

1. Consider the Gibbs free energy relationship

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

Circle the temperatures at which the following reactions would be spontaneous:

Reaction	ΔS	ΔH	Spontaneous ($\Delta G < 0$) at ...			
(A)	positive	negative	<u>all Temps</u>	high Temps	low Temps	no Temps
(B)	positive	positive	all Temps	<u>high Temps</u>	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 standard Gibbs free energy change (ΔG°) for the dissociation of ammonia in water using the following table of thermodynamic properties at 298.15 K.

	$\text{NH}_3(\text{aq})$	$\text{NH}_4^+(\text{aq})$	$\text{H}_2\text{O}(\text{l})$	$\text{OH}^-(\text{aq})$
$\Delta H^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	-80.3	-132.5	-285.8	-230.0
$\Delta S^\circ \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$	111.3	113.4	69.9	-10.8

First, write out the balanced chemical equation:



Second, calculate the standard enthalpy and entropy changes:

$$\Delta H^\circ = -132.5 \frac{\text{kJ}}{\text{mol}} + (-230.0 \frac{\text{kJ}}{\text{mol}}) - (-80.3 \frac{\text{kJ}}{\text{mol}}) - (-285.8 \frac{\text{kJ}}{\text{mol}}) = 3.6 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = 113.4 \frac{\text{J}}{\text{mol} \cdot \text{K}} + (-10.8 \frac{\text{J}}{\text{mol} \cdot \text{K}}) - 111.3 \frac{\text{J}}{\text{mol} \cdot \text{K}} - 69.9 \frac{\text{J}}{\text{mol} \cdot \text{K}} = -78.6 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Third, calculate the standard free energy change:

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

$$= \left(3.6 \frac{\text{kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \right) - (298.15 \text{ K}) \left(-78.6 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$

$$\Delta G^\circ = 2.7 \times 10^4 \frac{\text{J}}{\text{mol}}$$

B) Calculate the equilibrium constant (K_b) for NH_3 based on its ΔG° from part A.

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

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

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

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

- C) What are standard conditions? This is what the “°” symbol denotes in ΔG° . Is the dissociation of ammonia spontaneous under standard conditions?

Concentrations are 1.0 M, pressures are 1.0 atm, standard states, and temperature is 25 °C = 298.15 K
Nonspontaneous under standard conditions.

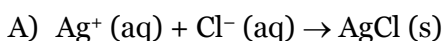
- D) Do you think typical aqueous solutions of weak acids/bases are at standard conditions? The answer is no! Why? Concentration of the conjugate-base/acid is not typically 1.0 M

Now calculate the Gibbs free energy change (ΔG) when $[\text{NH}_3] = 0.60 \text{ M}$ and $[\text{NH}_4^+] = [\text{OH}^-] = 0.0010 \text{ M}$ at 298.15 K. Is this process spontaneous now?

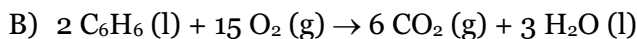
$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= 2.7 \times 10^4 \frac{\text{J}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) (298.15 \text{ K}) \ln \left[\frac{(0.0010)(0.0010)}{0.60}\right] \\ \Delta G &= -5.9 \times 10^3 \frac{\text{J}}{\text{mol}}\end{aligned}$$

Spontaneous under these conditions.

3. For each reaction, predict the sign of the entropy change.

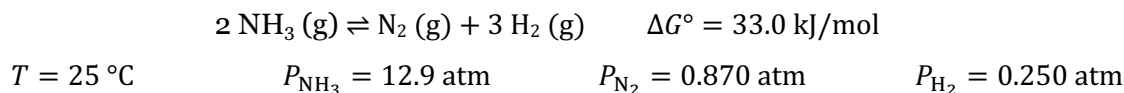


Entropy decreases going from reactants to products \rightarrow more ordered $\rightarrow \Delta S < 0$



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



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

$$Q = \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

And that we can calculate nonstandard free energy changes via:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= \left(33.0 \frac{\text{kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right) + \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) (298.15 \text{ K}) \ln \left[\frac{(0.870)(0.250)^3}{(12.9)^2}\right] \\ \Delta G &= 9680 \frac{\text{J}}{\text{mol}}\end{aligned}$$