Important announcement:
If you borrowed a clicker from me this semester, return it to me at the end of next lecture or at the final exam.
If you do not return it, you will receive an INC for your grade.

Today’s agenda

- Big picture of electrochemistry
  - Redox reactions and oxidation numbers (last lecture)
  - Charge flow in electrochemical cells and diagramming a cell
  - Using the mathematical model to predict current and voltage under standard and non-standard conditions
- Important points of thermodynamics for general chemistry
  - Enthalpy change (+endothermic, –exothermic)
  - Entropy change (+more disorder, –more order)
  - Gibbs free energy (+non-spontaneous, –spontaneous)
  - Connection to equilibrium
  - Connection to electrochemistry

Announcements

- Final exam is Tuesday, Dec 16, 3:00-6:00pm in S-1-006
Predicting voltage under standard conditions

- Voltage = cell potential \( (E_{o, \text{cell}}^\circ) \) = related to \( \Delta G \), which is related to \( \Delta H, T, \) and \( \Delta S \)
- 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
- Example of using standard reduction potentials to predict \( E_{o, \text{cell}}^\circ \)

Non-standard conditions: Nernst equation

- Concentrations of solutions not at standard 1.0 M
  \[
  E_{\text{cell}} = E_{o, \text{cell}}^\circ - \frac{0.0257}{n} \ln Q
  \]
  \[
  = E_{o, \text{cell}}^\circ - \frac{0.0592}{n} \log Q
  \]
- Temperature not at standard 25 °C
  \[
  E_{\text{cell}} = E_{o, \text{cell}}^\circ - \frac{RT}{nS} \ln Q
  \]

where \( F \) is the Faraday constant: \( F = 96,500 \text{ C/mol} \)

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/voltaicCellEMF.html set up Cu|Cu²⁺(0.001M)||Ag⁺(2.0M)|Ag cell
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. However, section 20.9 is required reading.
- **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
  - $\text{Cu}^{2+} (aq) + 2 \, \text{e}^- \rightarrow \text{Cu} (s)$
  - $\text{Au}^{3+} (aq) + 3 \, \text{e}^- \rightarrow \text{Au} (s)$
  - $\text{Ag}^+ (aq) + 1 \, \text{e}^- \rightarrow \text{Ag} (s)$
- 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 $\text{O}_2$ 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

Adapted from “Key Concept Summary” in McMurray & Fay, *Chemistry* (3rd edn)
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 flow
  - Endothermic = into the system (at constant p, $\Delta H$ is +)
  - Exothermic = out of the system (at constant p, $\Delta H$ is –)

- System vs. surroundings
  - Together, system + surroundings = universe
  - Heat flows from one to the other
    - If heat flows out of system (exothermic), then it goes into surroundings
    - If heat flows into system (endothermic), it is because it comes from the surroundings
  - Total energy of the universe remains constant

- Closed system
  - Heat can go in and out of system, but matter cannot

- Can be measured by calorimetry
  - Using equation $q = mC\Delta T$
  - At constant pressure, $q = \Delta H$
    - When heat flows into the system, the temperature goes up
    - When heat flows out of the system, the temperature goes down
Using Hess’s law to calculate $\Delta H_{\text{sys}}$

**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 $Fe\, (s)$).

\[
\Delta H^o = \sum \Delta H^o_{\text{formation}}^{\text{final components}} - \sum \Delta H^o_{\text{formation}}^{\text{initial components}}
\]

**Example**

$\Delta H^o$ for $H_2O\, (l) \rightleftharpoons H_2O\, (g)$ can be predicted from tabulated values (see Appendix C, pp. 1123-1125 in textbook).

\[
H_2O\, (l) \rightarrow H_2O\, (g)
\]

\[
\Delta H^o = \sum \Delta H^o_{\text{formation}}^{\text{final components}} - \sum \Delta H^o_{\text{formation}}^{\text{initial components}}
\]

\[
\begin{align*}
&= \left[ -241.83 \frac{kJ}{mol} \right] - \left[ -285.83 \frac{kJ}{mol} \right] = +44.00 \frac{kJ}{mol}
\end{align*}
\]

Absolute entropy ($S$)

- Entropy means disorder, or “spreadedness”
- The more disordered or spread out a material is, the greater the absolute entropy ($S$)
- The more ordered a material is, the lower the entropy
- 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

<table>
<thead>
<tr>
<th>State</th>
<th>$S^\circ$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid *</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>69.95</td>
</tr>
<tr>
<td>Gas</td>
<td>188.84</td>
</tr>
</tbody>
</table>

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


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 textbook, but the one here is a slightly nicer drawing.)

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

Arranged in order from lowest to highest absolute standard entropy \((S^0\) not \(\Delta S^0)\):

\begin{align*}
\text{a) } & \text{O}_2 (g) \text{ vs. O}_3 (g) \\
& \text{O}_2 \quad 205.1 \text{ J/mol-K} \\
& \text{O}_3 \quad 238.9 \\
\text{b) } & \text{NH}_4\text{Cl (s) vs. NH}_4\text{Cl (aq)} \\
& \text{NH}_4\text{Cl (s)} \quad 94.85 \text{ J/mol-K} \\
& \text{NH}_4\text{Cl (aq)} \quad 164.9 \\
\text{c) } & \text{F}_2 (g), \text{Cl}_2 (g), \text{Br}_2 (l), \text{I}_2 (s) \\
& \text{I}_2 (s) \quad 116.1 \text{ J/mol-K} \\
& \text{Br}_2 (l) \quad 152.2 \\
& \text{F}_2 (g) \quad 202.8 \\
& \text{Cl}_2 (g) \quad 223.1 \\
\text{d) } & \text{NaCl (s) vs. MgO (s)} \\
& \text{MgO (s)} \quad 26.85 \text{ J/mol-K} \\
& \text{NaCl (s)} \quad 72.11
\end{align*}
Entropy change
(Now we’re talking about $\Delta S^\circ$, not $S^\circ$)

