

# Chapter 19

## Chemical Thermodynamics

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### Chapter 19 suggested problems

10th Ed. - 19.x: 21, 29, 31, 33, 39, 47, 51, 53, 55, 59, 61, 73, 75, 90

also: review the following Chapter 5 problems: 37, 39, 45, 49, 51, 61, 63, 67, 69, 71, 73, 75, 101

11th Ed. - 19.x: 23, 31, 33, 35, 41, 49, 53, 55, 57, 61, 63, 75, 77, 92

also: review the following Chapter 5 problems: 41, 43, 45, 49, 51, 61, 63, 67, 69, 71, 73, 101, 105

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## Chapter Objectives

After completing this chapter, you should, *at a minimum*, be able to do the following. This information can be found in my lecture notes for this and other chapters and also in your text.

1. Correctly answer all of the questions suggested above and in the quiz for this chapter.
  2. Define basic terms such as thermodynamics, energy, system, surroundings, open system, closed system, isolated system, work, heat, PV work, internal energy, potential energy, kinetic energy, translational energy, vibrational energy, rotational energy, spin energy, state function, path function, extensive properties, intensive properties, conservation of energy, enthalpy, standard conditions, enthalpy of reaction, heat of reaction, standard enthalpy of formation, Hess's law, entropy, standard entropy, spontaneous, non-spontaneous, Gibbs free energy, standard Gibbs free energy of formation.
  3. Understand thermodynamic sign conventions.
  4. Articulate the three laws of thermodynamics.
  5. Describe various types of enthalpy.
  6. Calculate the heat of reaction using both Hess's law and enthalpies of formation.
  7. Calculate the entropy of phase change.
  8. Calculate the entropy change for a reaction using standard enthalpies.
  9. Express the temperature dependence of reaction spontaneity when given enthalpy and entropy information.
  10. Calculate the Gibbs free energy change for a reaction using enthalpy and entropy information or using standard Gibbs free energy of formation values.
  11. Calculate the equilibrium constants for reactions for which the Gibbs free energy change of reaction is known.
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## Class Notes

## I. Enthalpy

A. Thermodynamics: the study of the transformations of energy, especially the transformation of heat into work and work into heat

1. Ultimately energy considerations determine whether or not a reaction will occur, how rapidly it will occur, the products formed, and the equilibrium state of the reaction
2. Energy is the capacity to do work

B. System and surroundings

1. System: the part of the universe under observation
2. Surroundings: the rest of the universe, the place from which the system is observed
3. Types of systems
  - a. Open system: can exchange matter and energy with the surroundings
  - b. Closed system: can exchange energy but not matter with the surroundings
  - c. Isolated system: cannot exchange either matter or energy with the surroundings

C. Work and heat: there are two ways in which the energy of a closed system can be exchanged, by transferring energy either as work or heat

1. Work: a transfer of energy that can be used to change the height of a weight somewhere in the surroundings
2. Heat: a transfer of energy as a result of a temperature difference between a system and its surroundings
3. In chemistry work is most often performed as the consequence of a gas expanding against an external pressure
4. This kind of work is called PV work or expansion work

D. Internal energy (U, E): is equal to the sum of all of the potential and kinetic energies of all of the particles in the system: internal energy is the grand total energy in the system

1. Potential energy and chemical potential energy
2. Kinetic energy at a molecular level: translational, vibrational, rotational, and spin energies
3. When a system undergoes any physical or chemical change, the change in its internal energy is directly related to any heat gained or lost by the system and to any work done to or by the system

