

Chapter 16 Review Questions and Text Homework Solutions

Review Questions

- A spontaneous process is one that occurs without any outside intervention.
 - Entropy is a measure of disorder or randomness.
 - Positional probability is a type of probability that depends on the number of arrangements in space that yield a particular state. The more disordered state generally has the larger positional probability.
 - The system is the portion of the universe in which we are interested.
 - The surroundings are everything else in the universe besides the system.
 - The universe is everything; universe = system + surroundings.
- Second law of thermodynamics: in any spontaneous process, there is always an increase in the entropy of the universe. $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$; When both ΔS_{sys} and ΔS_{surr} are positive, ΔS_{univ} must be positive (so the process is spontaneous). ΔS_{univ} is always negative (so the process is nonspontaneous) when both ΔS_{sys} and ΔS_{surr} are negative. When the signs of ΔS_{sys} are opposite of each other [$(\Delta S_{\text{sys}} (+), \Delta S_{\text{surr}} (-)$ or vice versa], the process may or may not be spontaneous.
- ΔS_{surr} is primarily determined by heat flow. This heat flow into or out of the surroundings comes from the heat flow out of or into the system. In an exothermic process ($\Delta H < 0$), heat flows into the surroundings from the system. The heat flow into the surroundings increases the random motions in the surroundings and increases the entropy of the surroundings ($\Delta S_{\text{surr}} > 0$). This is a favorable driving force for spontaneity. In an endothermic reaction ($\Delta H > 0$), heat is transferred from the surroundings into the system. This heat flow out of the surroundings decreases the random motions in the surroundings and decreases the entropy of the surroundings ($\Delta S_{\text{surr}} < 0$). This is unfavorable. The magnitude of ΔS_{surr} also depends on the temperature. The relationship is inverse; at low temperatures, a specific amount of heat exchange makes a larger percent change in the surroundings than the same amount of heat flow at a higher temperature. The negative sign in the $\Delta S_{\text{surr}} = -\Delta H/T$ equation is necessary to get the signs correct. For an exothermic reaction where ΔH is negative, this increases ΔS_{surr} so the negative sign converts the negative ΔH value into a positive quantity. For an endothermic process where ΔH is positive, the sign of ΔS_{surr} is negative and the negative sign converts the positive ΔH value into a negative quantity.
- $\Delta S_{\text{univ}} = -\Delta G/T$ (at constant T and P); when ΔG is negative ($\Delta S_{\text{univ}} > 0$), the process is spontaneous. When ΔG is positive ($\Delta S_{\text{univ}} < 0$), the process is nonspontaneous (the reverse process is spontaneous). When $\Delta G = 0$, the process is at equilibrium.

 $\Delta G = \Delta H - T\Delta S$; see Table 16.5 of the text for the four possible sign conventions and the temperature dependence for these sign combinations. When the signs for ΔH and ΔS are both the same, then temperature determines if the process is spontaneous. When ΔH is positive

(unfavorable) and ΔS is positive (favorable), high temperatures are needed to make the favorable ΔS term dominate, which makes the process spontaneous ($\Delta G < 0$). When ΔH is negative (favorable) and ΔS is negative (unfavorable), low temperatures are needed so the favorable ΔH term dominates, which makes the process spontaneous ($\Delta G < 0$). Note that if ΔG is positive for a process, then the reverse process has a negative ΔG value and is spontaneous.

At the phase change temperature (melting point or boiling point), two phases are in equilibrium with each other so $\Delta G = 0$. The $\Delta G = \Delta H - T\Delta S$ equation reduces to $\Delta H = T\Delta S$ at the phase change temperature. For the $s \rightarrow l$ phase change, ΔG is negative above the freezing point because the process is spontaneous (as we know). For the $l \rightarrow g$ phase change, the sign of ΔG is positive below the boiling point as the process is nonspontaneous (as we know).

5. Third law of thermodynamics: The entropy of a perfect crystal at 0 K is zero. Standard entropy values (S°) represent the increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm pressure. The equation to calculate ΔS° for a reaction using the standard entropy values is: $\Delta S^\circ_{\text{rxn}} = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$.

