There are two contributions to the spontaneity of a chemical reaction. These contributions are enthalpy and entropy. Spontaneous (spontaneity) mean that a reaction will happen, but not necessarily at a fast rate!

a) A decrease in enthalpy is a favorable contribution toward the spontaneity of a chemical reaction.

A decrease in Enthalpy means \( \Delta H < 0 \), \( \Delta H \) is a negative number, the reaction is exothermic, \( H_F < H_I \), and the reaction is going toward a more stable energy state.

b) An increase in entropy is a favorable contribution toward the spontaneity of a chemical reaction.

An increase in entropy means \( \Delta S > 0 \), \( \Delta S \) is a positive number, the reaction is going from order to disorder (O-->D), and \( S_F > S_I \).

The spontaneity of a reaction depends on the balance between these two effects, enthalpy and entropy. The net effect of enthalpy and entropy contributions is measured in the free energy function.

\[
\text{Free Energy Change} = \Delta G = \Delta H - T \Delta S
\]

Note that:

\( \Delta H < 0 \), a negative number, is a favorable contribution to spontaneity

\( \Delta S > 0 \), a positive number, is a favorable contribution to spontaneity.

Therefore, \( \Delta G = \text{negative number} - T \text{ (positive number)} \) must be \(< 0\) for a spontaneous chemical reaction.
Since the entropy and enthalpy both can be positive or negative, there are four possible cases to be considered in the combining of entropy and enthalpy.

Table 1

<table>
<thead>
<tr>
<th>Case</th>
<th>ΔH</th>
<th>ΔS</th>
<th>-T ΔS</th>
<th>ΔG = ΔH - T ΔS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-, exo, favorable</td>
<td>+, O→D, favorable</td>
<td>-</td>
<td>- @ all Temperatures and favorable @ all Temperatures</td>
</tr>
<tr>
<td>2</td>
<td>-, exo, favorable</td>
<td>-, D→O, unfavorable</td>
<td>+</td>
<td>- @ Lower Temperatures and favorable @ lower Temperatures + @ Higher Temperatures and unfavorable @ higher Temperatures</td>
</tr>
<tr>
<td>3</td>
<td>+, endo, unfavorable</td>
<td>+, O→D, favorable</td>
<td>-</td>
<td>+ @ Lower Temperatures and unfavorable @ lower Temperatures - @ Higher Temperatures and favorable @ higher Temperatures</td>
</tr>
<tr>
<td>4</td>
<td>+, endo, unfavorable</td>
<td>-, D→O, unfavorable</td>
<td>+</td>
<td>+ @ all Temperatures and unfavorable @ all Temperatures</td>
</tr>
</tbody>
</table>

Note that:

- ΔG < 0  Spontaneous forward (Reactants --> Products)
- ΔG = 0  At equilibrium (Reactants <---> Products)
- ΔG > 0  Spontaneous in reverse (Reactants <-- Products)

So, how does one get the values of ΔH and ΔS for a chemical reaction? Well, there are two methods: measure their values in the laboratory or calculate from the laboratory measurements of others. The latter is most common and will be considered in this paper.
The enthalpy and entropy changes for a chemical reaction can be calculated from molar heats of formation and third law molar entropies.

\[ \Delta H^0_{\text{reaction}} = \sum \gamma_i H^o_f (\text{Products}) - \sum \gamma_j H^o_f (\text{Reactants}) \]

\[ \Delta S^0_{\text{reaction}} = \sum \gamma_i S^o_f (\text{Products}) - \sum \gamma_j S^o_f (\text{Reactants}) \]

where \( H^o_f \) and \( S^o_f \) are the molar heats of formation and entropies, respectively, and \( \gamma_i \) and \( \gamma_j \) coefficients in the chemical reaction.

So, where does one get molar heat of formation and molar entropies? Well, molar heats of formation and molar entropies are typically found in the appendix or body of texts of books in a table format. Perhaps a few comments on the origin of the molar heats of formation and molar entropies may be appropriate at this point.

Molar heats of formation are based on a standard state which assigns a value of zero to the molar heats of formation of the elements in their most stable form at 1 atm pressure and 298 K. Molar heats of formation are typically assigned a symbol of \( \Delta H^0_f \) or just \( H^0_f \).