- a.  $\Delta U = U_f - U_i = q + w$ 
    - i.  $w$ : work done by or on the system;  $w = P\Delta V$
    - ii.  $q$ : heat emitted or absorbed by the system
    - iii. Sign conventions
      - a. Heat flow from surroundings to system:  $q > 0$  (+ $q$ )
      - b. Heat flow system to surroundings:  $q < 0$  (- $q$ )
      - c. Work done by surroundings on system:  $w > 0$  (+ $w$ )
      - d. Work done by system on surroundings:  $w < 0$  (- $w$ )
    - iv. Implications
      - a. If  $q > 0$  and  $w > 0$  then  $\Delta U > 0$
      - b. If  $q < 0$  and  $w < 0$  then  $\Delta U < 0$
      - c. If  $q < 0$  and  $w > 0$  or if  $q > 0$  and  $w < 0$  then the sign of  $\Delta U$  depends
  4. Internal energy is a state function, i.e., it depends only on the present state of the system and not on how the state was arrived at
    - a. As compared to a path function
    - b. Altitude versus distance traveled to reach that altitude
  5. 1st law: the internal energy of an isolated system is constant
    - a. Energy is conserved (the law of conservation of energy)
- E. Defining enthalpy ( $H$ ; from Greek "enthalpein" meaning "to warm," or, "heat inside")
1. Enthalpy cannot be measured directly but the change in enthalpy of a system can be measured
    - a.  $\Delta H = H_f - H_i = \Delta U + P\Delta V$
    - b. At constant pressure  $\Delta H = q_p$
    - c. If we assume  $\Delta U = q + w$  and the system does  $P\Delta V$  work on the surroundings then, at constant pressure,  $\Delta U = q_p - P\Delta V = \Delta H - P\Delta V$
  2. There are various types of enthalpy: processes which result in a heat-related change in the internal energy of the system at constant pressure
    - a. Phase change -  $\Delta H_{\text{vaporization}}$ ,  $\Delta H_{\text{fusion}}$ ,  $\Delta H_{\text{sublimation}}$ , etc.
    - b. Ionization

- c. Electron affinity - the enthalpy of electron gain
- d. Bond enthalpies
- e. Enthalpies of formation: the change in enthalpy for the reaction that forms 1.00 mole of a compound from the elements with all substances in their standard states, usually at 298 K
3. Enthalpies of formation: elaboration and examples
- a. Examples
- $\text{C}_{(s)} + 2 \text{H}_2 (g) \rightarrow \text{CH}_4 (g) ; \Delta H^\circ_f = -74.8 \text{ kJ/mol}$
  - $2 \text{C}_{(s)} + 3 \text{H}_2 (g) + 1/2 \text{O}_2 (g) \rightarrow \text{C}_2\text{H}_5\text{OH} (l) ; \Delta H^\circ_f = -277.7 \text{ kJ/mol}$
- b. By definition the standard enthalpy of formation of the most stable form of any element is zero
- $\text{C}_{(s, \text{graphite})}: 0.0 \text{ kJ/mol}; \text{C}_{(s, \text{diamond})}: 2.9 \text{ kJ/mol}; \text{C}_{(g)}: +716.7 \text{ kJ/mol}$
  - $\text{Br}_2 (l): 0.0 \text{ kJ/mol}; \text{Br}_2 (g): 30.9 \text{ kJ/mol}$
- c. Can use standard enthalpy of formation values to calculate enthalpies of reaction:  $\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_{\text{f, prod}} - \sum n \Delta H^\circ_{\text{f, rxt}}$
- Calculate the  $\Delta H^\circ_{\text{rxn}}$  for the combustion of 1.00 mole of propane
    - $\text{C}_3\text{H}_8 (g) + 5 \text{O}_2 (g) \rightarrow 3 \text{CO}_2 (g) + 4 \text{H}_2\text{O}(l)$
    - |                            | $\Delta H^\circ_f$ (kJ/mol) |
|----------------------------|-----------------------------|
| $\text{C}_3\text{H}_8 (g)$ | -103.85                     |
| $\text{O}_2 (g)$           | 0.0                         |
| $\text{CO}_2 (g)$          | -393.5                      |
| $\text{H}_2\text{O}(l)$    | -285.8                      |
    - $\Delta H^\circ_{\text{rxn}} = [(3 \text{ moles})(-393.5 \text{ kJ/mol}) + (4 \text{ moles})(-285.8 \text{ kJ/mol})] - [(1 \text{ mole})(-103.85 \text{ kJ/mol}) + (5 \text{ moles})(0.0 \text{ kJ/mole})]$
    - $\Delta H^\circ_{\text{rxn}} = -2220 \text{ kJ/ mole propane}$
  - Calculate the  $\Delta H^\circ_{\text{rxn}}$  for the combustion of 1.00 grams of benzene
    - $\text{C}_6\text{H}_6 (l) + 15/2 \text{O}_2 (g) \rightarrow 6 \text{CO}_2 (g) + 3 \text{H}_2\text{O}(l)$
    - Note that enthalpy is an extensive property, i.e. it is related to amount, so fractional coefficients \*may\* be used in balancing thermochemical equations