This equation works because entropy is a state function of the system (it is not pathway-dependent). Because of this, one can manipulate chemical reactions with known ΔS° values to determine ΔS° for a different reaction. The entropy change for a different reaction equals the sum of the entropy changes for the reactions added together that yield the different reaction. This is utilizing Hess's law. The superscript $^\circ$ indicates conditions where $T = 25^\circ\text{C}$ and $P = 1 \text{ atm}$.

To predict signs for gas phase reactions, you need to realize that the gaseous state represents a hugely more disordered state (a state with much larger positional probability) as compared to the solid and liquid states. Gases dominate sign predictions for reactions. Those reactions that show an increase in the number of moles of gas as reactants are converted to products have an increase in disorder (an increase in positional probability) which translates into a positive ΔS° value. ΔS° values are negative when there is a decrease in the moles of gas as reactants are converted into products. When the moles of gaseous reactants and products are equal, ΔS° is usually difficult to predict for chemical reactions. However, predicting signs for phase changes can be done by realizing the solid state is the most ordered phase (lowest S° values, smallest positional probability). The liquid state is a slightly more disordered phase (has a higher positional probability) than the solid state, with the gaseous state being the most disordered phase (has the largest positional probability) by a large margin ($S^\circ_{\text{solid}} < S^\circ_{\text{liquid}} \ll S^\circ_{\text{gas}}$). Another process involving condensed phases whose sign is also easy to predict (usually) is the dissolution of a solute in a solvent. Here, the mixed up solution state is usually the more disordered state (has a larger positional probability) as compared to the solute and solvent separately.

6. Standard free energy change: the change in free energy that will occur for one unit of reaction if the reactants in their standard states are converted to products in their standard state. The standard free energy of formation (ΔG_f°) of a substance is the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements, with all reactants and products in their standard states. The equation that manipulates ΔG_f° values to determining $\Delta G^\circ_{\text{reaction}}$ is:

$$\Delta G^\circ = \sum n_p \Delta G_f^\circ (\text{products}) - \sum n_r \Delta G_f^\circ (\text{reactants}) .$$

Because ΔG° is a state function (path independent), chemical reactions with known ΔG° values can be manipulated to determine ΔG° for a different reaction. ΔG° for the different reaction is the sum of ΔG° for all the steps (reactions) added together to get the different reaction. This is Hess's law.

Another way to determine ΔG° for a reaction is to utilize the $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ equation. Here, you need to know ΔH° , ΔS° , and the temperature, then you can use the above equation to calculate ΔG° .

Of the functions ΔG° , ΔH° , and ΔS° , ΔG° has the greatest dependence on temperature. The temperature is usually assumed to be 25°C. However, if other temperatures are used in a reaction, we can estimate ΔG° at that different temperature by assuming ΔH° and ΔS° are temperature independent (which is not always the best assumption). We calculate ΔH° and ΔS° values for a reaction using Appendix 4 data, then use the different temperature in the $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ equation to determine (estimate) ΔG° at that different temperature.

7. No; when using ΔG_f° values in Appendix 4, we have specified a temperature of 25°C. Further, if gases or solutions are involved, we have specified partial pressures of 1 atm and solute concentrations of 1 molar. At other temperatures and compositions, the reaction may not be spontaneous. A negative ΔG° value means the reaction is spontaneous under standard conditions.

The free energy and pressure relationship is $G = G^\circ + RT \ln(P)$. The $RT \ln(P)$ term corrects for nonstandard pressures (or concentrations if solutes are involved in the reaction). The standard pressure for a gas is 1 atm and the standard concentration for solutes is 1 *M*. The equation to calculate ΔG for a reaction at nonstandard conditions is: $\Delta G = \Delta G^\circ + RT \ln Q$ where Q is the reaction quotient determined at the nonstandard pressures and/or concentrations of the gases and/or solutes in the reaction. The reaction quotient has the exact same form as the equilibrium constant K . The difference is that the partial pressures or concentrations used may or may not be the equilibrium concentrations.

All reactions want to minimize their free energy. This is the driving force for any process. As long as ΔG is a negative, the process occurs. The equilibrium position represents the lowest total free energy available to any reaction system. Once equilibrium is reached, the system cannot minimize its free energy anymore. Converting from reactants to products or products to reactants will increase the total free energy of the system which reactions do not want to do.

