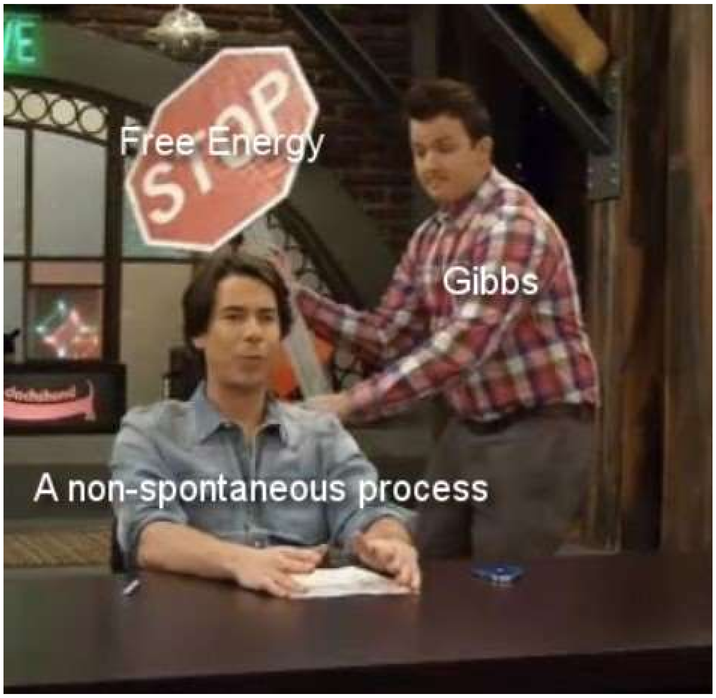
One more week until your spooky thermodynamics exam!



1. Which of the following compounds become less stable with respect to their elements as the temperature is raised?
    a. PCl_5(g)
    b. HCN(g)
    c. NO(g)
    d. SO_2(g)

2. A friend tells you "Free energy G and pressure P are directly related by the equation $G = G^o + RT\ln(P)$. Also, G is related to the equilibrium constant K in that when $G_{\text{products}} = G_{\text{reactants}}$, the system is at equilibrium. Therefore, it must be true that a system is at equilibrium when all pressures are equal." Do you agree with this friend? Explain.

3. Hydrogen cyanide (a highly toxic molecule whose toxicity is caused by the cyanide ion, which halts cellular respiration by acting as a non-competitive inhibitor for an enzyme in mitochondria called cytochrome c oxidase [but we digress]), is produced industrially by the following exothermic reaction:

$$2\ CH_4 + 2\ NH_3 + 3\ O_2 \rightarrow 2\ HCN + 6\ H_2O$$

It's run at 1000°C with a platinum-rhodium catalyst. Is the high temperature needed for thermodynamic or kinetic reasons? Or is there no reason? Maybe it's just fun to run reactions at high temperatures (spoiler: it's not).

4. Using data from Appendix 4, calculate ΔH^{o}, ΔG^{o}, and K (at 298 K) for the production of ozone from oxygen:

$$3O_2\ (g) \leftrightharpoons 2O_3\ (g)$$

At 30 km above the surface of the earth, the temperature is about 230. K and the partial pressure of oxygen is about 1.0×10^{-3} atm. Estimate the partial pressure of ozone in equilibrium with oxygen at 30 km above the earth's surface. Is it reasonable to assume that the equilibrium between oxygen and ozone is maintained under these conditions? Explain.

5. It is quite common for a solid to change from one structure to another at a temperature below its melting point. For example, sulfur undergoes a phase change from the rhombic crystal structure to the monoclinic crystal form at a temperature above 95°C. Predict the signs of ΔH and ΔS for this process. Which form of sulfur has the more ordered crystalline structure and therefore the smaller positional probability?