c.

	$\Delta H_f^\circ$ (kJ/mol)
$C_6H_6$ (l)	-49.0
$O_2$ (g)	0.0
$CO_2$ (g)	-393.5
$H_2O$ (l)	-285.8

d.  $\Delta H^\circ_{\text{rxn}} = [(6 \text{ moles})(-393.5 \text{ kJ/mol}) + (3 \text{ moles})(-285.8 \text{ kJ/mol})] - [(1 \text{ mole})(-49.0 \text{ kJ/mol}) + (15/2 \text{ moles})(0.0 \text{ kJ/mole})]$

e.  $\Delta H^\circ_{\text{rxn}} = -3267 \text{ kJ/mole benzene}$

f.  $(-3267 \text{ kJ/mole})(1 \text{ mole} / 78 \text{ g}) = -41.8 \text{ kJ/g benzene}$

## II. Entropy

### A. Two observations

1. The expansion of a gas from areas of high concentration to areas of low concentration is spontaneous, and although it is statistically possible for the gas particles to spontaneously re-order themselves, the likelihood is very low unless work is done by the surrounding on the system
2. The flow of heat from a system that is higher in temperature than it's surroundings is spontaneous, and to reheat the system once the heat is lost requires a transfer of heat from the surroundings to the system
  - a. Energy tends to disperse chaotically (in a random manner)

### B. Entropy: a measure of the dispersal of matter and energy (S)

1. Entropy is a synonym for the extent of chaotic dispersal of matter and energy
2. Entropy is also a measure of the randomness or disorder in a system
3. Entropy is a state property
4.  $\Delta S = S_f - S_i$

### C. The Second Law

1. The entropy of an isolated system increases during a spontaneous reaction
2. Or: the total entropy of a system and it's surroundings always increases during a spontaneous reaction
  - a. For a spontaneous process at a given temperature (K), at equilibrium  $\Delta S = q/T$
  - b. This permits calculation of  $\Delta S$  for phase changes

<b>transition</b>	<b>q</b>	<b><math>\Delta S</math></b>
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s → l	+	+
l → g	+	+
s → g	+	+
g → l	-	-
l → s	-	-
g → s	-	-

- c. At constant pressure  $q_p = \Delta H$  so at equilibrium  $\Delta S = \Delta H/T$  where  $\Delta H$  is the enthalpy of the particular phase change under observation
- d. Note that the calculation of values of  $\Delta S$  for phase changes indicate the change in entropy that results from the transition, not the entropy of either the initial or final state
- e. Examples
- What is the change in entropy associated with the melting of 1.00 mole of ice at  $0^\circ\text{C}$ ?  
 $\Delta S = \Delta H_{\text{melt}} / T_m = +6.01 \text{ kJ/mol} / 273.2 \text{ K} = +21.9 \text{ J/K}$
  - What is the change in entropy associated with the condensation of 1.00 mole of water at  $100^\circ\text{C}$ ?  
 $\Delta S = -\Delta H_{\text{vap}} / T_b = -40.7 \text{ kJ/mol} / 373.2 \text{ K} = -109.1 \text{ J/K}$

#### D. Are chemical reactions spontaneous?

- At equilibrium  $\Delta S = \Delta H/T \implies \Delta H/T - \Delta S = 0 \implies \Delta H - T\Delta S = 0$
- Assume constant temperature and pressure

