Definition of the enthalpy

The internal energy change is valid at constant volume

\[ \Delta E = q + w \]

The work is

\[ w = -P\Delta V \]

The enthalpy is a constant pressure function. As such it includes the work term for expansion against the atmosphere.

\[ \Delta H = \Delta E + P\Delta V \]

We often use enthalpy instead of internal energy under normal conditions because it includes the work automatically.
The specific heat

If we heat a substance, then its temperature will increase. The specific heat is a measure of how much heat it will take to increase one gram of the substance by 1 °C.

\( s \), the specific heat, has units of J/g·°C.

The heat transferred is \( q \), and this quantity can be positive or negative depending on whether the temperature of the system increases or decreases (see sign convention).

\[
q = ms\Delta T
\]

where \( m \) is the mass. The sign convention is actually built in. If the system temperature increases then \( DT > 0 \) and \( q > 0 \). If the system temperature decreases then \( DT < 0 \) and \( q < 0 \).
The Sign Convention

We can summarize the sign convention in the following table.

<table>
<thead>
<tr>
<th></th>
<th>+ (increased)</th>
<th>- (decreased)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Work done (w)</td>
<td>on system</td>
<td>by system</td>
</tr>
<tr>
<td>Heat flows (q)</td>
<td>into system</td>
<td>from system</td>
</tr>
</tbody>
</table>

Alternatively, we can depict the convention as follows.

\[ w < 0 \quad w > 0 \quad q < 0 \quad q > 0 \]
Relationship between enthalpy and internal energy

\[ \Delta_{\text{vap}} H = 44.0 \text{ kJ/mol for water at 25 } ^\circ\text{C.} \]

What is \( \Delta E \)?
Relationship between enthalpy and internal energy

$\Delta_{\text{vap}} H = 44.0 \text{ kJ/mol}$ for water at 25 °C.

What is $\Delta E$?

Solution:

$$\Delta \tilde{H} = \Delta \tilde{E} + P \Delta \tilde{V}$$
Relationship between enthalpy and internal energy

$\Delta_{\text{vap}} H = 44.0 \text{ kJ/mol}$ for water at $25 \, ^0\text{C}$.

What is $\Delta E$?

Solution: We can write the molar enthalpy using a bar

$$\Delta \bar{H} = \Delta \bar{E} + P \Delta \bar{V}$$

We recognize that

$$P \bar{V} = RT$$

and

$$\Delta \bar{H} = \Delta \bar{E} + RT$$

so

$$\Delta \bar{E} = \Delta \bar{H} - RT$$
Relationship between enthalpy and internal energy

$\Delta_{\text{vap}} H = 44.0 \text{ kJ/mol}$ for water at 25 °C. What is $\Delta E$?

Solution:

$$\Delta \bar{H} = \Delta \bar{E} + P \Delta \bar{V}$$

Now, plug in the numbers

$$\Delta \bar{E} = 44 \frac{kJ}{mol} - \left( 8.31 \frac{J}{molK} \right)(298 K)$$

$$\Delta \bar{E} = 44,000 \frac{J}{mol} - 2,480 \frac{J}{mol}$$

$$\Delta \bar{E} = 41,520 \frac{J}{mol}$$
Statistical definition of entropy

The statistical entropy was defined on a molecular basis using the Boltzmann constant $k_B$, where

$$k_B = \frac{R}{N_A}$$

The entropy is

$$S = k_B \ln W$$

Maximizing the distribution of molecules among the energy states maximizes the energy. The number of ways that $N$ Particles can be put into states with configurations $n_i$ is:

$$W = \frac{N!}{\prod_i n_i!}$$

The total number of possible states is

$$W = M^N$$
Statistical distribution in energy levels

The weight is

\[ W = \frac{N!}{\prod_i n_i!} \]

where the exclamation sign is the factorial.
Statistical distribution in energy levels

The weight is

$$W = \frac{N!}{\prod_i n_i!}$$

where the exclamationation sign is the factorial.