- The change from one state to another state (can be positive or negative)
- Difference between the final and initial entropy states
- Symbolized $\Delta S$
- 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

Entropy change is $\Delta S^\circ$ for $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

$\Delta S^\circ = \sum S^\circ(\text{H}_2\text{O}(g)) - \sum S^\circ(\text{H}_2\text{O}(l))$

$= \left[188.84 \text{ J/mol K}\right] - \left[69.95 \text{ J/mol K}\right] = +118.89 \text{ kJ/mol}$

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

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

(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 (at const. p):

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

- Depends on both enthalpy change term ($\Delta H$) and entropy change term ($T \Delta S$)
- Either term, or both, could drive the change to be spontaneous (spontaneous when $\Delta G$ is negative)
Example: $\text{H}_2\text{O} \ (l) \rightarrow \text{H}_2\text{O} \ (g)$ is a physical change

**Enthalpy:** The change, in the forward direction written, is endothermic ($\Delta H = 44 \text{ kJ/mol} > 0$, 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 ($\Delta S = 118.89 \text{ J/mol} \cdot \text{K} > 0$, gases are more disordered or “spread out” than liquids)

\[
\Delta G = \Delta H - T\Delta S
\]

<table>
<thead>
<tr>
<th>Conditions: $T = 90 \ ^\circ\text{C}$, $p = 1 \ \text{atm}$</th>
<th>Conditions: $T = 100 \ ^\circ\text{C}$, $p = 1 \ \text{atm}$</th>
<th>Conditions: $T = 110 \ ^\circ\text{C}$, $p = 1 \ \text{atm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G = \Delta H - T\Delta S$</td>
<td>$\Delta G = \Delta H - T\Delta S$</td>
<td>$\Delta G = \Delta H - T\Delta S$</td>
</tr>
<tr>
<td>$= 44 - (90 + 273)(0.119)$</td>
<td>$= 44 - (100 + 273)(0.119)$</td>
<td>$= 44 - (110 + 273)(0.119)$</td>
</tr>
<tr>
<td>$= 0.80 \text{ kJ/mol}$</td>
<td>$= 0 \text{ kJ/mol}$</td>
<td>$= -1.6 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>Non-spontaneous in direction written</td>
<td>At equilibrium</td>
<td>Spontaneous in direction written</td>
</tr>
</tbody>
</table>

Summarizing the example of water’s physical change from $\text{H}_2\text{O} \ (l)$ to $\text{H}_2\text{O} \ (g)$

- The spontaneity of the change depends on what temperature the change occurs at

<table>
<thead>
<tr>
<th></th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$T$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below normal b.p.</td>
<td>+0.80 kJ/mol = (non-spontaneous)</td>
<td>44 kJ/mol (endothermic)</td>
<td>(90$+273$ K)</td>
<td>(0.119 kJ/mol$\cdot$K$^\circ$) (increasing disorder)</td>
</tr>
<tr>
<td>At normal boiling point</td>
<td>0 = (at equilibrium)</td>
<td>same</td>
<td>(100$+273$ K)</td>
<td>same</td>
</tr>
<tr>
<td>Above normal b.p.</td>
<td>$-1.6 \text{ kJ/mol} = \text{(spontaneous)}$</td>
<td>same</td>
<td>(110$+273$ K)</td>
<td>same</td>
</tr>
</tbody>
</table>
Magnitudes and signs of terms in free energy

<table>
<thead>
<tr>
<th>TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ΔH</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>−</td>
</tr>
<tr>
<td>+</td>
</tr>
<tr>
<td>−</td>
</tr>
<tr>
<td>+</td>
</tr>
</tbody>
</table>

About the mathematical terms in this table:

- **ΔH** is the change of enthalpy. When ΔH > 0 (i.e., ΔH is positive), the change is endothermic. When ΔH < 0 (i.e., ΔH is negative), the change is exothermic.
- **ΔS** is the change of entropy. When ΔS > 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 −TΔS has the opposite sign of ΔS.

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,

\[ 2 \text{Fe}_2\text{O}_3 (s) + 3 \text{C (s, graphite)} \rightarrow 4 \text{Fe (s)} + 3 \text{CO}_2 (g) \]

the following information is available:

- \( \Delta H_{\text{rxn}}^o = +467.9 \text{ kJ} \)
- \( \Delta S_{\text{rxn}}^o = +560.7 \text{ J/K} \)

Show that it is necessary that this reaction be carried out at a high temperature.
Relationship between $\Delta G$ and $K_{eq}$

- At a temperature ($T$) other than standard temperature ($25^\circ C = 298K$), the Gibbs free energy is given by
  \[
  \Delta G = \Delta G^o + RT \ln Q
  \]
- At equilibrium, $\Delta G = 0$
- Also at equilibrium, $Q = K_{eq}$
- Substituting into the expression above, at equilibrium
  \[
  0 = \Delta G^o + RT \ln K_{eq}
  \]
- Therefore (rearranging):
  \[
  \Delta G^o = -RT \ln K_{eq}
  \]

How $\Delta G$ 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.

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

Then, use this result to calculate the equilibrium constant at 25 °C.
What’s left to cover this semester?

- Relating $\Delta G$, $E^o_{\text{cell}}$ and $K_{eq}$
- Predicting free energy changes under non-standard conditions
- Next class (last lecture this semester) we will do this in the context of going over selected problems from Assignment 13
  - Re-read chapter 19, and section 20.5, and attempt the homework before you come to the next lecture
  - Doing thermochemistry problems brings together nearly all of the topics you have learned this semester, and is in this sense a review of the semester