$\Delta H - T\Delta S < 0$	spontaneous
$\Delta H - T\Delta S > 0$	nonspontaneous
$\Delta H - T\Delta S = 0$	equilibrium

#### 3. Implications

$-\Delta H, +\Delta S$	always spontaneous
$+\Delta H, -\Delta S$	nonspontaneous
$-\Delta H, -\Delta S, +\Delta H, +\Delta S$	depends on T

#### E. The Third Law

- The entropy of a perfect crystalline material at  $T = 0\text{K}$  is zero
- Or: a substance that is perfectly crystalline at  $0\text{K}$  has  $S = 0$
- Or:  $0\text{K}$  can never be reached, since all molecular motion would have to stop
- The Three Laws restated
  - You can't win, you can only break even.

- b. You can only break even at absolute zero.
- c. You can never reach absolute zero.

#### F. Standard entropies

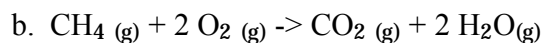
1. also known as absolute entropies
2.  $S^\circ$  is the entropy value for species in their standard state at 1 atm and a specific temperature, often 293 K or 298 K (see Table 19.1, p. 812 or Appendix C)
3. The elements in their elemental states do not have zero entropy values as is the case with enthalpies of formation; this is as stated by the 3rd Law.

#### G. Calculating $\Delta S$

1. Estimation: will  $\Delta S$  be "+" or "-" for a reaction?
  - a.  $\Delta S$  is positive if a reactant molecule is broken into two or more product molecules, as is the case in decomposition reactions
    - i.  $\text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{CO}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$
  - b.  $\Delta S$  is positive if the number of moles of gas in the product side is greater than the number of moles of gas on the reactant side
    - i.  $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$
2. Formal calculations: require tables of standard entropy values (Appendix C, p. 1112) and follow the equation  $\Delta S^\circ_{\text{rxn}} = \sum n \Delta S^\circ_{\text{prod}} - \sum n \Delta S^\circ_{\text{rxt}}$ 
  - a. Calculate  $\Delta S^\circ$  for the synthesis of ammonia from the elements
    - i.  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$
    - ii.  $\text{N}_2(\text{g})$ : 191.5 J/mol·K;  $\text{H}_2(\text{g})$ : 130.6 J/mol·K;  $\text{NH}_3(\text{g})$ : 193 J/mol·K
    - iii.  $\Delta S^\circ_{\text{rxn}} = [(2 \text{ moles})(193 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mole})(191.5 \text{ J/mol}\cdot\text{K}) + (3 \text{ moles})(130.6 \text{ J/mole}\cdot\text{K})]$
    - iv.  $\Delta S^\circ_{\text{rxn}} = -197 \text{ J/K}$
  - b. What is  $\Delta S^\circ$  for the combustion of ethanol?
    - i.  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$
    - ii.  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ : 161 J/mol·K;  $\text{O}_2(\text{g})$ : 205 J/mol·K;  $\text{CO}_2(\text{g})$ : 213.7 J/mol·K;  $\text{H}_2\text{O}(\text{l})$ : 69.91 J/mol·K
    - iii.  $\Delta S^\circ_{\text{rxn}} = [(2 \text{ moles})(213.7 \text{ J/mol}\cdot\text{K}) + (3 \text{ moles})(69.91 \text{ J/mole}\cdot\text{K})] - [(1 \text{ mole})(161 \text{ J/mol}\cdot\text{K}) + (3 \text{ moles})(205 \text{ J/mol}\cdot\text{K})]$
    - iv.  $\Delta S^\circ_{\text{rxn}} = -138.9 \text{ J/K}$