6. As $O_2(l)$ is cooled at 1 atm, it freezes at 54.5 K to form solid I. At a lower temperature, solid I rearrange to solid II, which has a different crystalline structure (similar to the different crystalline structures of sulfur at different temperatures and pressures). Thermal measurements show that ΔH for the I to II phase transition is -743.1 J/mol, and ΔS for the same transition is -17.0 J/K mole. At what temperature are solids I and II in equilibrium?

7. Recall previous worksheets we did where we look at the Mond reaction. Let's expand our Impure nickel, refined by smelting sulfide ores in a blast furnace, can be converted into metal from 99.90% to 99.99% purity by the Mond process. The primary reaction involved in the Mond process is

$$\mathrm{Ni}(s) + 4\,\mathrm{CO}(g) \rightleftharpoons \mathrm{Ni(CO)_4}(g)$$

   a. Without referring to Appendix 4, predict the sign of ΔS^o for the preceding reaction. Explain.

   b. The spontaneity of the preceding reaction is temperature-dependent. Predict the sign of ΔS_{surr} for this reaction. Explain.

c. For $Ni(CO)_4$(*g*), $\Delta H_f^o = -607$ kJ/mol and $S^o = 417$ J K^{-1} mol^{-1} at 298 K. Using these values and data in Appendix 4, calculate ΔH^o and ΔS^o for the preceding reaction.

d. Calculate the temperature at which $\Delta G^o = 0$ (K = 1) for the preceding reaction, assuming that ΔH^o and ΔS^o do not depend on temperature.

e. The first step of the Mond process involves equilibrating impure nickel with CO(*g*) and $Ni(CO)_4$(*g*) at about 50°C. The purpose of this step is to convert as much nickel as possible into the gas phase. Calculate the equilibrium constant for the preceding reaction at 50.°C.

f. In the second step of the Mond process, the gaseous $Ni(CO)_4$ is isolated and heated at 227°C. The purpose of this step is to deposit as much nickel as possible as pure solid (the reverse of the preceding reaction). Calculate the equilibrium constant for the preceding reaction at 227°C.

g. Why is temperature increased for the second step of the Mond process?

h. The Mond process relies on the volatility of $Ni(CO)_4$ for its success. Only pressures and temperatures at which $Ni(CO)_4$ is a gas are useful. A recently developed a variation of the Mond process carries out the first step at higher pressures and a temperature of 152°C. **Estimate the maximum pressure of $Ni(CO)_4(g)$ that can be attained before the gas will liquefy at 152°C**. The boiling point for $Ni(CO)_4$ is 42°C, and the enthalpy of vaporization is 29.0 kJ/mol. [*Hint*: The phase-change reaction and the corresponding equilibrium expression are

$$Ni(CO)_4(l) \rightleftharpoons Ni(CO)_4(g) \qquad K = P_{Ni(CO)4}$$

$Ni(CO)_4(g)$ will liquefy when the pressure of $Ni(CO)_4$ is greater than the *K* value]

8. Describe how the following changes affect the positional probability of a substance.
    a. Increase in volume of a gas at constant *T*
    b. Increase in temperature of a gas at constant *V*
    c. Increase in pressure of a gas at constant *T*

9. You have 1.00 mol of a monatomic ideal gas in a container fitted with a massless, frictionless piston at 1.00 atm and heat it to 400.0K. The gas, as expected, eventually cools to room temperature (in this case, 300.0K).
   [Note: at 400.0K, S° = 9.200 J/Kmol for this gas]
    a. Calculate ΔG (in kJ) for this process. Show all work.
    b. Why isn't ΔG an indication about the spontaneity of the cooling of the gas?

c. Provide mathematical support for the fact that the cooling of the gas is a spontaneous process.

10. When 1 mole of gaseous HI is sealed in a 1-Liter flask at 225°C, it decomposes to form 0.182 mole each of hydrogen and iodine:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

What is the value of the equilibrium constant K_{eq} at 225°C? Additionally, what is standard free energy change, ΔG^0?