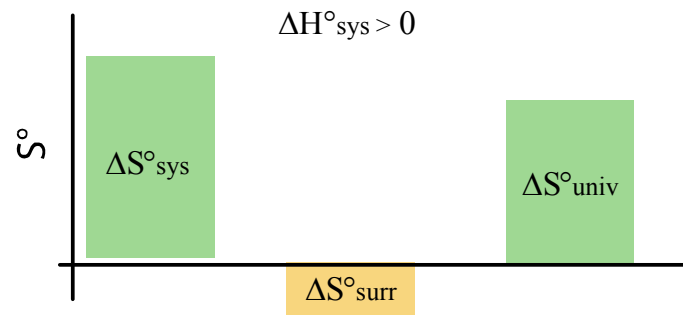
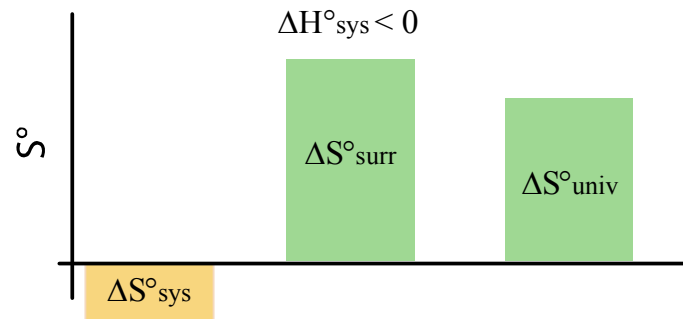
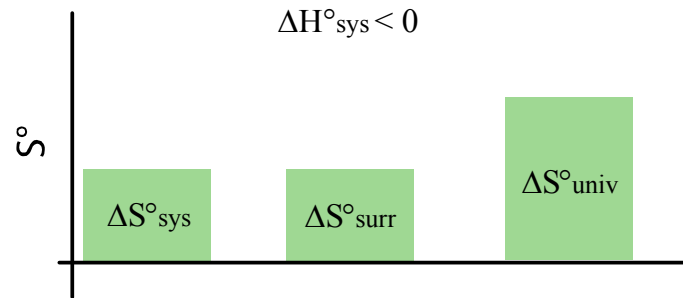


Lecture 8: Gibbs Free Energy

- Reading: Zumdahl 10.7, 10.9
- Outline
 - Defining the Gibbs Free Energy (ΔG)
 - Calculating ΔG
 - Pictorial Representation of ΔG
- Problems Z10.49-51, Z10.54, Z10.56-58

Entropy Summary

Three different ways the system and environment entropies can combine to produce spontaneous conditions.



Defining ΔG

- Recall, the second law of thermodynamics:

$$\Delta S_{\text{univ}} = \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

- Also:
$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T} = -\frac{q_P^{\text{rev}}}{T} \quad \Delta P = 0$$

Therefore

$$-T\Delta S_{\text{total}} = \Delta H - T\Delta S$$

Notice, when there is no subscript on H or S it means for the system.

ΔG as a state function; the other perspective

- G is a state function, because we define:

$$G = H - TS \quad \text{or} \quad \Delta G = \Delta H - \Delta(TS)$$

$$\text{@ constant } T: \Delta G = \Delta H - T\Delta S$$

- At constant Pressure then the heat out of the system is the heat into the surroundings (or environment).

$$\Delta S_{surr} = \frac{q_{rev}^{surr}}{T} = -\frac{q_{rev}^{system}}{T} = -\frac{\Delta H}{T}$$

$$\Delta H = -T\Delta S_{surr}$$

We used reversible heat. Does the reaction have to be done reversibly? No, because the state functions are independent of path, so these are the correct values of S , H and G regardless of path. {However, the actual amount of heat depends on path.}

Gibbs (Free) Energy and spontaneity

If a reaction (or physical change such as ice melting) is happening at constant temperature and pressure, the Gibbs energy of the system is:

$$\Delta G = \Delta H - T\Delta S = -T\Delta S_{total}$$

So the Gibbs energy (which is only of the system and does not mention the surroundings) is as valid a criterion of spontaneity as the total entropy (of the universe).

Notice that the sign of the criterion of spontaneity does change (between total entropy and Gibbs energy).

ΔG and Spontaneous Processes

- Recall from the second law the conditions of spontaneity:
 - **Three possibilities:**
 - If $\Delta S_{\text{univ}} > 0$process is spontaneous
 - If $\Delta S_{\text{univ}} < 0$process is spontaneous in opposite direction.
 - If $\Delta S_{\text{univ}} = 0$equilibrium
 - In our derivation of ΔG , we divided by $-T$; therefore, the direction of the inequality changes relative to entropy.

