

Unit 4 Review 3

THERMODYNAMICS: ENTROPY, FREE ENERGY, & EQUILIBRIUM

Entropy: Qualifying Entropy

In this class we expect you to understand entropy to three levels of sophistication, that I call: **qualifying entropy**, **defining entropy**, and **quantifying entropy**.

- **Qualifying Entropy:** although not quite accurate scientifically, we tend to think of entropy as disorder. More disordered phases of matter are higher in entropy.
- **We can easily see that the change in entropy correlates with the change in phase:**
Solids (low entropy) < Liquids < Gases (high entropy)
- **Or with volume** (consider 1 mole of gas at room temperature)
10L gas (lowest entropy) < 20L gas < 50L gas (highest entropy)
- **Or with temperature**
Gas at 100K (lowest entropy) < gas at 500K < gas at 1000K (highest entropy)

Entropy: Defining Entropy

- **Defining Entropy:** it is more appropriate to think of entropy as energy dispersal. This correlates specifically to the total number number of microstates in a system at a given temperature. This is given by the formula:

$$S = k \ln \Omega$$

Or one step further... $S = k \ln x^i$

- In the first equation, the omega term (Ω) is equal to the total number of microstates. The second equation clarifies this term by representing the omega variable as permutations (x^i). This means microstates are equal to the **number of orientations possible for a molecule** (x) raised to the power of the **total number of molecules** (i).

Entropy: Defining Entropy

- The relationship between entropy and microstates is given by the formulas:

$$S = k \ln \Omega$$

$$S = k \ln x^i$$

- However, it is more important to understand what these mean instead of calculating absolute entropy.
 - Entropy depends on the **“complexity” of the molecule**, represented by the orientations possible (x)
 - CH_3Cl is more complex than CO_2
 - Entropy depends on the total number of particles, represented by i
 - More particles (or more moles) leads to a higher entropy

Factors that affect Entropy

- **In summation, you can compare entropy by comparing:**
 1. Phase
 2. Volume
 3. Temperature
 4. Complexity of your molecule
 5. Complexity of your solution * we don't really talk about this
 6. Number of particles

Entropy: Quantifying Entropy

$$\Delta S = \frac{q_{rev}}{T}$$

- **Quantifying Entropy:** lastly, we must understand how to calculate entropy changes in different experimental conditions.
 - The trick to understanding how to quantify entropy is understanding the equations from which it is derived. **The key here is understanding the units of entropy: J/K**
 - **Entropy of a temperature change**

$$q = mC_s \Delta T$$

If we integrate with respect to T to get entropy:

$$\Delta S = mC_s \ln \frac{T_f}{T_i}$$

- **Entropy of a phase change**

$$q = \Delta H_{trans}$$

If we divide by the temperature we get:

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

- **Entropy of isothermal expansion**

$$q = nRT \ln \frac{V_f}{V_i}$$

If we divide by the temperature we get:

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Entropy: Quantifying Entropy

- **Remember: entropy is a state function, so it is path independent. If you have absolute entropy data, you can use your reliable “products minus reactants” formula.**

$$\Delta S_{rxn} = \sum nS^{\circ}(\text{products}) - \sum nS^{\circ}(\text{reactants})$$

Note: something strange you might notice is that entropy is often provided in tables as J. Enthalpy is provided in tables as kJ. Make sure to adjust your units if you use the two state functions together!

Entropy: Quantifying Entropy (surroundings)

- All of the previous calculations will tell you the change in entropy of the surroundings. However, if we define that $q_{sys} = -q_{surr}$ we can apply one last equation:

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}}$$

Note: this does NOT mean $\Delta S_{surr} = -\Delta S_{sys}$
Understand that T_{surr} is not equal to T_{sys} unless you are at equilibrium (example: phase change)

The 2nd Law of Thermodynamics

- **The second law of thermodynamics states that the entropy of the universe is always increasing.**

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

- This law gives us three conditions for ΔS_{total} :
 1. $\Delta S < 0$ (negative) ; your reaction is nonspontaneous
 2. $\Delta S = 0$ (zero) ; your reaction is at equilibrium / reversible
 3. $\Delta S > 0$ (positive) ; your reaction is spontaneous

2nd Law Homework Question

- You drop a sugar cube in water and it dissolves (endothermic reaction). What are the signs of $\Delta S_{\text{universe}}$, ΔS_{system} , and ΔS_{surr} ?