_______  W is greater

_______  at a given T

_______  if levels are

_______  more closely

_______  spaced
Statistical distribution
Statistical distribution

The weight is

\[ W = \frac{N!}{\prod_i n_i!} \]

\[ W = \frac{6!}{3! \cdot 2! \cdot 1! \cdot 0!} = 60 \]
The entropy is

\[ S = k_B \ln W = \left(1.38 \times 10^{-23} \frac{J}{K}\right) \ln(60) \]

\[ = 5.65 \times 10^{-23} \frac{J}{K} \]
The molar entropy is

\[ S = R \ln W = \left( 8.31 \frac{J}{\text{molK}} \right) \ln(60) \]

\[ S = 34 \frac{J}{\text{molK}} \]
Classical definition of entropy

The classical definition of entropy change is the heat transferred per unit temperature.

\[ \Delta S \geq \frac{q}{T} \]

The equal sign applies to reversible (equilibrium) changes. The greater-than sign applies to irreversible changes. A special case of equilibrium is a phase change. Since \( \Delta G = 0 \), and the latent heat of the phase change is the enthalpy change (\( q = \Delta H \)). We have,

\[ \Delta S = \frac{\Delta H}{T} \]
Thermodynamic Efficiency

We define the efficiency as the work extracted divided by the total heat input.

\[
\text{efficiency} = \frac{\text{work done}}{\text{heat used}}
\]

\[
\eta = \frac{|w_{\text{total}}|}{q_{\text{input}}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}
\]
Calculate the entropy starting at \( S = 0 \) at \( T = 0 \) K.
Equilibration

The heat capacity is $C_p = ms$ ($m = \text{mass}$, $s = \text{specific heat}$)

$q_1 = -q_2$

$$C_{p,1}(T_{eq} - T_1) = -C_{p,2}(T_{eq} - T_2)$$

Now we solve for the equilibrium temperature $T_{eq}$.

$$T_{eq}(C_{p,1} + C_{p,2}) = C_{p,1}T_1 + C_{p,2}T_2$$

$$T_{eq} = \frac{C_{p,1}T_1 + C_{p,2}T_2}{C_{p,1} + C_{p,2}}$$
Equilibration

The heat capacity is $C_p = ms$ (m = mass, s = specific heat)

$q_1 = -q_2$

$m_1 s_1 (T_{eq} - T_1) = -m_2 s_2 (T_{eq} - T_2)$

Now we solve for the equilibrium temperature $T_{eq}$.

$$(m_1 s_1 + m_2 s_2)T_{eq} = m_1 s_1 T_1 + m_2 s_2 T_2$$

$$T_{eq} = \frac{m_1 s_1 T_1 + m_2 s_2 T_2}{m_1 s_1 + m_2 s_2}$$
Equilibration

To measure the specific heat of a compound we can heat it and then add it to water. By measuring the temperature change we can obtain the unknown specific heat.
Equilibration

Example: An unknown sample with a mass of 2 grams is heated to 180 °C and then added to 100 grams water at 25 °C. The water heats to 27 °C. What is the specific heat of the unknown?
Equilibration

Example: An unknown sample with a mass of 2 grams is heated to 180 °C and then added to 100 mg water at 25 °C. The water heats to 27 °C.

