out matter is
   - If a system gains/loses disorder, then the surroundings must do so in a way such that both system and surroundings together net an increase in the universe’s disorder
3. Zero disorder is defined as a perfect crystal at zero absolute temperature.
   - Zero absolute temperature is impossible to achieve

Additional important implications

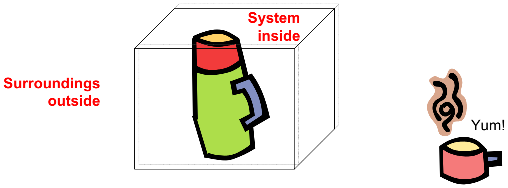
- If a chemical or physical change written in one direction is non-spontaneous, then written in the opposite direction it is spontaneous
  - “Spontaneous” means that once a process begins (after activation barrier is surmounted) it continues without intervention
  - Spontaneous and non-spontaneous are opposites
- Whether a given change is spontaneous depends on the experimental conditions (e.g., temperature, pressure)
  - A change that is spontaneous under one set of conditions may be non-spontaneous under a different set of conditions
- Spontaneous change always progresses toward a condition of equilibrium

Enthalpy: what you have already learned

- Heat energy flow
- System vs. surroundings
- Closed system
- Can be measured by calorimetry

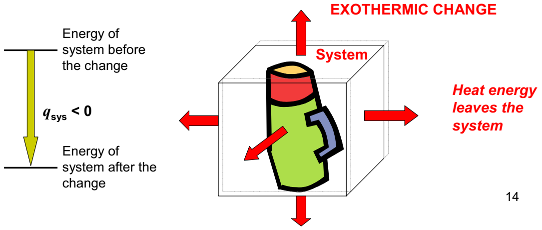
What is a System?

- A “system” is a 3-dimensional space, surrounded by an imaginary surface boundary, such that no matter passes through the boundary, but heat energy can transfer freely across the boundary



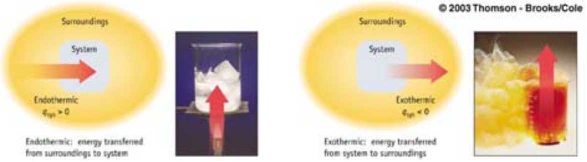
What happens to the SYSTEM when heat transfer occurs?

- As coffee eventually cools, heat energy is transferred to the air around the thermos and the counter beneath it.
- System: Particles in the coffee slow down their motion.
- Surroundings: Particles in the air, and particles in the counter, speed up their motion.



Endothermic vs. Exothermic

<u>Endothermic</u>	<u>Exothermic</u>
Example: ice melting	Example: fire burning
Heat enters system	Heat exits system
System gains energy	System loses energy
$q_{sys} > 0$	$q_{sys} < 0$



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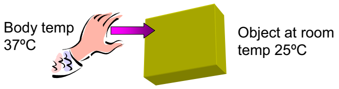
Quantitative measure of heat energy transfer

- How do we measure heat lost or gained by a system?



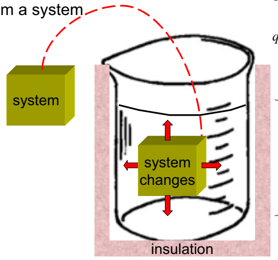
- What does the quantity of heat transferred depend on?
  - Quantity of material in the object
  - Size of temperature change
  - Identity of the material the object is made from

$$q = m\ C\ \Delta T$$

Liquid Water's Capacity to Absorb Heat Energy

Can be used as the standard for comparison: Calorimetry!

Measuring heat transferred from a system



Problem Solving Strategy

$$q_w = m_w C_w \Delta T_w$$

$$\text{where} \quad \Delta T_w = \textit{temp change of } \mathrm{H_2O}$$

$$q_{sys} \textit{ is opposite of } q_w$$

ΔH_{sys} is just q_{sys} per mole of reactant

Known quantity (mass, m_w) of water in beaker

Beaker image: core.ecu.edu/chem/chemlab/ equipment/ebeaker.htm

Using Hess's law to calculate ΔH_{sys}

Hess's law: enthalpy is a "state function" and as such its value does not depend on the path taken to get from initial to final state

Reference state has enthalpy change of zero – "reference state" defined to be elements in the states they exist in naturally at standard conditions (*e.g.,* hydrogen is H_2 (g), carbon is C (s), iron is Fe (s))

$$\textit{initial state} \rightarrow \textit{final state}$$

$$\Delta H^o = \sum_{\textit{final components}} \Delta H^o_{\textit{formation}} - \sum_{\textit{initial components}} \Delta H^o_{\textit{formation}}$$

