Lecture 4 – Chapter 14
New and Improved Thermodynamics

- Spontaneity
- Entropy – 2nd Law of Thermodynamics
- 3rd Law of Thermodynamics
- Calculating Entropy Changes
Thermodynamics

- Studying the flow of energy from one substance or phase to another
- Previously we discussed energy \( (E) \) and enthalpy \( (H) \)
- Remember 1\(^{st}\) Law of Thermodynamics?
  \[
  \Delta E_{\text{Total}} = 0 \quad \text{or} \quad \text{Energy is conserved}
  \]
- This is great, but it isn’t everything
- Observe most sophisticated demo of the year…
Things tend toward dispersal or disorder

Energy tends to disperse, become disordered around the room
  • Ball stays on floor

Particles tend to disperse

Just as energy never reorganizes into the ball, the gas never reorganizes into one of the bulbs
Entropy

• We need something to explain why energy and particles like to be dispersed
• Entropy \( (S) \) measures how many possible ways there are to arrange our system.
  – Many arrangements == high entropy
    \[ S = k \ln W \]  (Eq 14-1, Boltzmann 1877 – HUGE)

26 balls in 36 spaces
Not many arrangements
Not much entropy
\( W = 2.5 \times 10^8 \)
\( S = 19.4k \)

26 balls in 72 spaces
Lots more arrangements
Lots more entropy
\( W = 2.8 \times 10^{19} \)
\( S = 45k \)
2\textsuperscript{nd} Law of Thermodynamics

- The 2\textsuperscript{nd} law says that the most likely thing will be the one that actually occurs.
- Things with many arrangements are more likely to happen than things with few arrangements
  - It is more likely that energy will be distributed randomly among all the particles in the floor
  - It is extremely unlikely that a bunch of energy will spontaneously flow from all around the room into the ball, giving it a huge kick of kinetic energy
- Therefore the 2\textsuperscript{nd} law says that particles will distribute evenly throughout a volume (not congregate together)
- The 2\textsuperscript{nd} law says the ball will stay on the floor.

\[ \Delta S_{Total} > 0 \]
Entropy related to heat flow

- In practice, $W$ is hard to quantify
- We know $S$ is related to heat flow

$$\Delta S = \frac{q}{T} \text{ at constant Temp (Eq 14-2)}$$

Example: You put 3 moles of water outside at -10 °C. What is entropy change of water, of the ‘outside’ and total?
  - P is constant. So we can use $q = \Delta H$
  - T is constant in the freezing ice (phase change) and in the surroundings (because they are so big).
  - So, we can use Eq 14-2
Example: freeze 3 moles water at -10 °C

Enthalpy change for 3 moles of water going to ice:

\[ q = n \Delta H_{Fusion} = 3 \times 6.01 \times 10^3 \text{ J/mol} = 1.803 \times 10^4 \text{ J} \]

\[ q_{water-ice} = -1.803 \times 10^4 \text{ J} \quad \text{ (must remove energy from water to freeze)} \]

\[ q_{surroundings} = 1.803 \times 10^4 \text{ J} \]

\[ \Delta S_{water-ice} = q / T = -1.803 \times 10^4 \text{ J} / 273.15 \text{ K} = -6.601 \text{ J/K} \]

\[ \Delta S_{surroundings} = 1.803 \times 10^4 \text{ J} / 263.15 \text{ K} = 6.852 \text{ J/K} \]

\[ \Delta S_{total} = \Delta S_{water-ice} + \Delta S_{surroundings} = 0.251 \text{ J/K} \]

\[ \Delta S_{total} > 0 \quad \text{so water spontaneously freezes when it is cold outside!} \]
What is total entropy change if 1 mole of ice melts sitting on your desk (298 K)?

\[ \Delta H_{\text{Fusion}} = 6.01 \times 10^3 \text{ J/mol} \]

0%  1.  \(-22.0 \text{ J/K}\)
13% 2.  \(-20.2 \text{ J/K}\)
7%  3.  \(-1.83 \text{ J/K}\)
78% 4.  \(1.83 \text{ J/K}\)
2%  5.  \(22.0 \text{ J/K}\)
Absolute Entropy
3rd Law of Thermodynamics

- Entropy is zero for a system with only one possible arrangement
  \[ S = k \ln W \quad \text{and} \quad \ln 1 = 0 \]
- Third Law of Thermodynamics: a pure, perfect crystal at 0 K has zero entropy.
  \[ S_{(\text{pure, perfect crystal; } T = 0 \text{ K})} = 0 \]
Standard Molar Entropy ($S^\circ$)

- Never 0

- More freedom to move means large entropy
  - Gas $S^\circ >$ Liquid $S^\circ >$ Solid $S^\circ$
  - Hot something $>$ cold something