8. At equilibrium, $\Delta G = 0$ and $Q = K$ (the reaction quotient equals the equilibrium constant value). From the $\Delta G^\circ = -RT \ln K$ equation, when a reaction has $K < 1$, the $\ln K$ term is negative, so ΔG° is positive. When $K > 1$, the $\ln K$ term is positive, so ΔG° is negative. When $\Delta G^\circ = 0$, this tells us that K for the process is equal to one ($K = 1$) because $\ln(1) = 0$.

The sign of ΔG (positive or negative) tells us which reaction is spontaneous (the forward or reverse reaction). If $\Delta G < 0$, then the forward reaction is spontaneous, and if $\Delta G > 0$, then the reverse reaction is spontaneous. If $\Delta G = 0$, then the reaction is at equilibrium (neither the forward or reverse reactions are spontaneous). ΔG° gives the equilibrium position by determining K for a reaction utilizing the equation $\Delta G^\circ = -RT \ln K$ can only be used to predict spontaneity when all reactants and products are present at standard pressures of 1 atm and/or standard concentrations of 1 *M*.

10. $w_{\max} = \Delta G$; when ΔG is negative, the magnitude of ΔG is equal to the maximum possible useful work obtainable from the process (at constant T and P). When ΔG is positive, the magnitude of ΔG is equal to the minimum amount of work that must be expended to make the process spontaneous. Due to waste energy (heat) in any real process, the amount of useful work obtainable from a spontaneous process is always less than w_{\max} , and for a non-spontaneous reaction, an amount of work greater than w_{\max} must be applied to make the process spontaneous.

Reversible process: A cyclic process carried out by a hypothetical pathway, which leaves the universe the same as it was before. No real process is reversible.

Text Homework

22. The sign of ΔG tells us if a reaction is spontaneous or not at whatever concentrations are present (at constant T and P). The magnitude of ΔG equals w_{\max} . When $\Delta G < 0$, the magnitude tells us how much work, in theory, could be harnessed from the reaction. When $\Delta G > 0$, the magnitude tells us the minimum amount of work that must be supplied to make the reaction occur. ΔG° gives us the same information only when the concentrations for all reactants and products are at standard conditions (1 atm for gases, 1 M for solute). These conditions rarely occur.

$\Delta G^\circ = -RT \ln K$; from this equation, one can calculate K for a reaction if ΔG° is known at that temperature. Therefore, ΔG° gives the equilibrium position for a reaction. To determine K at a temperature other than 25°C , one needs to know ΔG° at that temperature. We assume ΔH° and ΔS° are temperature-independent and use the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to estimate ΔG° at the different temperature. For $K = 1$, we want $\Delta G^\circ = 0$, which occurs when $\Delta H^\circ = T\Delta S^\circ$. Again, assume ΔH° and ΔS° are temperature-independent; then solve for T ($= \Delta H^\circ/\Delta S^\circ$). At this temperature, $K = 1$ because $\Delta G^\circ = 0$. This only works for reactions where the signs of ΔH° and ΔS° are the same (either both positive or both negative). When the signs are opposite, K will always be greater than 1 (when ΔH° is negative and ΔS° is positive) or K will always be less than 1 (when ΔH° is positive and ΔS° is negative). When the signs of ΔH° and ΔS° are opposite, K can never equal 1.

32. Of the three phases (solid, liquid, and gas), solids are most ordered (have the smallest positional probability) and gases are most disordered (have the largest positional probability). Thus a, b, and f (melting, sublimation, and boiling) involve an increase in the entropy of the system since going from a solid to a liquid or from a solid to a gas or from a liquid to a gas increases disorder (increases positional probability). For freezing (process c), a substance goes from the more disordered liquid state to the more ordered solid state; hence, entropy decreases. Process d (mixing) involves an increase in disorder (an increase in positional probability), while separation (phase e) increases order (decreases positional probability). So, of all the processes, a, b, d, and f result in an increase in the entropy of the system.