ΔG criterion of spontaneous

- Three possibilities: (for any process)
 - If $\Delta S_{\text{univ}} > 0$process is spontaneous
 - If $\Delta S_{\text{univ}} < 0$process is spontaneous in opposite direction.
 - If $\Delta S_{\text{univ}} = 0$equilibrium
- In terms of ΔG : (only for constant T, P processes)
 - If $\Delta G < 0$process is spontaneous
 - If $\Delta G > 0$process is spontaneous in opposite direction.
 - If $\Delta G = 0$equilibrium

ΔG and Spontaneous Processes

- Note that ΔG is composite of both ΔH and ΔS

$$\boxed{\boxed{\Delta G = \Delta H - T\Delta S}}$$

- A reaction is spontaneous if $\Delta G < 0$. Such that:

If $\Delta H < 0$ and $\Delta S > 0$spontaneous at any T

If $\Delta H > 0$ and $\Delta S < 0$not spontaneous at any T

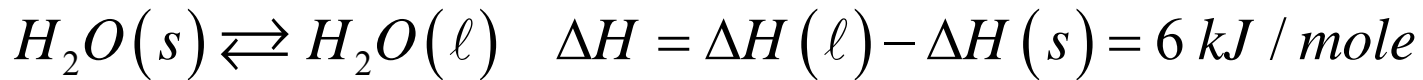
If $\Delta H < 0$ and $\Delta S < 0$spontaneous at low T

If $\Delta H > 0$ and $\Delta S > 0$spontaneous at high T

Ice Melting

- Know ice melts above 0C, and water freezes below 0C.
- Why? What does thermodynamics tell us about this process?
- It is a trade off of two (large) competing tendencies. Ice (like all solids) is the stable form at low temperatures because melting is endothermic (the ice must have heat to melt). Melting is not enthalpically favorable.
- We found that the enthalpy for melting and boiling were rather independent of temperature.
- Competing with this is the entropy which (statistically) was the tendency to disorder (greater positional possibilities). If possible, if the water molecules can have more places to go they will do that. Liquid water affords molecules an opportunity to migrate (unlike solid water). So the melting should be entropically favorable. But need to raise T to some critical value so that the entropy can take over and melt ice.
- This is a model (we can remember) for any chemical transformation

The entropy of melting



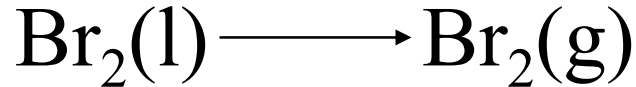
- Ice melts at 0C. The latent heat of fusion is 6kJ/mole. Notice it is positive; breaking water-water bonds.
- What is the entropy change for ice to melt?
- At the transition temperature, the two phases are in equilibrium, so $\Delta G=0=\Delta H-T\Delta S$. Solve for the entropy difference:

$$\Delta S = \frac{\Delta H}{T} = \frac{6 \cdot 10^3}{273} = 22 \text{ J / mol} \cdot \text{K}$$

- Notice Entropy change is positive, as one expect, so the Gibbs Energy becomes negative at higher temperatures, and the liquid form is favored (by entropic terms).
- The favorable bonding of water to water (enthalpically favored) is broken by the randomization forces of entropy.

Esoteric Example (A liquid boils)

- At what T is the following reaction spontaneous?



$$\Delta H^\circ = 30.91 \text{ kJ/mol}, \quad \Delta S^\circ = 93.2 \text{ J/mol.K} \quad @T=25^\circ\text{C}$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ only } @T=25^\circ\text{C}$$

The criterion of spontaneity is Gibbs Energy Change is zero.

Assume that the enthalpy and entropy changes upon boiling are rather independent of temperature, then

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

$$T_{\text{boiling}} = \frac{\Delta H}{\Delta S} \approx \frac{\Delta H^\circ}{\Delta S^\circ} = 331\text{K}$$

Boiling Example

- Try 298 K just to see:

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

$$\Delta G^\circ = 30.91 \text{ kJ/mol} - (298\text{K})(93.2 \text{ J/mol.K})$$

$$\begin{aligned}\Delta G^\circ &= (30.91 - 27.78) \text{ kJ/mol} \\ &= 3.13 \text{ kJ/mol} > 0\end{aligned}$$

Not spontaneous at 298 K, but the two big numbers are just about canceling, we need to go up from 300 to 330 to get cancellation. Above that temperature the process will be spontaneous (i.e. Br₂ will boil.)

Gibbs Energy for reactions

- Cannot have a change in the gas in a box for a process at constant T and P. Need more going on, such as the number of moles changing. This is where a chemical reaction comes in.
- For a chemical reaction at constant T and P the only contributions to the changing free energy are due to the changes in the concentrations of the various species.
- We wrote the enthalpy in terms of the molar enthalpies of formation of each of the species; now write the total Gibbs energy as the sum of the molar Gibbs energies for each of the species.