The molar enthalpies of compounds are calculated from the standard states of their elements. Consider one simple example, the formation of ammonia gas. The heat of reaction for the formation of ammonia is measured at -46.19 kJ/mole of ammonia formed at 298 K and 1 atm.

\[ \frac{3}{2} \text{H}_2 (g) + \frac{1}{2} \text{N}_2 (g) \longrightarrow \text{NH}_3 (g); \Delta H^0_{\text{reaction}}(298 \text{ K}) = -46.19 \text{ kJ/mole} \]

\[ \Delta H^0_{\text{reaction}} = \sum \gamma_i H^o_f (\text{Products}) - \sum \gamma_j H^o_f (\text{Reactants}) \]

where \( \gamma_i \) and \( \gamma_j \) are reaction coefficients and the superscripted little "o" means at 1 atm pressure.

\[ \Delta H^0_{\text{reaction}} = -46.19 \text{ kJ/mole} = H^o_f (\text{NH}_3) - \frac{3}{2} H^o_f (\text{H}_2) - \frac{1}{2} H^o_f (\text{N}_2) \]

so, if both \( H^o_f (\text{H}_2) \) and \( H^o_f (\text{N}_2) \) are assigned values of zero and one has the measured value for the formation of ammonia from its elements, then \( H^o_f (\text{NH}_3) \) must be -46.19 kJ/mole.
The molar entropies of elements and compounds are based on a standard state that is described by the third law of thermodynamics: all elements and compounds in a perfect crystal at 0 K have entropies of zero. The entropy of a substance at 298 K is simply the entropy change that takes place when that substance is raised in temperature from 0 K to 298 K.

$$\Delta S^o(0 K \rightarrow 298 K) = S^o_f \text{(compound @ 298 K)} - S^o_f \text{(compound @ 0 K)}$$

but $$S^o_f \text{(compound @ 0 K)} = 0$$ by the third law

so

$$\Delta S^o(0 K \rightarrow 298 K) = S^o_f \text{(compound @ 298 K)}$$

If one can evaluate the entropy change resulting from raising the temperature of a compound from 0 K to 298 K, one can determine the molar entropy of that compound at 298 K. Most certainly the entropy change for this process can be determined; however, a discussion of this issue will not be considered in this paper. It is enough to say that it can be done and that is where molar entropies come from.

For the applications and problems in Chemistry 107, molar entropies and heats of formation will be found in the tables in our text books.

Let consider an example so that we can see all of this "stuff" at work.

Consider the reaction: $3 \text{H}_2 (g) + \text{N}_2 (g) \rightarrow 2 \text{NH}_3 (g)$

So, we go to a book and look up the heats of formations and the molar entropies. What we find is the following:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$H_f^o$ kJ/mole</th>
<th>$S_f^o$ kJ/mole deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>0.131</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>0.192 (0.191.5)</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-46.1</td>
<td>0.192 (0.192.3)</td>
</tr>
</tbody>
</table>

therefore

$$\Delta H_f^o \text{reaction} = 2 H_f^o (\text{NH}_3) - 3 H_f^o (\text{H}_2) - 1 H_f^o (\text{N}_2)$$

$$2 (-46.1) - 3 (0) - 1 (0) = -92.2 \text{ kJ/reaction as written at 298 K}$$

So! The reaction is exothermic, going toward a more stable state, and a positive contribution to spontaneity!
and

$$\Delta S^0_{\text{reaction}} = 2 S_f^0 (\text{NH}_3) - 3 S_f^0 (\text{H}_2) - 1 S_f^0 (\text{N}_2)$$

2 (0.192) - 3 (0.131) - 1(0.192) = -0.201 kJ/deg reaction as written at 298 K

So! The reaction has a negative entropy change, D-->O (disorder toward order), and is unfavorable toward spontaniety!

This reaction is case # 2 in Table 1 (enthalpy favorable and entropy unfavorable).

So, let us consider the net effect, the combination of entropy and enthalpy, which is called free energy.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G^0 = (-92.2) - 298 (-0.201) = -92.2 + 59.6$$

$$\Delta G^0 = - 32.6 \text{ kJ/ reaction at 298 K}$$

Note that \( \Delta H = -92.2 \) and \(- T \Delta S = +59.6 \) are of opposite sign which means that one is favorable (\( \Delta H \)) and one unfavorable (\( \Delta S \)).

So, what is next. Well, the values of \( \Delta H^0 \) and \( \Delta S^0 \) for a chemical reaction and are actually slightly dependent on temperature. In this class we will assume that these values are independent of temperature. If the temperature is not too far away from room temperature (298 K), the approximations is quite good. If \( \Delta H^0 \) and \( \Delta S^0 \) are assumed to be temperature independent, then the free energy at any other temperature is given by the following:

$$\Delta G^0_T = \Delta H^0_{298 K} - T \Delta S^0_{298 K}$$

and therefore

At \( T = 298 \text{ K} \) \( \Delta G^0_{298 \text{ K}} = -92.2 - (298) (-0.201) = -32.6 \text{ kJ} \)