34. a.
$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{-(-2221 \text{ kJ})}{298 \text{ K}} = 7.45 \text{ kJ/K} = 7.45 \times 10^3 \text{ J/K}$$

b.
$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{-112 \text{ kJ}}{298 \text{ K}} = -0.376 \text{ kJ/K} = -376 \text{ J/K}$$

36. $\Delta G = \Delta H - T\Delta S$; a process is spontaneous when $\Delta G < 0$. For the following, assume ΔH and ΔS are temperature-independent.

- a. When ΔH and ΔS are both negative, ΔG will be negative below a certain temperature where the favorable ΔH term dominates. When $\Delta G = 0$, then $\Delta H = T\Delta S$. Solving for this temperature:

$$T = \frac{\Delta H}{\Delta S} = \frac{-18,000 \text{ J}}{-60. \text{ J/K}} = 3.0 \times 10^2 \text{ K}$$

At $T < 3.0 \times 10^2 \text{ K}$, this process will be spontaneous ($\Delta G < 0$).

- b. When ΔH and ΔS are both positive, ΔG will be negative above a certain temperature where the favorable ΔS term dominates.

$$T = \frac{\Delta H}{\Delta S} = \frac{18,000 \text{ J}}{60. \text{ J/K}} = 3.0 \times 10^2 \text{ K}$$

At $T > 3.0 \times 10^2 \text{ K}$, this process will be spontaneous ($\Delta G < 0$).

- c. When ΔH is positive and ΔS is negative, this process can never be spontaneous at any temperature because ΔG can never be negative.
- d. When ΔH is negative and ΔS is positive, this process is spontaneous at all temperatures because ΔG will always be negative.

38. At the boiling point, $\Delta G = 0$, so $\Delta H = T\Delta S$. $T = \frac{\Delta H}{\Delta S} = \frac{58.51 \times 10^3 \text{ J/mol}}{92.92 \text{ J/K} \cdot \text{mol}} = 629.7 \text{ K}$

40. $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{C}_2\text{H}_5\text{OH}(g)$; at the boiling point, $\Delta G = 0$ and $\Delta S_{\text{univ}} = 0$. For the vaporization process, ΔS is a positive value, whereas ΔH is a negative value. To calculate ΔS_{sys} , we will determine ΔS_{surr} from ΔH and the temperature; then $\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$ for a system at equilibrium.

$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{38.7 \times 10^3 \text{ J/mol}}{351 \text{ K}} = -110. \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{\text{sys}} = -\Delta S_{\text{surr}} = -(-110.) = 110. \text{ J/K} \cdot \text{mol}$$

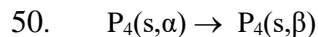
42. a. Decrease in positional probability ($\Delta n < 0$); $\Delta S^\circ(-)$
b. Decrease in positional probability ($\Delta n < 0$); $\Delta S^\circ(-)$
c. Increase in positional probability; $\Delta S^\circ(+)$
d. Increase in positional probability; $\Delta S^\circ(+)$

44. a. He (10 K); $S = 0$ at 0 K

- b. N_2O ; more complicated molecule, so has the larger positional probability.

c. $\text{NH}_3(\text{l})$; the liquid state is more disordered (has a larger positional probability) than the solid state.

48. $\text{CS}_2(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{SO}_2(\text{g}); \Delta S^\circ = S_{\text{CO}_2}^\circ + 2S_{\text{SO}_2}^\circ - [3S_{\text{O}_2}^\circ + S_{\text{CS}_2}^\circ]$
 $-143 \text{ J/K} = 214 \text{ J/K} + 2(248 \text{ J/K}) - 3(205 \text{ J/K}) - (1 \text{ mol})S_{\text{CS}_2}^\circ, S_{\text{CS}_2}^\circ = 238 \text{ J/K}\cdot\text{mol}$



a. At $T < -76.9^\circ\text{C}$, this process is spontaneous, and the sign of ΔG is (-). At -76.9°C , $\Delta G = 0$, and above -76.9°C , the sign of ΔG is (+). This is consistent with ΔH (-) and ΔS (-).

b. Because the sign of ΔS is negative, the β form has the more ordered structure (has the smaller positional probability).