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Definition of Free Energy

- **Free Energy (G):** another “mythological” state function that describes the stability of a system. Like enthalpy, we are concerned most with the ΔG because of the conclusions we can make using its **sign** and **magnitude**.
- **The change in free energy of a reaction (ΔG) is related to the enthalpy, entropy, and temperature of the system.**

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

$$\Delta G_{rxn} = \Delta H_{sys} - T \Delta S_{sys}$$

Remember: something strange you might notice is that entropy is often provided in tables as J. Enthalpy is provided in tables as kJ. Make sure to adjust your units if you use the two state functions together! (stated again for emphasis)

Calculating Free Energy

- You should be very familiar with the formula:

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

- However, remember that free energy is still a state function. So we can also use the formula:

$$\Delta G_{rxn} = \sum n \Delta G_f^\circ(\text{prod}) - \sum n \Delta G_f^\circ(\text{react})$$

Free Energy Conclusions

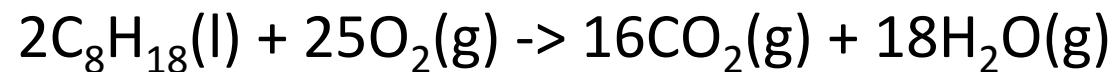
- **The final and most important lesson in thermodynamics is that there is a finite amount of “Free Energy” in the universe and that spontaneous reactions lower the free energy.**
- This point gives us three conditions for ΔG :
 1. $\Delta G < 0$ (negative) ; your reaction is spontaneous
 2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
 3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous
- We understand these ideas conceptually with a few familiar terms:
 - **Lower energy products** will be more **stable** (a reaction will tend to be spontaneous and form these products)
 - We can set up conditions that are “**favorable**” or “**unfavorable**” for a reaction, meaning they are conducive to lowering the free energy

Free Energy: $-\Delta H$, $+\Delta S$

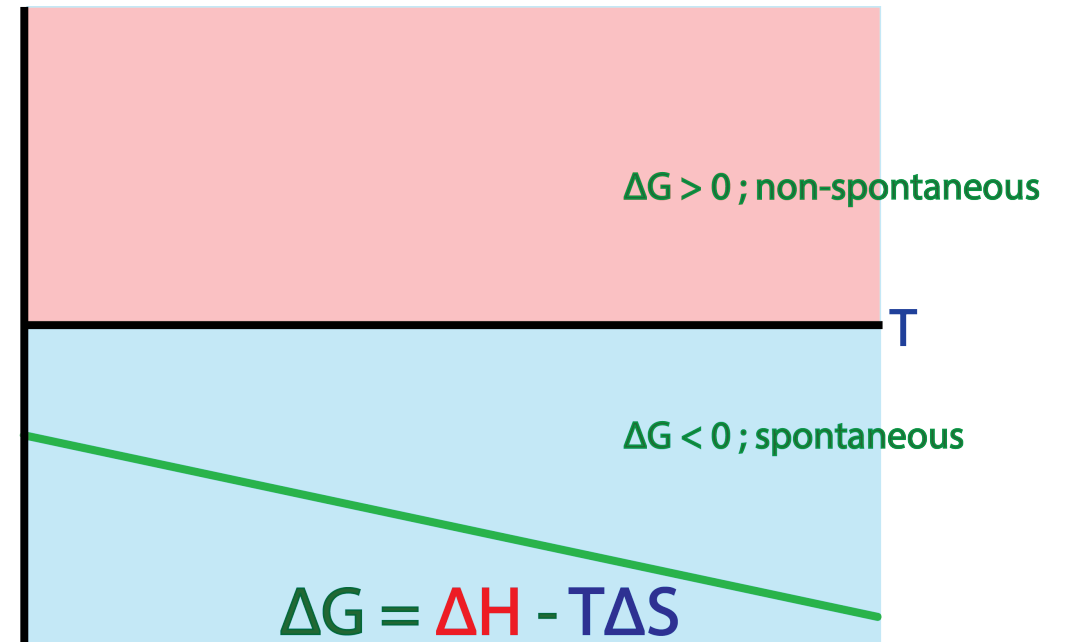
In this case, our enthalpy and entropy are “favorable” for a spontaneous reaction.

Therefore, this reaction will be **spontaneous** at all temperatures.