Use the heat transfer equation.

\[ m_1 s_1 (T_{eq} - T_1) = -m_2 s_2 (T_{eq} - T_2) \]

Now we solve for the unknown \( s_1 \).

\[ s_1 = -\frac{m_2 s_2 (T_{eq} - T_2)}{m_1 (T_{eq} - T_1)} \]

Insert the values from the given information.

\[ s_1 = -\frac{(100)(4.184)(27 - 25)}{2(27 - 180)} = 2.73 \ \frac{J}{g - K} \]
Alternative form for free energy

Since

\[ \Delta G = \Delta G^\circ + RT \ln Q \]

And

\[ \Delta G^\circ = -RT \ln K \]

we can also write

\[ \Delta G = -RT \ln K + RT \ln Q \]

which can be rearranged to

\[ \Delta G = RT \ln \left( \frac{Q}{K} \right) \]
Standard state

We can tabulate the values of free energy, $\Delta G^o$, and enthalpy, $\Delta H^o$, at a standard concentration. The standard state is

1 atmosphere of pressure for a gas
1 molar of concentration for a solution

We do not include solids in the definition of standard state. Note that the free energy, $\Delta G^o$, and the enthalpy $\Delta H^o$, both have the same standard state.

The free energy of formation follows the same definition for the reference state as the enthalpy. $\Delta_f G^o = 0$ for elements in their most stable chemical form.
Definition of free energy of formation

The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of that substance from its component elements, at their standard states.

The standard state is defined as the most stable form of the element at 25 degrees Celsius and 1 bar.

The symbol is $\Delta_f G^\circ$. All elements in their standard states ($O_2$, graphite, Hg liquid etc.) have 0 standard Gibbs free energy change of formation, as there is no change involved.
Example of free energy of formation

We consider the reaction

\[ N_2(g) + O_2(g) \leftrightarrow 2NO(g) \]

The data for NO from thermodynamic tables are:

\[ \Delta_f H^o = 90.1 \text{ kJ/mol} \quad \Delta_f G^o = 86.6 \text{ kJ/mol} \quad S^o = 209.8 \text{ J/molK} \]

The data for O\(_2\) and N\(_2\) are:

\[ S^o = 205.1 \text{ J/molK} \quad S^o = 191.6 \text{ J/molK} \]

The use the following forms of enthalpy and entropy:

\[ \Delta_{rxn} H^o = 2\Delta_f H^o(NO) - \Delta_f H^o(O_2) - \Delta_f H^o(N_2) \]

\[ \Delta_{rxn} S^o = 2S^o(NO) - S^o(O_2) - S^o(N_2) \]
Example of free energy of formation

We consider the reaction

\[ N_2(g) + O_2(g) \leftrightarrow 2NO(g) \]

The enthalpy of reaction is twice the enthalpy of formation since the reaction produces two moles of NO:

\[ \Delta_{rxn}H^o = 2\Delta_fH^o = 2(90,100 \text{ J/mol}) \]

Note that the enthalpies of formation of O\(_2\) and N\(_2\) are 0.

\[
\Delta_{rxn}S^o = 2 \left( 209.80 \frac{J}{\text{mol} \cdot \text{K}} \right) - 205.1 \frac{J}{\text{mol} \cdot \text{K}} - 191.6 \frac{J}{\text{mol} \cdot \text{K}} \\
= 22.9 \frac{J}{\text{mol} \cdot \text{K}}
\]

\[ \Delta_{rxn}G^o = 180,200 - (300K) \left( 22.9 \frac{J}{\text{mol} \cdot \text{K}} \right) \\
= 173,300 \text{ J/mol} \]
Example of free energy of formation

We consider the reaction

\[ N_2(g) + O_2(g) \leftrightarrow 2NO(g) \]

If we now compare the free energy calculated from the Enthalpy of formation and the absolute entropy on a per mole basis (i.e. divide by two to get the equation that corresponds to the formation reaction),

\[ \Delta_{rxn}G^o = 173,300 \text{ J/mol} \]

It compares perfectly with the tabulated free energy of formation

\[ \Delta_fG^o = 86.6 \text{ kJ/mol} \]
Conditions for Spontaneity

There are four possible combinations of the sign of $\Delta H$ and $\Delta S$ in the Gibbs free energy change:

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>Description of process</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;0</td>
<td>&gt;0</td>
<td>Endothermic, spontaneous for $T &gt; \Delta H/\Delta S$</td>
</tr>
<tr>
<td>&lt;0</td>
<td>&lt;0</td>
<td>Exothermic, spontaneous for $T &lt; \Delta H/\Delta S$</td>
</tr>
<tr>
<td>&lt;0</td>
<td>&gt;0</td>
<td>Exothermic, spontaneous for all $T$</td>
</tr>
<tr>
<td>&gt;0</td>
<td>&lt;0</td>
<td>Never spontaneous</td>
</tr>
</tbody>
</table>

Wertz uses the word extensive to apply the idea of $\Delta H^o$ and $\Delta S^o$:

<table>
<thead>
<tr>
<th>$\Delta H^o$</th>
<th>$\Delta S^o$</th>
<th>Description of process</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;0</td>
<td>&gt;0</td>
<td>Endothermic, extensive for $T &gt; \Delta H^o/\Delta S^o$</td>
</tr>
<tr>
<td>&lt;0</td>
<td>&lt;0</td>
<td>Exothermic, extensive for $T &lt; \Delta H^o/\Delta S^o$</td>
</tr>
<tr>
<td>&lt;0</td>
<td>&gt;0</td>
<td>Exothermic, extensive for all $T$</td>
</tr>
<tr>
<td>&gt;0</td>
<td>&lt;0</td>
<td>Never extensive</td>
</tr>
</tbody>
</table>
Calculating $\Delta G$ and $\Delta G^\circ$

The free energy is

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where $Q$ is defined from the sample reaction

$$a \, A + b \, B \leftrightarrow x \, X + y \, Y$$

As

$$Q = \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Under standard conditions

$$Q = \frac{[1M]^x[1M]^y}{[1M]^a[1M]^b} = 1$$

and

$$\Delta G = \Delta G^\circ$$
The temperature dependence of $\Delta G^\circ$

As we have shown previously, $\Delta G$, will decrease until it reaches 0. Then we have reached equilibrium. The equilibrium condition is

$$\Delta G^\circ = -RT \ln K$$

If we assume that $\Delta H^\circ$ and $\Delta S^\circ$ are independent of temperature, then we can write,

$$\Delta H^\circ - T_1 \Delta S^\circ = -RT_1 \ln K_1$$
$$\Delta H^\circ - T_2 \Delta S^\circ = -RT_2 \ln K_2$$

We can divide by temperature and subtract temperature $T_2$ from $T_1$ to obtain.

$$\Delta H^\circ \left(1/T_1 - 1/T_2\right) = -R \ln(K_1/K_2)$$

$$\ln(K_2/K_1) = -\Delta H^\circ / R \left(1/T_2 - 1/T_1\right)$$
The temperature dependence of $\Delta G^o$

Then we can divide each equation by its respective temperature to obtain,

\[
\frac{\Delta H^o}{T_1} - \Delta S^o = -R \ln K_1 \\
\frac{\Delta H^o}{T_2} - \Delta S^o = -R \ln K_2
\]

We subtract temperature $T_2$ from $T_1$.

\[
\Delta H^o \left(\frac{1}{T_1} - \frac{1}{T_2}\right) = -R \ln \left(\frac{K_1}{K_2}\right)
\]

\[
\ln \left(\frac{K_2}{K_1}\right) = -\Delta H^o / R \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

This equation says that if we plot $\ln(K)$ vs $1/T$, we obtain a line, and the slope of that line is $-\Delta H^o / R$. 
Using equilibrium data to obtain \( \Delta H^\circ \) and \( \Delta S^\circ \)

Solution: starting with the equation

\[
\ln \left( \frac{K_2}{K_1} \right) = - \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Solve for \( \Delta H^\circ \)

\[
\Delta H^\circ = \frac{-R \ln \left( \frac{K_2}{K_1} \right)}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)}
\]

We can make a plot if we have more than two data points.
Temperature dependent problem