At \( T = 350 \text{ K} \) \( \Delta G^0_{350 \text{ K}} = -92.2 - (350) (-0.201) = -21.9 \text{ kJ} \)
At $T = 500$ K  

$$
\Delta G^{0}_{500 \text{K}} = -92.2 - (500)(-0.201) = +8.3 \text{ kJ}
$$

What does all of this mean? Well, the reaction has negative values for $\Delta G^{0}$ at 298 and 350 K and is spontaneous. At 500 K the entropy term has become more important and the value of $\Delta G^{0}$ has become positive and the reaction is now nonspontaneous (actually, spontaneous in the reverse direction). Somewhere between 350 and 500 K the value of $\Delta G^{0}$ switches from positive to negative and the reaction changes from spontaneous to nonspontaneous. One can find that value of T where $\Delta G^{0}$ switches from positive to negative in the following way. Note that going from positive to negative requires passing through zero. Yep, let's set $\Delta G^{0}$ equal to zero and solve for T.

$$
0 = \Delta H^{0}_{298 \text{K}} - T_x \Delta S^{0}_{298 \text{K}}
$$

where $T_x$ is called the cross over temperature

$$
0 = -92.2 - T_x (-0.201)
$$

and

$$
T_x = 459 \text{ K}
$$

The cross over temperature is the temperature where the reaction goes from spontaneous forward through equilibrium to spontaneous backwards. Consider the following data and graph.

<table>
<thead>
<tr>
<th>Temp</th>
<th>$\Delta G^{0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-32.302</td>
</tr>
<tr>
<td>325</td>
<td>-26.875</td>
</tr>
<tr>
<td>350</td>
<td>-21.85</td>
</tr>
<tr>
<td>375</td>
<td>-16.825</td>
</tr>
<tr>
<td>400</td>
<td>-11.8</td>
</tr>
<tr>
<td>425</td>
<td>-6.775</td>
</tr>
<tr>
<td>450</td>
<td>-1.75</td>
</tr>
<tr>
<td>459</td>
<td>0.059</td>
</tr>
<tr>
<td>475</td>
<td>3.275</td>
</tr>
<tr>
<td>500</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Guess how this was done!
Note that
If $T < 459$ K then $\Delta G^0 < 0$ and the reaction is spontaneous forward

$$3 \text{ H}_2 (g) + \text{ N}_2 (g) \longrightarrow 2 \text{ NH}_3 (g)$$

If $T = 459$ K then $\Delta G^0 = 0$ and the reaction is at equilibrium

$$3 \text{ H}_2 (g) + \text{ N}_2 (g) \longleftrightarrow 2 \text{ NH}_3 (g)$$

If $T > 459$ K then $\Delta G^0 > 0$ and the reaction is spontaneous backwards

$$3 \text{ H}_2 (g) + \text{ N}_2 (g) \not\longleftarrow 2 \text{ NH}_3 (g)$$

So, is there anything else? Well, yes of course! So far we have learned to calculate the enthalpy, entropy, and free energy changes under the condition of 1 atm for each reagent. The conditions of 1 atm is the little "o" in the upper right of the symbol - i.e. $\Delta G^0$. So what if the reagents in the reaction are not at 1 atm? Well, that is the next topic!

We have already said that both $\Delta H$ and $\Delta S$ are fairly independent of temperature. At least for introductory chemistry we will assume that $\Delta H$ and $\Delta S$ have values that do not change with temperature. It turns out that $\Delta H$ is also fairly independent of
pressure. That means $\Delta H = \Delta H^0$; that is easy. The entropy term is another issue. While entropy is independent of temperature (at least for this class), it is not independent of pressure. So we need correct for pressure. I’ll just give the correction factor; you know ITO!

$$\Delta S = \Delta S^0 - R \ln MA;$$

where $R$ is the gas constant and $MA$ is the mass action expression for the reaction.

One other bit of simple math needs to be done.

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

also

$$\Delta H = \Delta H^0$$

and

$$\Delta S = \Delta S^0 - R \ln MA$$

SO!

$$\Delta G = \Delta H^0 - T (\Delta S^0 - R \ln MA)$$

or

$$\Delta G = (\Delta H^0 - T \Delta S^0 ) + T R \ln MA)$$

and

$$\Delta G = \Delta G^0 + RT \ln MA$$

(an equation worth remembering)

So let’s see how this all works. Let’s do a problem. Consider again the ammonia formation reaction again.

$$3 \text{H}_2 (g, 1 \text{ atm}) + \text{N}_2 (g, 1 \text{ atm}) \rightarrow 2 \text{NH}_3 (g, 1\text{atm})$$

$\Delta H^0_{\text{reaction}} = -92.2 \text{ kJ/ reaction as written at 298 K}$

$\Delta S^0_{\text{reaction}} = -0.201 \text{ kJ/ deg reaction as written at 298 K}$

$\Delta G^0 = -32.6 \text{ kJ/ reaction as written at 298 K}$
What are the values of the enthalpy, entropy, and free energy for the following reactions (not all 1 atm) at 298 K.