Example

ΔH^o for H_2O (l) ⇆ H_2O (g) can be predicted from tabulated values (see Appendix C, pp. 1123-1125 in text book)

$$\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$$

$$\Delta H^o = \sum_{\textit{final components}} \Delta H^o_f(\mathrm{H_2O}\,(g)) - \sum_{\textit{initial components}} \Delta H^o_f(\mathrm{H_2O}\,(l))$$

$$= \left[-241.83\frac{kJ}{mol}\right] - \left[-285.83\frac{kJ}{mol}\right] = +44.00\frac{kJ}{mol}$$

Absolute entropy

- The amount of disorder ("spreadedness") in a material
- Must always be a comparison
- Ultimate comparison is to absolute order, which is a perfect crystal lattice structure with no motion (zero absolute temperature)
- Impossible for absolute entropy to be zero (except at reference state of absolute order, which is unachievable)

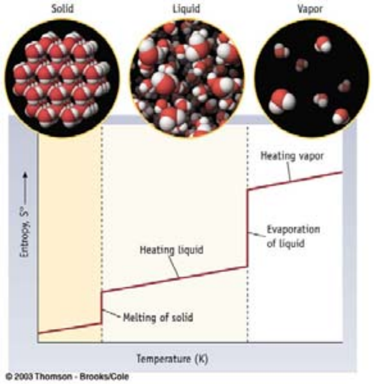
Examples (comparison per mole of the chemical)

- Water in different states
- Homologous series of alkanes

Comparing absolute entropy of water in different physical states

State	S^o (J/mol·K)
Solid	*
Liquid	69.95
Gas	188.84

*No value because S° by definition means "at standard conditions of 25 ºC and 1 atm" and solid water does not exist under these conditions



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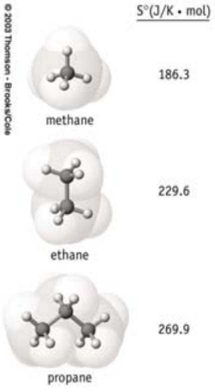
Comparing absolute entropy of different alkanes under standard conditions

- The more complex the molecular structure, the higher the absolute entropy of the substance
- More complicated molecules have more options for configurations, rotations, vibrations, etc.

(This is the same as Fig 19.15 in your text book, but the one here is a slightly nicer drawing.)



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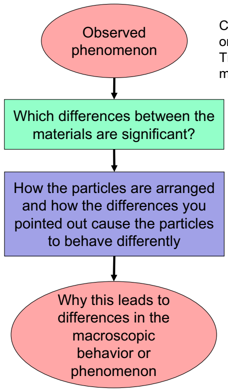
The structure of scientific explanations (in chemistry)



Observed phenomenon

Comparison of properties exhibited by two materials
or
Trend in properties exhibited by a series of related materials

Which differences between the materials are significant?

What things are the same about the materials?
What things are different?

How the particles are arranged and how the differences you pointed out cause the particles to behave differently

What kinds of behaviors are there?
Which of these are affected by the differences in the materials?

Why this leads to differences in the macroscopic behavior or phenomenon

Questions to help you think about what to say

Molecular interpretation of entropy (*S*)

$S = k \ln W$

W is the number of microstates available, *k* is a constant

So, as *W* increases, the absolute entropy (*S*) increases

Factors that influence *W* (for making qualitative comparisons)

- Temperature
- Volume
- Number of independently moving particles

Compare absolute entropies

Arrange in order from lowest to highest <u>absolute</u> <u>standard</u> entropy and explain your reasoning ($S°$ not $\Delta S°$):

a) O_2 (*g*) vs. O_3 (*g*)

b) NH_4Cl (*s*) vs. NH_4Cl (*aq*)

c) F_2 (*g*), Cl_2 (*g*), Br_2 (*l*), I_2 (*s*)

d) NaCl (*s*) vs. MgO (*s*)

O_2	205.1 J/mol·K
O_3	238.9

NH_4Cl (*s*)	94.85 J/mol·K
NH_4Cl (*aq*)	164.9

I_2 (*s*)	116.1 J/mol·K
Br_2 (*l*)	152.2
F_2 (*g*)	202.8
Cl_2 (*g*)	223.1

MgO (*s*)	26.85 J/mol·K
NaCl (*s*)	72.11

Note: in the boxes are literature values, which you can use to confirm your logic *after* you have made predictions

Entropy change
(Now we're talking about ΔS^o, not S^o)

- The change from one state to another state (can be positive or negative)
- Difference between the final and initial entropy states
- Symbolized ΔS
- When $\Delta S > 0$ it means disorder ("spreadedness") of the system increases during the change
- Hess's law applies because entropy is also a state function