If the equilibrium constant increases by factor of two between 290 and 300 K, calculate $\Delta H^o$ for the reaction.
Temperature dependent problem

If the equilibrium constant increases by factor of two between 290 and 300 K, calculate $\Delta H^o$ for the reaction.

\[
\ln \left( \frac{K_2}{K_1} \right) = - \frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\Delta H^o = \frac{-R \ln \left( \frac{K_2}{K_1} \right)}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)}
\]

\[
\Delta H^o = \frac{-(8.31 \frac{J}{molK}) \ln(2)}{\left( \frac{1}{300K} - \frac{1}{290K} \right)} = 50.1 \text{ kJ/mol}
\]
Calculating equilibrium values

If the equilibrium constant is very large or very small, this tells us that the equilibrium lies far to the right (products) or left (reactants), respectively.

If the equilibrium constant is somewhere between 0.001 and 1000, then significant concentrations of both reactants and products will be present at equilibrium.

We can calculate the equilibrium amounts using the ICE method. Set up a table with Initial, Change, and Equilibrium values of concentration.
Application to Haber-Bosch

For example, if we consider the important Haber-Bosch process (think about how important this is next time you eat food!). To catalyze the reaction:

\[
\frac{1}{2} \text{N}_2 (g) + \frac{3}{2} \text{H}_2 (g) \rightarrow \text{NH}_3(g)
\]

We must both heat and apply high pressure. While heating is essential to accelerate the kinetics, it actually shifts the equilibrium unfavorably. Let’s first consider both the temperature dependent equilibrium and ICE analysis to understand the competing factors in this reaction.
Equilibrium shift in Haber-Bosch

Let’s consider the ICE analysis for this process. Assuming we have 0.8 atom N\(_2\), 2.4 atm H\(_2\) and no NH\(_3\) initially, what are the equilibrium pressures.

\[
\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \leftrightarrow NH_3(g)
\]

<table>
<thead>
<tr>
<th>ICE</th>
<th>N(_2)</th>
<th>H(_2)</th>
<th>NH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.8</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-0.5x</td>
<td>-1.5x</td>
<td>x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.8-0.5x</td>
<td>2.4-1.5x</td>
<td>x</td>
</tr>
</tbody>
</table>

Insert the equilibrium values into K and solve for x:

\[
K = \frac{P_{NH_3}}{P^{1/2}_{N_2}P^{3/2}_{H_2}}
\]
Equilibrium shift in Haber-Bosch

\[ K = \frac{x}{(0.8 - 0.5x)^2 (2.4 - 1.5x)^2} \]

\[ K = \frac{1}{3^{3/2}} \frac{x}{(0.8 - 0.5x)^2} \]

\[ K(0.64 - 0.8x + 0.25x^2) = \frac{x}{3^{3/2}} \]

\[ 0.64 - \left(0.8 + \frac{0.192}{K}\right)x + 0.25x^2 = 0 \]

\[ x = \left(0.8 + \frac{0.192}{K}\right) \pm \sqrt{\left(0.8 + \frac{0.192}{K}\right)^2 - 0.64} \]

\[ \frac{0.5}{0.5} \]
Equilibrium shift in Haber-Bosch

Suppose we heat the system up to the temperature where the equilibrium constant is $K = 1$.

\[
x = \frac{0.8 + \frac{0.192}{K}}{0.5} \pm \sqrt{\left(0.8 + \frac{0.192}{K}\right)^2 - 0.64}
\]

\[
x = \frac{0.992 \pm \sqrt{0.992^2 - 0.64}}{0.5}
\]

\[
x = \frac{0.992 \pm 0.5865}{0.5}
\]

\[x = 3.2 \text{ or } 0.8
\]

\[P_{N_2} = 0.4 \text{ atm}; \ P_{H_2} = 1.2 \text{ atm}; \ P_{NH_3} = 0.8 \text{ atm}
\]
Equilibrium shift in Haber-Bosch