\[ 3 \text{H}_2 (g, 1 \text{ atm}) + \text{N}_2 (g, 1 \text{ atm}) \rightleftharpoons 2 \text{NH}_3 (g, 0.1 \text{ atm}) \]

\[
\text{Mass Action} = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}^2} = \frac{0.1^2}{1^3 \cdot 1} = 0.01
\]

\[ \Delta H_{\text{reaction}} = \Delta H^0_{\text{reaction}} = -92.2 \text{ kJ/reaction} \]

(enthalpy change is independent of P)

\[ \Delta S = \Delta S_0 - R \ln MA = -0.201 \text{ kJ/reaction} - R \ln (0.01) \]

\[ \Delta S = -0.201 \text{ kJ/deg reaction} - (0.008314 \text{ kJ/mole deg}) \ln (0.01) \]

\[ \Delta S = -0.201 \text{ kJ/deg reaction} + 0.038 \text{ kJ/deg} = -0.163 \text{ kJ/deg reaction} \]

(entropy change increased)

\[ \Delta G = \Delta G^0 + RT \ln MA = -32.6 \text{ kJ/reaction} + (0.008314 \text{ kJ/mole deg}) (298) \ln (0.01) \]

-32.6 kJ/reaction - 11.3 kJ/reaction

-43.9 kJ/reaction

(free energy change - more spontaneous)

Let's consider a couple more issues before we stop!

\[ \Delta G = \Delta G^0 + RT \ln MA \]

but at equilibrium \( \Delta G = 0 \) and \( MA = K \) (equilibrium Constant)

then

\[ 0 = \Delta G^0 + RT \ln K \]

If one knows \( \Delta G^0 \), one can calculate \( K \) (equilibrium). Just like the following:

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>( \Delta G^0 ) kJ/reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-32.302</td>
</tr>
<tr>
<td>350</td>
<td>-21.85</td>
</tr>
<tr>
<td>500</td>
<td>+8.3</td>
</tr>
</tbody>
</table>

\[ 0 = \Delta G^0 + RT \ln K \]

0 = \(-32.3\) + (0.008314 kJ/mole deg) \((298) \ln K\); --> \( K = 4.5 \times 10^5 \) at 298

0 = \(-21.85\) + (0.008314 kJ/mole deg) \((350) \ln K\); --> \( K = 1.8 \times 10^3 \) at 350

0 = \(+8.3\) + (0.008314 kJ/mole deg) \((500) \ln K\); --> \( K = 0.136 \) at 500

note that when \( \Delta G^0 \) is negative \( K > 1 \) and when \( \Delta G^0 \) is positive \( K < 1 \)
One last thought.

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

\[
\Delta H^0_{\text{reaction}} = -92.2 \text{ kJ/ reaction as written at 298 K}
\]

\[
\Delta S^0_{\text{reaction}} = -0.201 \text{ kJ/ deg reaction as written at 298 K}
\]

\[
\Delta G^0 = -32.6 \text{ kJ/ reaction as written at 298 K}
\]

\[K_{\text{eq}} = K = 4.5 \times 10^5 \text{ at 298 K}
\]

Let \(P(\text{N}_2) = P(\text{H}_2) = 1 \text{ atm}\) and \(P(\text{NH}_3)\) be a variable.

\[\text{MA} = P^2(\text{NH}_3)\]

<table>
<thead>
<tr>
<th>(P(\text{NH}_3))</th>
<th>MA</th>
<th>RT \text{Ln MA}</th>
<th>(\Delta G^0 + \text{RT Ln MA} -32.6 + \text{RT Ln MA})</th>
<th>(K \text{ vs MA})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>10^{-4}</td>
<td>-22.8</td>
<td>-55.4</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>0.1</td>
<td>10^{-2}</td>
<td>-11.4</td>
<td>-44.0</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>-32.6</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>11.42</td>
<td>-21.1</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>100</td>
<td>10^{+4}</td>
<td>22.8</td>
<td>-9.7</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>400</td>
<td>16 \times 10^{+4}</td>
<td>29.7</td>
<td>-2.8</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>500</td>
<td>25 \times 10^{+4}</td>
<td>30.8</td>
<td>-1.7</td>
<td>K&gt;MA</td>
</tr>
<tr>
<td>678</td>
<td>45 \times 10^{+4} ***</td>
<td>32.6</td>
<td>0 ************</td>
<td>K=MA ****</td>
</tr>
<tr>
<td>1000</td>
<td>100 \times 10^{+4}</td>
<td>34.2</td>
<td>1.9</td>
<td>K&lt;MA</td>
</tr>
<tr>
<td>1500</td>
<td>225 \times 10^{+4}</td>
<td>36.2</td>
<td>3.67</td>
<td>K&lt;MA</td>
</tr>
</tbody>
</table>