Example

ΔS^o for $H_2O\,(l) \leftrightarrows H_2O\,(g)$ can be predicted from tabulated values (see Appendix C in text book)

$$\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$$

$$\Delta H^o = \sum_{final} S^o\left(\mathrm{H_2O}\,(g)\right) - \sum_{initial} S^o\left(\mathrm{H_2O}\,(l)\right)$$

$$= \left[188.84\,\frac{J}{mol \bullet K}\right] - \left[69.95\,\frac{J}{mol \bullet K}\right] = +118.89\,\frac{kJ}{mol}$$

Example: $H_2O\,(l) \leftrightarrows H_2O\,(g)$ is a physical change

Enthalpy: The change, in the forward direction written, is endothermic (ΔH = 44 kJ/mol > 0, the system requires energy input from the surroundings for the change to proceed)

Entropy: The change, in the forward direction written, represents an increase in the system's disorder (ΔS = 118.89 J/mol·K> 0, gases are more disordered or "spread out" than liquids)

$$\Delta G = \Delta H - T\Delta S$$

Conditions:	Conditions:	Conditions:
T = 90 ºC, p = 1 atm	T = 100 ºC, p = 1 atm	T = 110 ºC, p = 1 atm
$\Delta G = \Delta H - T\Delta S$	$\Delta G = \Delta H - T\Delta S$	$\Delta G = \Delta H - T\Delta S$
$= 44 - (90 + 273)(0.119)$	$= 44 - (100 + 273)(0.119)$	$= 44 - (110 + 273)(0.119)$
$= +0.80\ kJ/mol$	$= 0\ kJ/mol$	$= -1.6\ kJ/mol$
Non-spontaneous in direction written	At equilibrium	Spontaneous in direction written

Gibbs free energy

- Derives from the idea that the entropy change to the universe resulting from a change in a system and its surroundings, under conditions of constant temperature and pressure, is

$$\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$$

(see pp. 822-823 in your text book)

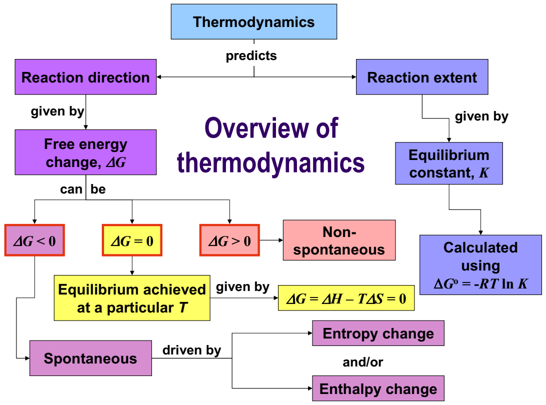
- Measures absolute entropy change to the entire universe, which always increases for any change that occurs spontaneously
- Results in an equation in terms of the system of interest:

$$\Delta G = \Delta H - T\,\Delta S$$

ΔG: Gibbs free energy
ΔH: Enthalpy change
T: Absolute temperature
ΔS: Entropy change

- Depends on both enthalpy change term (ΔH) and entropy change term ($T\Delta S$) – either one, or both, could drive the change to be spontaneous (spontaneous only when $\Delta G < 0$)

Overview of thermodynamics



Thermodynamics
predicts
Reaction direction
Reaction extent
given by
Free energy change, ΔG
given by
Equilibrium constant, K
can be
$\Delta G < 0$
$\Delta G = 0$
$\Delta G > 0$
Non-spontaneous
Calculated using $\Delta G^o = -RT \ln K$
Equilibrium achieved at a particular T
given by
$\Delta G = \Delta H - T\Delta S = 0$
Spontaneous
driven by
Entropy change
and/or
Enthalpy change

Adapted from "Key Concept Summary" in McMurray & Fay, Chemistry (3rd edn)

ΔG information

- Graphically (fig 19.18, p. 824)
- Comparing magnitudes and signs of the terms in the ΔG equation (table 19.4, p. 828)
- Spontaneous? Which direction?
- Relating it to K via $\Delta G^o = -RT \ln K$
- Relating these to E^o_{cell} for an electrochemical cell

- Important note: "standard" temperature in thermodynamic systems is T = 25ºC = 298 K. It is easy to confuse this with "standard" temperature in the kinetic theory of gases, which was T = 0ºC = 273 K.