The enthalpy and entropy of this reaction are $\Delta_{rxn}^{o}H^{o} = -45.9 \text{ kJ/mol}$ and $\Delta_{rxn}^{o}S^{o} = -55.9 \text{ J/mol-K}$. If we heat the reaction to 500 K the equilibrium shifts in an unfavorable direction. Let’s investigate.

$$\Delta_{rxn}^{o}G^{o} = \left(-45,900 \frac{J}{mol}\right) - (500 \text{ K})\left(-55.9 \frac{J}{molK}\right)$$

$$\Delta_{rxn}^{o}G^{o} = -17.9 \text{ kJ/mol}$$

$$K = \exp\left\{-\frac{\Delta_{rxn}^{o}G^{o}}{RT}\right\} \quad K = \exp\left\{-\frac{-17900}{(8.31)(500)}\right\}$$

$$K = 74$$

This is much smaller than the value of 191,000 at 298 K. But, heating is required so...
Actually, the change in the equilibrium constant is not as bad as you might think. Obviously, this has been studied quite carefully. The temperature 500 K was chosen since it is below the crossover temperature (can you use $\Delta_{\text{rxn}}H^0$ and $\Delta_{\text{rxn}}S^0$ to calculate it?). We can see the effect of the change of equilibrium constant for 191,000 to 74 by using the equation:

$$K = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}}$$
Equilibrium shift in Haber-Bosch

In the last lecture we showed that a general expression for the reaction progress variable is:

\[
x = \frac{0.8 + \frac{0.192}{K}}{0.5} \pm \sqrt{\left(0.8 + \frac{0.192}{K}\right)^2 - 0.64}
\]

If \( K = 191,600 \)

\[
x = \frac{0.800001 \pm \sqrt{0.800001^2 - 0.64}}{0.5}
\]

\[x = 1.597 \text{ or } 1.603\]

\[P_{N_2} = 0.0015 \text{ atm} ; \ P_{H_2} = 0.0045 \text{ atm} ; \ P_{NH_3} = 1.597 \text{ atm}\]

If \( K = 74 \)

\[
x = \frac{0.80042 \pm \sqrt{0.80042^2 - 0.64}}{0.5}
\]

\[x = 1.548 \text{ or } 1.652\]

\[P_{N_2} = 0.026 \text{ atm} ; \ P_{H_2} = 0.078 \text{ atm} ; \ P_{NH_3} = 1.548 \text{ atm}\]
Equilibrium shift in Haber-Bosch

Up to this point we have assumed that the pressure is not constant. However, if we wish to apply a constant pressure then we can write the equilibrium constant as:

\[
K = \frac{X_{\text{NH}_3}}{X_{\text{N}_2}^{1/2} X_{\text{H}_2}^{3/2}} \frac{1}{P_{\text{tot}}}
\]

Thus, the ratio of mole fractions is:

\[
KP_{\text{tot}} = \frac{X_{\text{NH}_3}}{X_{\text{N}_2}^{1/2} X_{\text{H}_2}^{3/2}}
\]
Applying Haber-Bosch at Constant P

The reaction:

\[
\frac{1}{2} \text{N}_2 (g) + \frac{3}{2} \text{H}_2 (g) \rightarrow \text{NH}_3 (g)
\]

has the following ICE table:

<table>
<thead>
<tr>
<th>ICE</th>
<th>( \text{N}_2 )</th>
<th>( \text{H}_2 )</th>
<th>( \text{NH}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P Initial</td>
<td>0.8</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>P Change</td>
<td>-0.5x</td>
<td>-1.5x</td>
<td>x</td>
</tr>
<tr>
<td>P Equil.</td>
<td>0.8-0.5x</td>
<td>2.4-1.5x</td>
<td>x</td>
</tr>
<tr>
<td>x Equil.</td>
<td>( \frac{0.8-0.5x}{3.2-x} )</td>
<td>( \frac{2.4-1.5x}{3.2-x} )</td>
<td>( \frac{x}{3.2-x} )</td>
</tr>
</tbody>
</table>