Calculating ΔG°_{rxn}

- Can evaluate all reaction energies at standard thermodynamic conditions (1 Atm 25C) where the superscript “naught” is applied.
- Previously we needed to determine ΔH°_{rxn} and ΔS°_{rxn} to determine ΔG°_{rxn}
- Now, ΔG is a state function; therefore, we can use known ΔG° for each of the chemical species to determine ΔG°_{rxn} using:

$$\Delta G^\circ_{rxn} = \sum c_{prod} \Delta G^\circ_{prod.} - \sum c_{react} \Delta G^\circ_{react.}$$

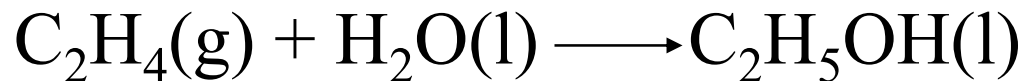
Standard ΔG of Formation: ΔG_f°

- (Like ΔH_f° and S°)
- ΔG_f° is defined as the “change in free energy that accompanies the formation of 1 mole of that substance for its constituent elements with all reactants and products in their standard state.”
- Like ΔH_f° , $\Delta G_f^\circ = 0$ for an element in its standard state:



Gibbs Energy of Reaction (Example)

- Determine the $\Delta G^\circ_{\text{rxn}}$ for the following:



- Tabulated $\Delta G^\circ_{\text{f}}$ from Appendix 4:

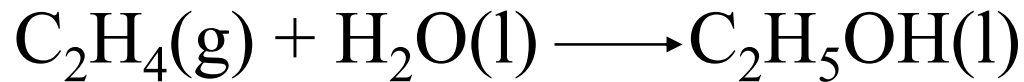
$$\Delta G^\circ_{\text{f}}(\text{C}_2\text{H}_5\text{OH}(\text{l})) = -175 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{f}}(\text{C}_2\text{H}_4(\text{g})) = 68 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{f}}(\text{H}_2\text{O}(\text{l})) = -237 \text{ kJ/mol}$$

Partially Burn a Hydrocarbon (see Z10.56)

- Using these values:



$$\Delta G^\circ_{\text{rxn}} = \sum c_{\text{prod}} \Delta G^\circ_{\text{prod}} - \sum c_{\text{react}} \Delta G^\circ_{\text{react}}$$

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f}}(\text{C}_2\text{H}_5\text{OH}(\text{l})) - \Delta G^\circ_{\text{f}}(\text{C}_2\text{H}_4(\text{g})) - \Delta G^\circ_{\text{f}}(\text{H}_2\text{O}(\text{l}))$$

$$\Delta G^\circ_{\text{rxn}} = -175 \text{ kJ} - 68 \text{ kJ} - (-237 \text{ kJ})$$

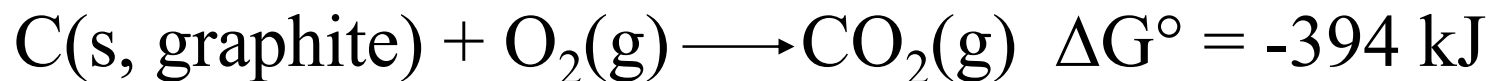
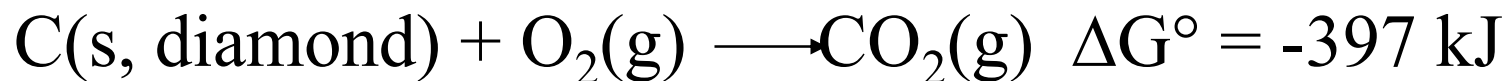
$$\Delta G^\circ_{\text{rxn}} = -6 \text{ kJ} < 0 ; \text{ therefore, spontaneous}$$

Why is it spontaneous and for what temperatures is this true?

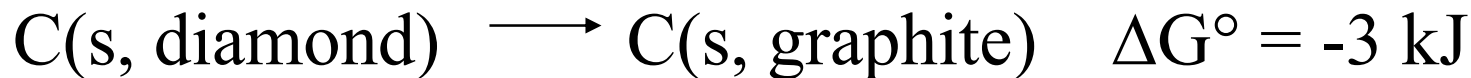
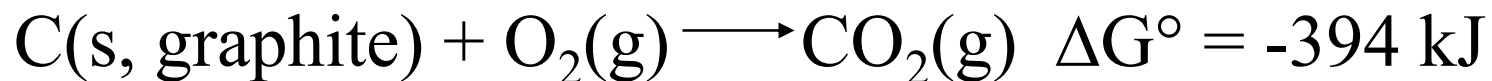
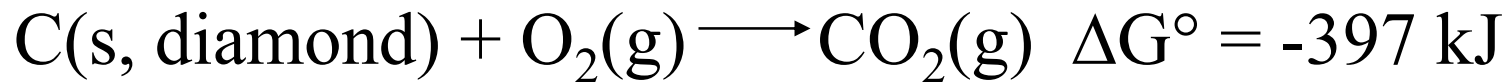
$\Delta H^\circ_{\text{rxn}} = -44 \text{ kJ}$; from this get $\Delta S^\circ_{\text{rxn}} = -120 \text{ J/K}$. Spontaneous at low T.

