Lecture 6 – Chapter 14, Sections 5-6
Thermodynamics – Applied

- Nitrogenase
- Phase changes
- Bioenergetics
Nitrogen

- All organisms need nitrogen
- BUT triple bond in N\(_2\) is very hard to break
- Most organisms can only use NO\(_3^-\) or NH\(_3\)

- Why? Let’s look in terms of \(\Delta G\)
- What if we want to make a simple amino acid – glycine?
  - Start with something very similar – acetic acid – as reactant

\[
4\text{CH}_3\text{CO}_2\text{H} + 2\text{N}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{NCH}_2\text{CO}_2\text{H} + \text{O}_2
\]

\[
\Delta G_f^\circ(\text{H}_2\text{NCH}_2\text{CO}_2\text{H}) = -367 \text{ kJ/mol} \quad \Delta G_f^\circ(\text{O}_2) = 0 \text{ kJ/mol} \\
\Delta G_f^\circ(\text{CH}_3\text{CO}_2\text{H}) = -389 \text{ kJ/mol} \quad \Delta G_f^\circ(\text{N}_2) = 0 \text{ kJ/mol} \\
\Delta G_f^\circ(\text{H}_2\text{O}) = -237 \text{ kJ/mol}
\]
What is $\Delta G_{rxn}$ for the formation of glycine from $N_2$? (per mole of glycine)

$$4\text{CH}_3\text{CO}_2\text{H} + 2\text{N}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{NCH}_2\text{CO}_2\text{H} + \text{O}_2$$

$\Delta G_f^\circ(\text{H}_2\text{NCH}_2\text{CO}_2\text{H}) = -367 \text{ kJ/mol}$

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$\Delta G_f^\circ(\text{O}_2) = 0 \text{ kJ/mol}$

$\Delta G_f^\circ(\text{N}_2) = 0 \text{ kJ/mol}$

25% 1. 64.8 kJ/ mol

25% 2. 141 kJ/mol

25% 3. 259 kJ/mol

25% 4. 562 kJ/mol
Ammonia better than N$_2$

- If we do the same thing, but use ammonia as our N-source
  \[ \text{CH}_3\text{CO}_2\text{H} + \text{NH}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{NCH}_2\text{CO}_2\text{H} + \text{H}_2\text{O} \]
  \[ \Delta G_{rxn} = -198 \text{ kJ/mol} \]

- So, production of ammonia is big business – fertilizer
  – 5 of the top 15 industrial chemicals (in amount produced) are primarily used in fertilizer production

- Industrial ammonia is made from N$_2$ and H$_2$ gases
  \[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \quad \Delta G_{rxn} = -32.8 \text{ kJ/mol} \]
H$_2$ gas is tough

- H$_2$ gas is rare on earth – must be manufactured
- Made from methane (‘natural gas’ mostly methane)

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

\[ \Delta H^\circ_{\text{rxn}} = +205.9 \text{ kJ/mol} \]
\[ \Delta S^\circ_{\text{rxn}} = +214.6 \text{ J/mol·K} \]

\[ \Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} = 205.9 \text{ kJ/mol} - (298 \text{ K})(0.2146 \text{ kJ/mol·K}) \]

\[ \Delta G^\circ_{\text{rxn}} = +142 \text{ kJ/mol} \]
Using \( \Delta G_{\text{rxn}} = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ \)
and \( \Delta H_{\text{rxn}}^\circ = +205.9 \text{ kJ/mol} \)
\( \Delta S_{\text{rxn}}^\circ = +214.6 \text{ J/mol} \cdot \text{K} \)

At what temperature does the reaction become spontaneous?

25% 1. 0.9595 K
25% 2. 8.7 K
25% 3. 959.5 K
25% 4. 1042 K
Nitrogen Fixation

• So, NH$_3$ production is expensive because H$_2$ needs lots of heat

• Sources of ‘fixed’ nitrogen:
  – 1% is N$_2$ converted to NO$_3^-$ by lightning
  – 30 % is man-made – N$_2$ converted to NH$_3$ for fertilizer
  – 70 % is N$_2$ converted to NH$_3$ by bacteria – nitrogenase
Phase Changes

- The spontaneous direction of a phase change depends on pressure
- This is obvious for the liquid-vapor equilibrium
  - Free energy (entropy) of vapor depends strongly on pressure
- At any temperature, there is some pressure at which $\Delta G_{\text{vap}} = 0$. 
Clausius-Clapeyron Equation

\[ \ln \nu p = -\frac{\Delta H_{vap}}{RT} + \frac{\Delta S^o_{vap}}{R} \]

- Describes pressure-dependence of liquid-vapor phase line
- For instance look at normal boiling of water: \( \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \)

\[ \Delta H^o_{f \text{H}_2\text{O}(l)} = -285.83 \text{ kJ/mol} \]

\[ \Delta H^o_{f \text{H}_2\text{O}(g)} = -241.83 \text{ kJ/mol} \]

\[ \Delta S^o_{\text{H}_2\text{O}(l)} = 69.95 \text{ J/mol·K} \]

\[ \Delta S^o_{\text{H}_2\text{O}(g)} = 188.835 \text{ J/mol·K} \]

\[ \Delta H^o_{\text{vap}} = (-241.83 \text{ kJ/mol}) - (-285.83 \text{ kJ/mol}) = 44.00 \text{ kJ/mol} \]

\[ \Delta S^o_{\text{vap}} = (188.835 \text{ J/mol·K}) - (69.95 \text{ J/mol·K}) = 118.89 \text{ J/mol·K} \]

\[ \ln \nu p = -\frac{44,000 \text{ J/mol}}{(8.314 \text{ J/mol·K})(373.15 \text{ K})} + \frac{118.89 \text{ J/mol·K}}{8.314 \text{ J/mol·K}} = 0.1167 \]

\[ \nu p = 1.124 \text{ bar} \]
We got 1.124 bar, but actual answer is 1 atm = 1.013 bar. What’s the deal?

<table>
<thead>
<tr>
<th>%</th>
<th>1. The $\Delta H_{vap}^\circ$ isn’t very accurate anymore at 373 K</th>
<th>2. The $\Delta S_{vap}^\circ$ isn’t very accurate anymore at 373 K</th>
<th>3. The $\Delta G_{vap}^\circ$ is not actually 0 when water is boiling at 373 K</th>
<th>4. The Clausius-Clapeyron equation isn’t valid for water</th>
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<tbody>
<tr>
<td>25%</td>
<td>1.</td>
<td>2.</td>
<td>3.</td>
<td>4.</td>
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</table>
\( \Delta G \) is the currency for biological reactions

- Glucose oxidation gives off energy \( \Rightarrow \Delta G_{\text{rxn}}^\circ = -2870 \text{ kJ/mol} \)
- Used to convert ADP into ATP \( \Rightarrow \Delta G_{\text{rxn}}^\circ = +30.6 \text{ kJ/mol} \)

- ATP is easily transported and easily hydrolyzed back into ADP
- Each mole of ATP provides 30 kJ of energy to do biological work

- Note that 1 mole of glucose (2870 kJ) should yield over 90 moles of ATP
  - In reality the yield is only about 36 moles of ATP – significant loss
Glucose comes from the sun, or maybe the air.
Today

• Finish CAPA #3

Wednesday

• Dive into Chapt 15
• Fall in love with kinetics
• Start CAPA #4