Example: most combustion reactions



ΔG

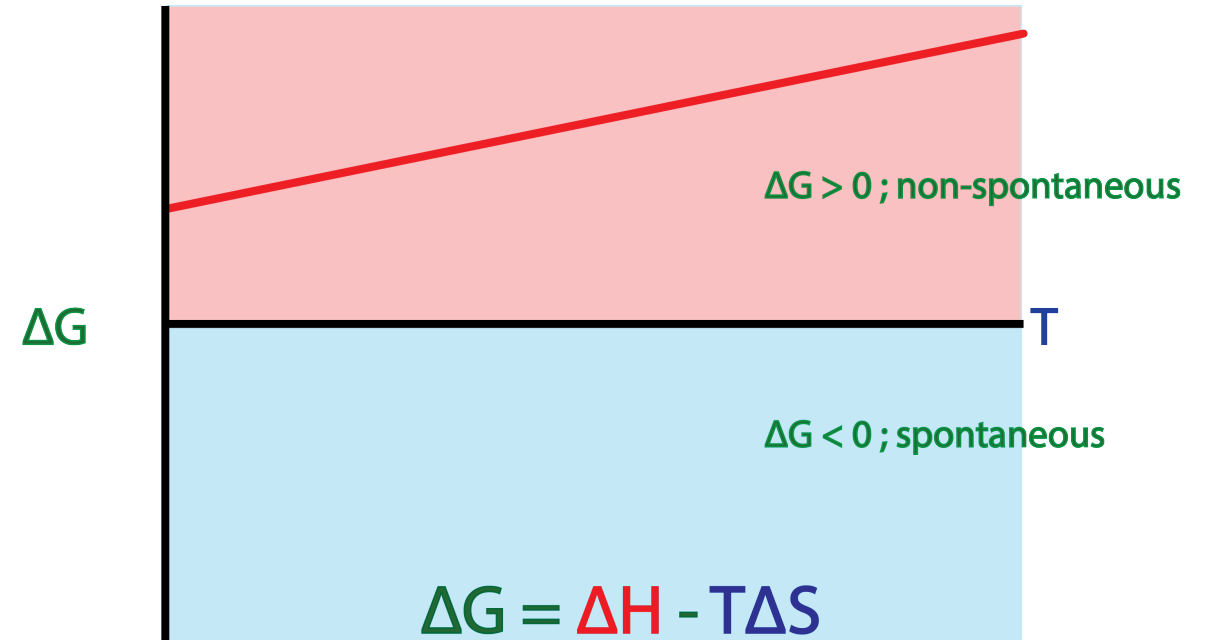


$\Delta S > 0$, $\Delta H < 0$; spontaenous at all temperatures

Free Energy: $+\Delta H$, $-\Delta S$

In this case, our enthalpy and entropy are “unfavorable” for a spontaneous reaction.

Therefore, this reaction will be **nonspontaneous** at all temperatures.



$\Delta S < 0$, $\Delta H > 0$; non-spontaneous at all temperatures

Note on spontaneity: a positive ΔG does not mean that a reaction can't happen. It means that it doesn't happen without the continuous input of energy.