More $\Delta G^\circ_{\text{rxn}}$

- Similar to ΔH° , one can use the ΔG° for various reactions to determine ΔG° for the reaction of interest (a “Hess’ Law” for ΔG°)
- Example:



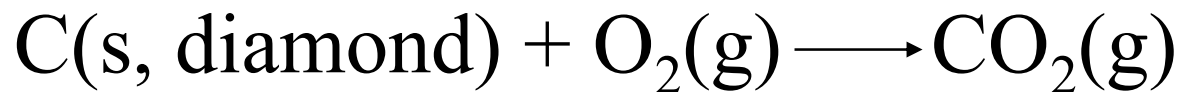
$\Delta G^\circ_{\text{rxn}}$ Calculations



$\Delta G^\circ_{\text{rxn}} < 0 \dots \text{rxn is spontaneous}$

$\Delta G^\circ_{\text{rxn}} \neq \text{Reaction Rate}$

- Although $\Delta G^\circ_{\text{rxn}}$ can be used to predict if a reaction will be spontaneous as written, it does not tell us how fast a reaction will proceed.
- Example:



$$\Delta G^\circ_{\text{rxn}} = -397 \text{ kJ} \lll 0$$

But diamonds are forever?.... $\Delta G^\circ_{\text{rxn}} \neq \text{rate}$

Example Problem

- Is the following reaction spontaneous under standard conditions?



	ΔH°_f (kJ/mol)	S° (J/mol.K)
$\text{KClO}_3(s)$	-397.7	143.1
$\text{KClO}_4(s)$	-432.8	151.0
$\text{KCl}(s)$	-436.7	82.6

What would you guess qualitatively, first?

Example Problem Solution

- Calculating $\Delta H^\circ_{\text{rxn}}$



$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 3\Delta H^\circ_f(\text{KClO}_4) + \Delta H^\circ_f(\text{KCl}) - 4\Delta H^\circ_f(\text{KClO}_3) \\ &= 3(-432.8\text{kJ}) + (-436.7\text{kJ}) - 4(397.7\text{kJ}) \\ &= -144\text{kJ}\end{aligned}$$

- Calculating $\Delta S^\circ_{\text{rxn}}$

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 3S^\circ(\text{KClO}_4) + S^\circ(\text{KCl}) - 4S^\circ(\text{KClO}_3) \\ &= 3(151.0\text{J/K}) + (82.6\text{J/K}) - 4(143.1\text{J/K}) \\ &= -36.8\text{J/K}\end{aligned}$$

Example Problem Solution

- Calculating $\Delta G^\circ_{\text{rxn}}$

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} \\ &= -144\text{kJ} - (298\text{K})(-38.6\text{J/K})\left(\frac{1\text{kJ}}{1000\text{J}}\right) \\ &= -133\text{kJ}\end{aligned}$$

$\Delta G^\circ_{\text{rxn}} < 0$;therefore, reaction is spontaneous. The entropic term is very weak, so it is enthalpically driven. Notice entropy and enthalpy have the same sign. Yes, there is a temperature above which it will not be spontaneous, but that must be very large. See also Z10.57-58.

Example Problem (End)

For what temperatures will this reaction be spontaneous?

Answer: For T in which $\Delta G_{rxn} < 0$.

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

$$0 = \Delta H_{rxn} - T \Delta S_{rxn}$$

$$\Delta H_{rxn} \approx \Delta H_{rxn}^{\circ} \text{ and } \Delta S_{rxn} \approx \Delta S_{rxn}^{\circ}$$

$$T = \frac{\Delta H_{rxn}}{\Delta S_{rxn}} \approx \frac{\Delta H_{rxn}^{\circ}}{\Delta S_{rxn}^{\circ}} = \frac{-133kJ}{\left(-38.6 \frac{J}{K}\right) \left(\frac{1kJ}{1000J}\right)} = 3446K$$

Spontaneous as long as $T < 3446 \text{ K}$.

Whenever the enthalpy and the entropy have the same sign, there is always a temperature at which equilibrium will exist. However, it is so large that it is very approximate.