Magnitudes and signs of terms in free energy

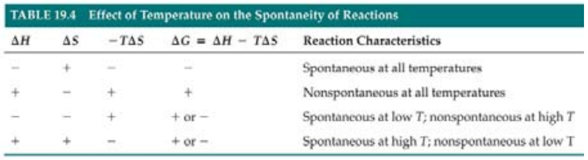


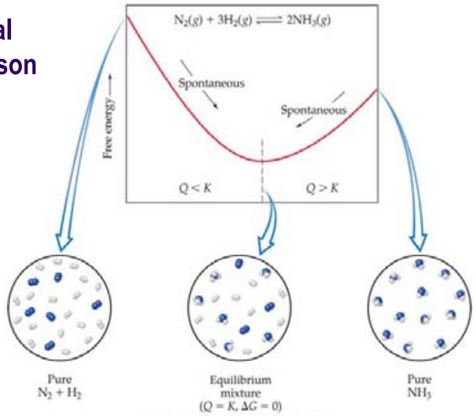
TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics
−	+	−	−	Spontaneous at all temperatures
+	−	+	+	Nonspontaneous at all temperatures
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T
+	+	−	+ or −	Spontaneous at high T; nonspontaneous at low T

About the mathematical terms in this table:

- ❖ ΔH is the change of enthalpy. When $\Delta H > 0$ (i.e., ΔH is positive), the change is endothermic. When $\Delta H < 0$ (i.e., ΔH is negative), the change is exothermic.
- ❖ ΔS is the change of entropy. When $\Delta S > 0$ (i.e., ΔS is positive), the entropy increases during the process (the system becomes more disordered). And vice versa.
- ❖ T is the absolute temperature (i.e., Kelvin scale). It is always a number larger than zero.
- ❖ Therefore, the term $-T\Delta S$ has the opposite sign of ΔS.

Graphical comparison



Effect of temperature on spontaneity

Similar to Exercise 19.8, p. 829

Metallic iron is produced in a blast furnace by reducing iron oxide (mined from the earth) using carbon. For the reaction,

$$2\ Fe_2O_3\ (s) + 3\ C\ (s,\ \text{graphite}) \rightarrow 4\ Fe\ (s) + 3\ CO_2\ (g)$$

the following information is available:

$$\Delta H^o_{rxn} = +467.9\ \text{kJ}$$

$$\Delta S^o_{rxn} = +560.7\ \text{J/K}$$

Show that it is necessary that this reaction be carried out at a high temperature.

How ΔG indicates reaction extent

Similar to Exercise 19.11, p. 834

Determine the standard free energy change for the reaction

$$C\ (s) + CO_2\ (g) \rightarrow 2\ CO\ (g)$$

from the following thermodynamic data.

$C\ (s)$ $\Delta G_f^o = 0$ kJ/mol
$CO_2\ (g)$ $\Delta G_f^o = -394.359$ kJ/mol
$CO\ (g)$ $\Delta G_f^o = -137.168$ kJ/mol

Then, use this result to calculate the equilibrium constant at 25 ºC.

What's next?

- Relating ΔG, E^o_{cell} and K_{eq}
- Predicting free energy changes under non-standard conditions

Relating ΔG, E^o_{cell} and K_{eq}

(see section 20.5, pp. 868-871 in text)

- In electrochemistry, cells only operate spontaneously (with the reaction going in one direction) when Q is not equal to K
- An electrochemical cell "goes" in the direction toward equilibrium, and stops changing concentrations when it gets to equilibrium
- The chemistry and thermodynamics are governed by all the same equations as all the rest of chemistry
- At equilibrium, the cell voltage drops to zero because the reaction is not moving forward any faster than it is moving in reverse

$$\Delta G^o = \Delta H^o - T\,\Delta S^o$$

$$\Delta G^o = -RT \ln K_{eq}$$

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

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log Q$$

Therefore, at equilibrium
$E_{cell} = 0$ and $Q = K_{eq}$

$$\log K_{eq} = \frac{n\,E^o_{cell}}{0.0592}$$

Electrochemistry and equilibrium: an example

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/voltaicCellEMF.html

$$2\ Ag^+\ (aq) + Cu\ (s) \leftrightarrows Cu^{2+}\ (aq) + 2\ Ag\ (s)$$

Reduction: $Ag^+\ (aq) + 1e^- \leftrightarrows Ag\ (s)$ $E^o = +\ 0.799$ V
Oxidation: $Cu\ (s) \leftrightarrows Cu^{2+}\ (aq) + 2e^-$ $E^o = -\ (+0.337$ V$)$

$n = 2$

$E^o_{cell} = +0.462$ V

Method 1 to get to K_{eq}

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

$$\Delta G^o = -RT \ln K_{eq}$$

or

Method 2 to get to K_{eq}

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log Q$$

$$\log K_{eq} = \frac{n\,E^o_{cell}}{0.0592}$$