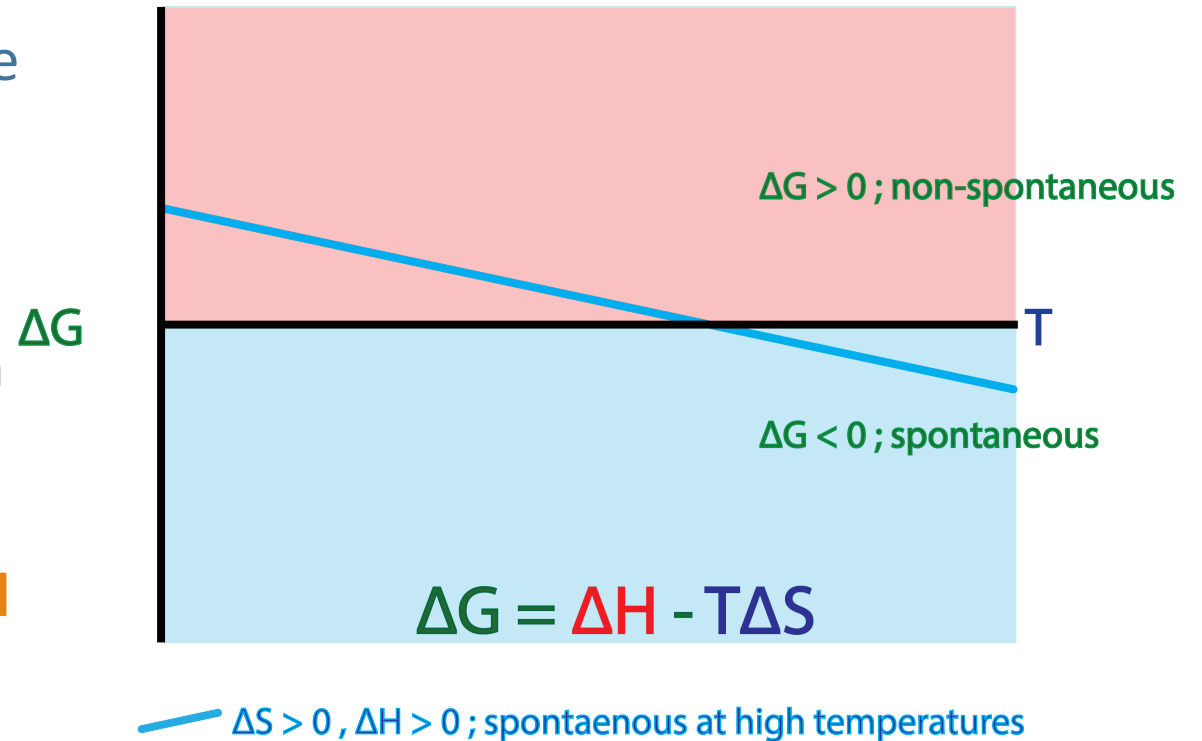
Free Energy: $+\Delta H$, $+\Delta S$

In this case, our enthalpy is unfavorable and our entropy is favorable.

This means that our $T\Delta S$ term must be greater in magnitude than our ΔH term in order for our ΔG to be negative.

In other words, our reaction is favored only at high enough temperatures.

Example: dissolution (favored at High T)
 $\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$

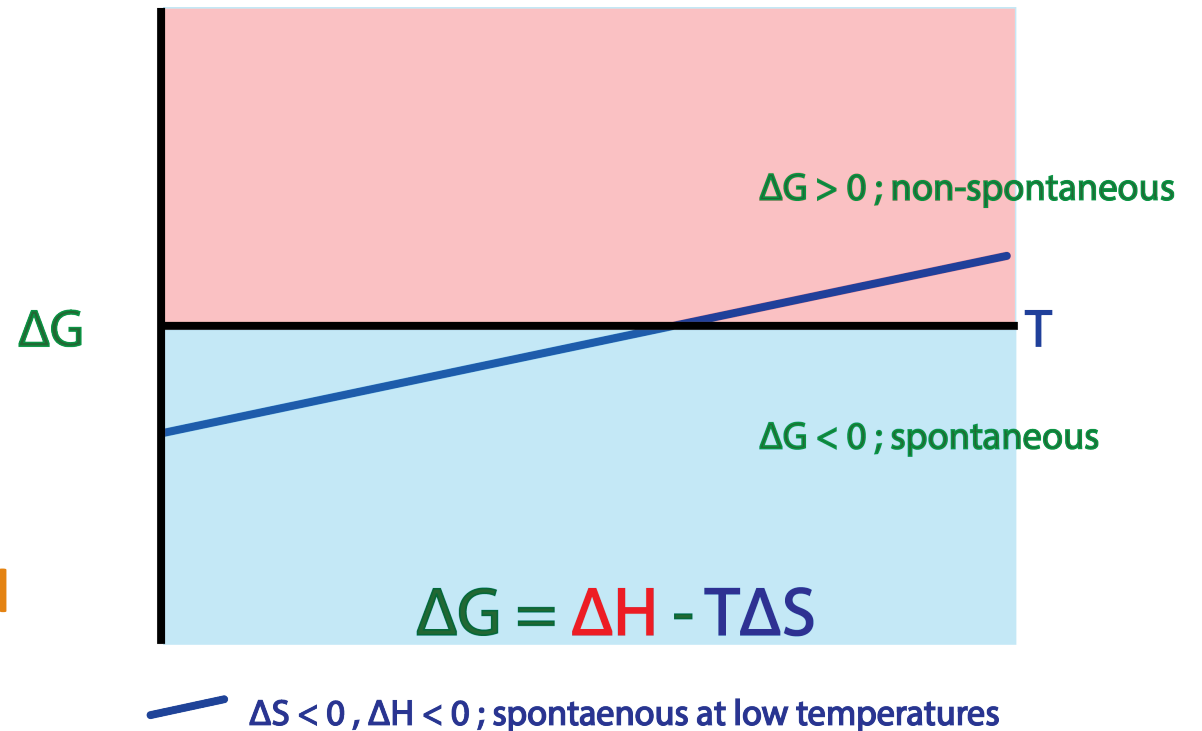


Free Energy: $-\Delta H$, $-\Delta S$

In this case, our entropy is unfavorable and our enthalpy is favorable.