### III. Gibbs free energy and spontaneity

- A. As previously demonstrated, the spontaneity of a reaction can be predicted if  $\Delta H$  and  $\Delta S$  for the reaction are known
- B. The thermodynamic property defined by enthalpy, entropy, and temperature is called Gibbs Free energy according to the relationship  $\Delta G = \Delta H - T\Delta S$
- At a given temperature and pressure, if  $\Delta G$  is negative the reaction will be spontaneous
  - At a given temperature and pressure, if  $\Delta G$  is positive the reaction will be nonspontaneous
  - At a given temperature and pressure, if  $\Delta G$  is zero the reaction is at equilibrium
- C. For a reaction the value of  $\Delta G$  gives the maximum amount of non-expansion (i.e., nonPV) work that can be obtained from a system undergoing change at a constant temperature and pressure
- Proof
    - non PV work =  $w'$
    - $w = w' - P\Delta V$
    - $\Delta G = \Delta H - T\Delta S$
    - $\Delta G = \Delta U + P\Delta V - T\Delta S$
    - $\Delta G = q + w + P\Delta V - T\Delta S$
    - $\Delta G = q + w' - P\Delta V + P\Delta V - T\Delta S = q + w' - T\Delta S$
    - Since  $\Delta S = q/T$  then  $q = T\Delta S$  and  $\Delta G = T\Delta S + w' - T\Delta S$
    - $\Delta G = w'$
  - An example: Given the reaction  $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$  ( $\Delta G = -237 \text{ kJ}$ ) in a fuel cell, the formation of 1.0 mole of water can generate 237 kJ of electrical energy
- D. The difference between  $\Delta G$  and  $\Delta H$  is that energy must be discarded by the system into the surroundings as heat to ensure that the process is spontaneous and can produce work, especially non-PV work
- $\Delta G$  represents the energy free for use in non-expansion work, hence the name "free energy"
  - $\Delta G$  is a measure of the "driving force" of a reaction
  - The values of  $\Delta G$  for individual compounds is a relative index of their stability
- E. Calculations with  $\Delta G$

1. Calculating  $\Delta G$  from  $\Delta H$  and  $\Delta S$ a. Calculate  $\Delta G$  for the combustion of methane at  $25^\circ\text{C}$ 

c.

	<b>CH<sub>4</sub> (g)</b>	<b>O<sub>2</sub> (g)</b>	<b>CO<sub>2</sub> (g)</b>	<b>H<sub>2</sub>O(l)</b>	<b>source (BLB)</b>
<b><math>\Delta H_f^\circ</math> (kJ/mol)</b>	-74.9	0	-393.5	-285.8	Appendix C, p. 1112
<b><math>\Delta S^\circ</math> (J/mol·K)</b>	186.1	205	213.7	69.91	

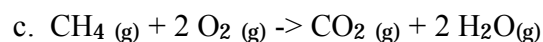
d.  $\Delta H_f^\circ = [(1 \text{ mole})(-393.5 \text{ kJ/mol}) + (2 \text{ moles})(-285.5 \text{ kJ/mol})] - [(1 \text{ mole})(-74.9 \text{ kJ/mol}) + (2 \text{ moles})(0.0 \text{ kJ/mole})] = -890.2 \text{ kJ}$

e.  $\Delta S^\circ = [(1 \text{ mole})(213.7 \text{ J/mol}\cdot\text{K}) + (2 \text{ moles})(69.91 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mole})(186.1 \text{ J/mol}\cdot\text{K}) + (2 \text{ moles})(205 \text{ J/mole}\cdot\text{K})] = -242.6 \text{ J/K}$

f.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-802.2 \text{ kJ}) - (298.15 \text{ K})(-5.00 \text{ J/K}) = -800.7 \text{ kJ}$

2. Calculating  $\Delta G$  from standard free energy of formation values:  $\Delta G^\circ_{\text{rxn}} = \sum n \Delta G^\circ_{\text{prod}} - \sum n \Delta G^\circ_{\text{rxt}}$ a. Standard free energy of formation: the free energy change that occurs when 1 mole of substance is formed from the elements in their most stable states at 1 atm and a specific temperature (usually  $25^\circ\text{C}$ )

b. A table of these values is found in Appendix C, p. 1112 ff



1.  $\text{CH}_4(\text{g}): -50.8 \text{ kJ/mol}$

2.  $\text{O}_2(\text{g}): 0 \text{ kJ/mol}$

3.  $\text{CO}_2(\text{g}): -394.4 \text{ kJ/mol}$

4.  $\text{H}_2\text{O}(\text{g}): -237.1 \text{ kJ/mol}$

d.  $\Delta G^\circ_{\text{rxn}} = [(1 \text{ mol})(-394.4 \text{ kJ/mol}) + (2 \text{ mol})(-237.1 \text{ kJ/mol})] - [(1 \text{ mol})(-50.8 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})] = -817.8 \text{ kJ}$

