1. Consider the Gibbs free energy relationship

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

Determine the <u>temperature</u> at which the following reaction conditions would be spontaneous:

Reaction	ΔS	ΔH	Spontaneous ($\Delta G < 0$) at …			
A)	positive	positive	all Temps	<u>high Temps</u>	low Temps	no Temps
B)	positive	negative	<u>all Temps</u>	high Temps	low Temps	no Temps
C)	negative	positive	all Temps	high Temps	low Temps	<u>no Temps</u>
D)	negative	negative	all Temps	high Temps	<u>low Temps</u>	no Temps

2. Ammonia (NH_3) is a weak base in water with a $K_b = 1.8 \times 10^{-5}$.

   A) Calculate the Gibbs free energy change ($\Delta G°$) for the dissociation of ammonia in water from the table of thermodynamic properties at 298.15 K.

	NH_3 (aq)	NH_4^+ (aq)	H_2O (l)	OH^- (aq)
$\Delta H_f° \left(\dfrac{kJ}{mol}\right)$	−80.3	−132.5	−285.8	−230.0
$\Delta S° \left(\dfrac{J}{mol \cdot K}\right)$	111.3	113.4	69.9	−10.8

First, write out the balanced chemical equation:
$$NH_3 \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons NH_4^+ \text{ (aq)} + OH^- \text{ (aq)}$$

Second, calculate the standard enthalpy and entropy changes:
$$\Delta H° = -132.5\frac{kJ}{mol} + \left(-230.0\frac{kJ}{mol}\right) - \left(-80.3\frac{kJ}{mol}\right) - \left(-285.8\frac{kJ}{mol}\right) = 3.6\frac{kJ}{mol}$$
$$\Delta S° = 113.4\frac{J}{mol \cdot K} + \left(-10.8\frac{J}{mol \cdot K}\right) - 111.3\frac{J}{mol \cdot K} - 69.9\frac{J}{mol \cdot K} = -78.6\frac{J}{mol \cdot K}$$

Third, calculate the standard free energy change:
$$\Delta G° = \Delta H° - T\Delta S°$$
$$= \left(3.6\frac{kJ}{mol} \times \frac{1000\,J}{1\,kJ}\right) - (298.15\,K)\left(-78.6\frac{J}{mol \cdot K}\right)$$
$$\Delta G° = 2.7 \times 10^4\,\frac{J}{mol}$$

   B) Is the dissociation of NH_3 in water spontaneous or nonspontaneous?

   Nonspontaneous

C) Calculate the equilibrium constant (K_b) for NH_3 based on its $\Delta G°$ from part A. Recall that:

$$\Delta G° = -RT \ln K \quad K = e^{-\Delta G°/RT} \quad R = 8.314 \frac{J}{mol \cdot K}$$

$$K_b = \exp\left\{-\frac{\Delta G°}{RT}\right\}$$

$$= \exp\left\{-\frac{2.7 \times 10^4 \frac{J}{mol}}{\left(8.314 \frac{J}{mol \cdot K}\right)(298.15 \text{ K})}\right\}$$

$$K_b = 1.8 \times 10^{-5}$$

D) The phrases "spontaneous" and "nonspontaneous" may <u>mislead</u> you into believing that certain reactions will or will not take place. This is a misconception though.

What does the magnitude and sign of the $\Delta G°$ value tell us about the reaction?

Hint: Consider the relationship between $\Delta G°$ and K in part C.

The sign of $\Delta G°$ tells us whether the equilibrium favors the reactants ($\Delta G° > 0$) or the products ($\Delta G° > 0$) at equilibrium. In other words, this is simply a transformation of the equilibrium constant, K.

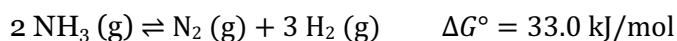3. For each reaction, predict the sign of the entropy change.
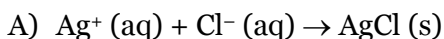
A) Ag^+ (aq) + Cl^- (aq) $\rightarrow$ AgCl (s)

Entropy decreases going from reactants to products $\rightarrow$ more ordered $\rightarrow \Delta S < 0$

B) $2 C_6H_6$ (l) + 15 O_2 (g) $\rightarrow 6 CO_2$ (g) + 3 H_2O (l)
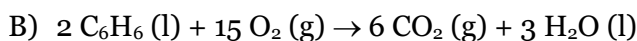
Entropy decreases going from reactants to products $\rightarrow$ more ordered $\rightarrow \Delta S < 0$

4. What is the free energy change (ΔG) for the process shown under the specified conditions?

$$2 NH_3 \text{ (g)} \rightleftharpoons N_2 \text{ (g)} + 3 H_2 \text{ (g)} \qquad \Delta G° = 33.0 \text{ kJ/mol}$$

$$T = 25\,°C \qquad P_{NH_3} = 12.9 \text{ atm} \qquad P_{N_2} = 0.870 \text{ atm} \qquad P_{H_2} = 0.250 \text{ atm}$$

Recall that the reaction quotient for this reaction can be expressed as:

$$Q = \frac{P_{N_2} P_{H_2}^3}{P_{NH_3}^2}$$

And that we can calculate nonstandard free energy changes via:

$$\Delta G = \Delta G° + RT \ln Q$$

$$= \left(33.0 \frac{kJ}{mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right) + \left(8.314 \frac{J}{mol \cdot K}\right)(298.15 \text{ K}) \ln\left[\frac{(0.870)(0.250)^3}{(12.9)^2}\right]$$

$$\Delta G = 9680 \frac{J}{mol}$$