- Things with more atoms or more particles have larger entropy
  - $C_6H_{14} > C_6H_6 > C_2H_6 > CH_4$
  - $2NO_2(g) > N_2O_4(g)$

- If otherwise similar, massive things have more entropy than tiny things
  - aircraft carrier $>$ car $>$ Ar $>$ He
Examples of $S^\circ$

<table>
<thead>
<tr>
<th>Substance</th>
<th>Phase</th>
<th>$S^\circ$ (J mol$^{-1}$K$^{-1}$)</th>
<th>Substance</th>
<th>Phase</th>
<th>$S^\circ$ (J mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Solid (diamond)</td>
<td>2.4</td>
<td>He</td>
<td>Gas</td>
<td>126.153</td>
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<tr>
<td>C</td>
<td>Solid (graphite)</td>
<td>5.74</td>
<td>Ar</td>
<td>Gas</td>
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<tr>
<td>Si</td>
<td>Solid</td>
<td>18.8</td>
<td>Xe</td>
<td>Gas</td>
<td>169.685</td>
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<tr>
<td>Al</td>
<td>Solid</td>
<td>28.3H</td>
<td>$H_2$</td>
<td>Gas</td>
<td>130.680</td>
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<tr>
<td>Cu</td>
<td>Solid</td>
<td>33.2</td>
<td>CO</td>
<td>Gas</td>
<td>197.660</td>
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<td>Ag</td>
<td>Solid</td>
<td>42.6F</td>
<td>$H_2$</td>
<td>Gas</td>
<td>202.79</td>
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<td>SiO$_2$</td>
<td>Solid</td>
<td>41.5</td>
<td>$Cl_2$</td>
<td>Gas</td>
<td>223.08</td>
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<td>NaCl</td>
<td>Solid</td>
<td>72.1</td>
<td>$CO_2$</td>
<td>Gas</td>
<td>213.78</td>
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<td>I$_2$</td>
<td>Solid</td>
<td>116.1</td>
<td>$CH_4$</td>
<td>Gas</td>
<td>184.3</td>
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<td>H$_2$O</td>
<td>Liquid</td>
<td>69.95</td>
<td>$C_2H_2$</td>
<td>Gas</td>
<td>200.9</td>
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<td>Hg</td>
<td>Liquid</td>
<td>75.9</td>
<td>$C_2H_4$</td>
<td>Gas</td>
<td>219.3</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>Liquid</td>
<td>152.2</td>
<td>$C_2H_6$</td>
<td>Gas</td>
<td>229.2</td>
</tr>
</tbody>
</table>

Table 14-2  Standard Molar Entropy at 298 K
Arrange in order from the most entropy to the least. (Assume all are gas phase at the same temp)

Note that all of these have 6 carbon atoms

A) 1 mole Hexane           B) 1 mole Cyclohexane
C) 1 mole Benzene          D) 2 moles Propane

1. A B C D
2. D A B C
3. C B A D
4. A D B C
Entropy and conditions

- $S$ increases at $T$ increases
- $S$ increases as available $V$ increases
  - $S$ decreases as concentration or partial pressure increase

\[
S_{(p \neq 1 \text{ bar})} = S^\circ - R \ln p
\]

\[
S_{(c \neq 1 \text{ M})} = S^\circ - R \ln c
\]

$p$ MUST be in bar and $c$ MUST be in molarity
Entropy Change During a Reaction

- Just \textit{products} – \textit{reactants}
- Exactly the same as Hess’s Law for $\Delta H$!

$$
\Delta S^\circ_{\text{reaction}} = \sum \text{coeff}_{\text{products}} S^\circ_{\text{products}} - \sum \text{coeff}_{\text{reactants}} S^\circ_{\text{reactants}}
$$

- Don’t forget to balance the equation before you start and then use the correct coefficients.
- Standard entropies are always given as J/mol K, so you must account for how many moles are reacting
For next time….

Consider the breakdown of glucose \( \text{C}_6\text{H}_{12}\text{O}_6(s) \)
into carbon dioxide \( (g) \) and water \( (l) \).

Calculate the standard molar entropy change

AND

The standard molar enthalpy change

Assume that all products and reactants are at STP

\[
\Delta H_f \alpha\text{-glucose} = -1274.5 \text{ kJ/mol}
\]

\[
\Delta S_f \alpha\text{-glucose} = 210.3 \text{ J/mol K}
\]

Don’t work alone!
Today

• Finish up CAPA #2

Friday

• Don’t be late to lecture
• Finish reading Chapt 14
• Go to seminar
• Make plans for attending the research celebration the following Friday (the 27\textsuperscript{th})