F.  $\Delta G$  and equilibrium1.  $\Delta G^\circ$  for a reaction can be calculated from the data in thermodynamic tables when all reactants and products are in their standard states2. If reactants/products are in non-standard states then an adjusted value of  $\Delta G$  can be calculated:  $\Delta G = \Delta G^\circ + RT \ln Q$ 3. At equilibrium  $\Delta G = 0$  and  $Q = K$ , therefore  $0 = \Delta G^\circ + RT \ln K$ 

4.  $\Delta G^\circ = -RT \ln K$  ( $R = 8.314 \text{ J/mol}\cdot\text{K}$ )

5. Example 1

- a. Given the Haber process, if  $\Delta G^\circ = -33.3 \text{ kJ/mol}$ , calculate  $\Delta G$  for a reaction mixture of 1.00 atm nitrogen, 3.00 atm nitrogen, and 0.50 mole ammonia, all at  $25^\circ\text{C}$
- b.  $Q = P_{\text{NH}_3}^2 / P_{\text{N}_2} \cdot P_{\text{H}_2}^3 = (0.50)^2 / (1) \cdot (3)^3 = 9.26 \times 10^{-3}$
- c.  $\Delta G = \Delta G^\circ + RT \ln Q = (-33.3 \text{ kJ}) + (8.314 \text{ J/mol}\cdot\text{K}) \cdot (298 \text{ K}) \ln (9.26 \times 10^{-3}) = -44.9 \text{ kJ/mol}$

## 6. Example 2

- a. Calculate  $K_p$  at  $25^\circ\text{C}$  for the Haber process
- b. At equilibrium  $\Delta G = 0$  and  $Q = K_p$ , therefore  $0 = \Delta G^\circ + RT \ln K_p$
- c. Since  $\Delta G^\circ = -RT \ln K_p$ ,  $K_p = \exp(-\Delta G^\circ / RT)$
- d.  $K_p = \exp[-(-33.3 \text{ kJ}) / (8.314 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}) \cdot (298 \text{ K})] = e^{13.4} = 6.87 \times 10^5$

7. A note on the relationship between  $\Delta G$  and  $K$ 

- a. If  $\Delta G^\circ < 0$  then  $K > 1$ , product-favored
- b. If  $\Delta G^\circ > 0$  then  $K < 1$ , reactant-favored
- c. If  $\Delta G^\circ = 0$  then  $K = 1$ , eqb

G. The dependence of  $\Delta G$  on temperature

1. If we assume  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature then  $\Delta G^\circ$  can be calculated at any temperature using  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

## 2. Example 1

- a. Calculate  $\Delta G^\circ$  for the Haber process at  $-100^\circ\text{C}$  and  $500^\circ\text{C}$  ( $\Delta H^\circ = -92.35 \text{ kJ/mol}$ ,  $\Delta S^\circ = -198.3 \text{ J/K}$ )
- b. At  $-100^\circ\text{C}$  (173 K):  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-92.35 \text{ kJ/mol}) - (173 \text{ K})(-198.3 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}) = -58.1 \text{ kJ/mol}$
- c. At  $500^\circ\text{C}$  (773 K):  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-92.35 \text{ kJ/mol}) - (773 \text{ K})(-198.3 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}) = 60.9 \text{ kJ/mol}$

## 3. Example 2

- a. At what temperature will this reaction be at equilibrium? ( $K = 1$ ,  $\Delta G^\circ = 0$ ):  $T = 465.9 \text{ K}$

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