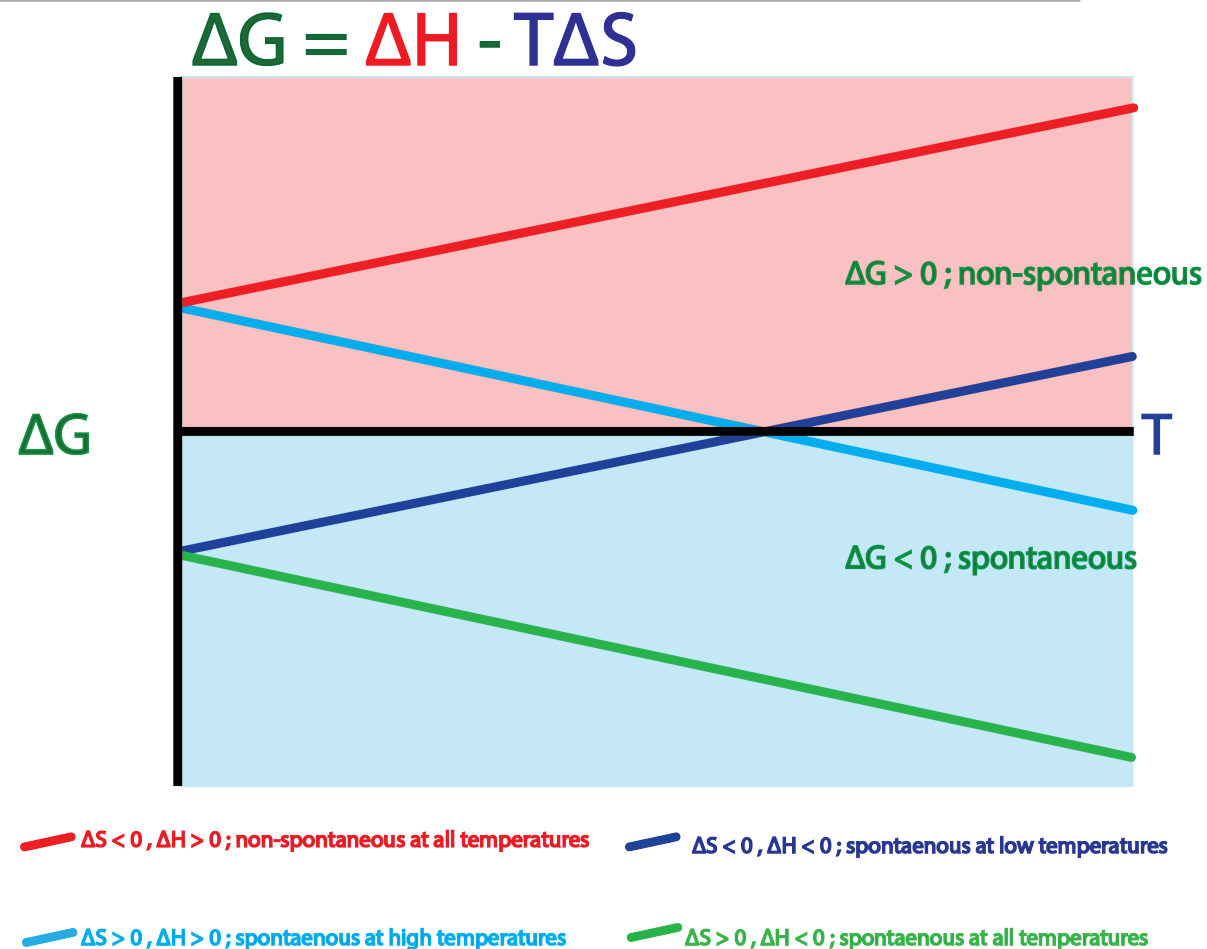
This means that our $T\Delta S$ term must be smaller in magnitude than our ΔH term in order for our ΔG to be negative.

In other words, our reaction is favored only at low enough temperatures.



Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

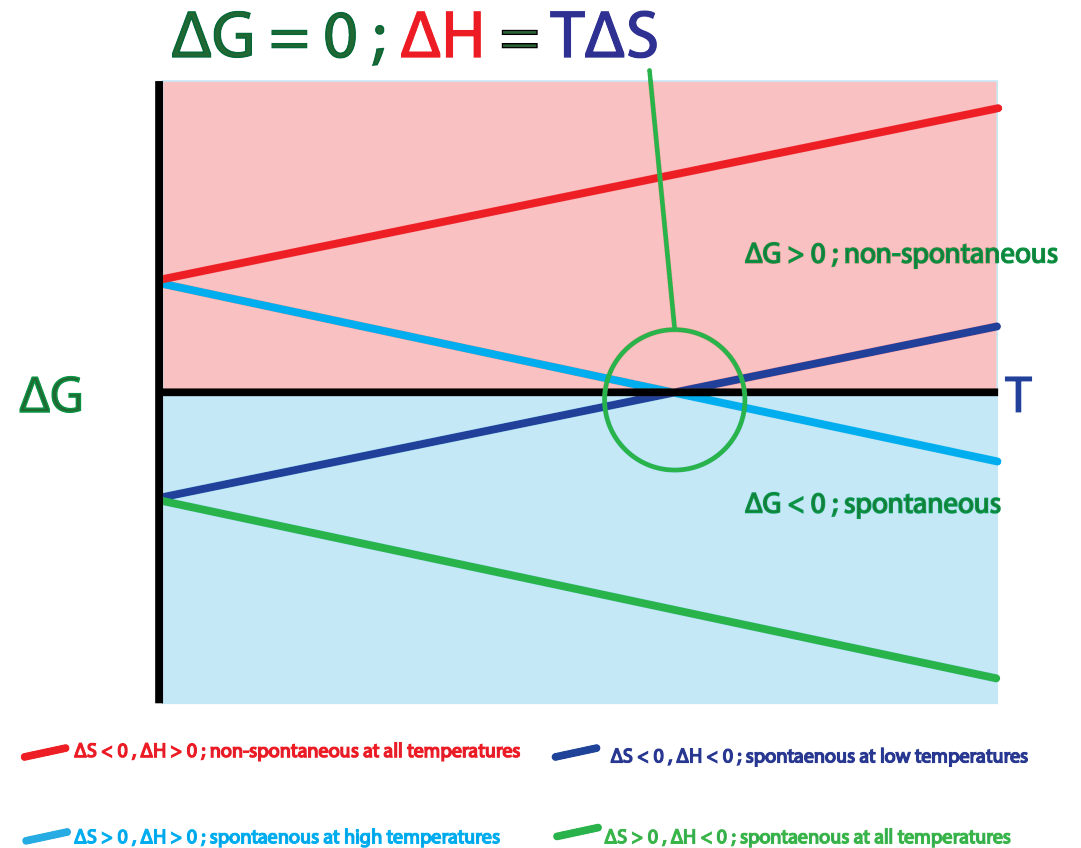


Free Energy: Equilibrium

For the conditions that are temperature dependent, it is possible to have a ΔG value equal to 0. This is, by definition, equilibrium.

In this class we are focused on one main equilibrium condition: phase change.

$$T_{trans} = \frac{\Delta H_{rxn}}{\Delta S_{rxn}}$$



Free Energy Homework Question

The vaporization of bromine is 34kJ/mol and the standard entropy change is 98J/mol K . What is the lowest temperature at which this process is spontaneous in degrees Celsius?

Free Energy: Final Conclusions

Ultimately, the change in free energy tells us about the stability of the products with respect to the reactants. We know that things in the universe tend toward high stability (low energy), so this also correlates with spontaneity.

In summation, we should now be able to compare reactions using stability and spontaneity. For example:

Reaction 1, $\Delta G_{\text{rxn}} = 11 \text{ kJ/mol}$

Reaction 2, $\Delta G_{\text{rxn}} = -52 \text{ kJ/mol}$

Reaction 3, $\Delta G_{\text{rxn}} = -4 \text{ kJ/mol}$

Reaction 4, $\Delta G_{\text{rxn}} = 211 \text{ kJ/mol}$

Reactions 2 and 3 are spontaneous. Reactions 1 and 4 are nonspontaneous. Furthermore, reaction 2 is the “most” spontaneous, meaning that the products have a greater increase in stability from the reactants than in reaction 3.