Note that we converted to mole fraction on the bottom row. We used the fact that the total pressure is

\[
P_{\text{tot}} = 0.8 - 0.5x + 2.4 - 1.5x + x
\]

Therefore, \( P_{\text{tot}} = 3.2 - x \)
When we substitute the mole fractions into:

\[ KP_{\text{tot}} = \frac{X_{\text{NH}_3}}{X_{\text{N}_2}^{1/2} X_{\text{H}_2}^{3/2}} \]

We have:

\[ KP_{\text{tot}} = x(3.2 - x) \]

\[ (0.8 - 0.5x)^2 (2.4 - 1.5x)^2 \]

And the solution is:

\[ x = \frac{(0.8 + 0.614) \pm \sqrt{(0.8 + 0.614)^2 - 0.64 \left(0.25 + \frac{0.768}{KP_{\text{tot}}}ight)}}{2 \left(0.25 + \frac{0.192}{KP_{\text{tot}}}ight)} \]

as \( P_{\text{tot}} \) increases \( x \) approaches the maximum value of 1.6 atm. This is Le Chatelier’s principle in a single mathematical equation.
The conversion from glucose to mannose occurs via an epimerization and is known as the Lobry de Bruyn-van Ekenstein transformation.

\[ \Delta_f G^o = -910.5 \text{ kJ/mol} \quad \text{and} \quad \Delta_f G^o = -904.2 \text{ kJ/mol} \]

Given the free energies of formation, and assuming an initial concentration of 0.2 M mannose, what is the final concentration of glucose at equilibrium? What is the percent conversion from mannose to glucose?
Lobry de Bruyn–van Ekenstein transformation

The reaction is:

\[ \text{Glucose} \overset{\leftrightarrow}{\longrightarrow} \text{Mannose} \]

Step 1. Calculate the free energy change for the reaction.

\[ \Delta_{rxn} G^o = -904.2 - (-910.5) \text{ kJ/mol} \]

\[ \Delta_{rxn} G^o = +6.3 \text{ kJ/mol} \]
Lobry de Bruyn–van Ekenstein transformation

The reaction is:

\[
\text{Glucose} \rightleftharpoons \text{Mannose}
\]

Step 1. Calculate the free energy change for the reaction.

\[
\Delta_{\text{rxn}} G^o = -904.2 - (-910.5) \text{ kJ/mol} \\
\Delta_{\text{rxn}} G^o = +6.3 \text{ kJ/mol}
\]

Step 2. Calculate the equilibrium constant

\[
K = \exp \left\{ -\frac{\Delta_{\text{rxn}} G^o}{RT} \right\} \quad K = \exp \left\{ -\frac{6300}{(8.31)(298)} \right\} \quad K = 0.0785
\]
Lobry de Bruyn–van Ekenstein transformation

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\]

Step 3. Create an ICE table.

<table>
<thead>
<tr>
<th></th>
<th>Glucose</th>
<th>Mannose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Change</td>
<td>x</td>
<td>-x</td>
</tr>
<tr>
<td>Equil.</td>
<td>x</td>
<td>0.2 - x</td>
</tr>
</tbody>
</table>
The reaction is:

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\]

Step 4. Substitute the values from the ICE table into the equilibrium constant.

\[
K = \frac{[\text{mannose}]}{[\text{glucose}]}
\]

Step 5. Solve for \(x\). This is the glucose concentration.

\[
K = \frac{(0.2 - x)}{x} \quad (K + 1)x = 0.2 \quad x = \frac{0.2}{K + 1}
\]

\[
x = \frac{0.2}{1.0785} = 0.185 \text{ M}
\]

The concentration of glucose is 0.185 M. This is 92.5% conversion from mannose to glucose.