54. a. $\Delta H^\circ = 2(-46 \text{ kJ}) = -92 \text{ kJ}; \Delta S^\circ = 2(193 \text{ J/K}) - [3(131 \text{ J/K}) + 192 \text{ J/K}] = -199 \text{ J/K}$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92 \text{ kJ} - 298 \text{ K}(-0.199 \text{ kJ/K}) = -33 \text{ kJ}$$

b. ΔG° is negative, so this reaction is spontaneous at standard conditions.

c. $\Delta G^\circ = 0$ when $T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92 \text{ kJ}}{-0.199 \text{ kJ/K}} = 460 \text{ K}$

At $T < 460 \text{ K}$ and standard pressures (1 atm), the favorable ΔH° term dominates, and the reaction is spontaneous ($\Delta G^\circ < 0$).

62. a. $\Delta G^\circ = 2(-270. \text{ kJ}) - 2(-502 \text{ kJ}) = 464 \text{ kJ}$

b. Because ΔG° is positive, this reaction is not spontaneous at standard conditions at 298 K.

c. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = 464 \text{ kJ} + 298 \text{ K}(0.179 \text{ kJ/K}) = 517 \text{ kJ}$

We need to solve for the temperature when $\Delta G^\circ = 0$:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ, T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{517 \text{ kJ}}{0.179 \text{ kJ/K}} = 2890 \text{ K}$$

This reaction will be spontaneous at standard conditions ($\Delta G^\circ < 0$) when $T > 2890 \text{ K}$. Here the favorable entropy term will dominate.

66. $\Delta G^\circ = 3(0) + 2(-229) - [2(-34) + 1(-300.)] = -90. \text{ kJ}$

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2\text{S}}^2 \times P_{\text{SO}_2}} = -90. \text{ kJ} + \frac{(8.3145)(298)}{1000} \text{ kJ} \left[\ln \frac{(0.030)^2}{(1.0 \times 10^{-4})(0.010)} \right]$$

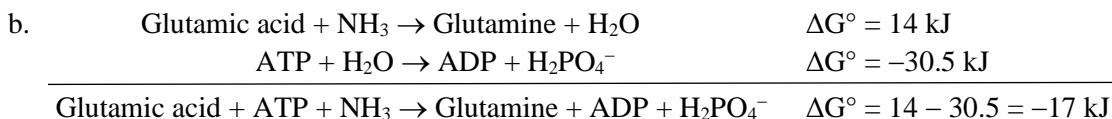
$$\Delta G = -90. \text{ kJ} + 39.7 \text{ kJ} = -50. \text{ kJ}$$

70. $\Delta G^\circ = 2 \text{ mol}(-229 \text{ kJ/mol}) - [2 \text{ mol}(-34 \text{ kJ/mol}) + 1 \text{ mol}(-300. \text{ kJ/mol})] = -90. \text{ kJ}$

$$K = \exp \frac{-\Delta G^\circ}{RT} = \exp \left[\frac{-(-9.0 \times 10^4 \text{ J})}{8.3145 \text{ J/K} \cdot \text{mol}(298 \text{ K})} \right] = e^{36.32} = 5.9 \times 10^{15}$$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; because there is a decrease in the number of moles of gaseous particles, ΔS° is negative. Because ΔG° is negative, ΔH° must be negative. The reaction will be spontaneous at low temperatures (the favorable ΔH° term dominates at low temperatures).

76. a. $\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-14,000 \text{ J}}{(8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = -5.65, K = e^{-5.65} = 3.5 \times 10^{-3}$



$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-17,000 \text{ J})}{8.3145 \text{ J/K} \cdot \text{mol}(298 \text{ K})} = 6.86, K = e^{6.86} = 9.5 \times 10^2$$

78. $2 \text{ SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ SO}_3(\text{g}); \Delta G^\circ = 2(-371 \text{ kJ}) - [2(-300. \text{ kJ})] = -142 \text{ kJ}$

$$\Delta G^\circ = -RT \ln K, \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-142,000 \text{ J})}{8.3145 \text{ J/K} \cdot \text{mol} (298 \text{ K})} = 57.311$$

$$K = e^{57.311} = 7.76 \times 10^{24}$$

$$K = 7.76 \times 10^{24} = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = \frac{(2.0)^2}{P_{\text{SO}_2}^2 \times (0.50)}, P_{\text{SO}_2} = 1.0 \times 10^{-12} \text{ atm}$$

From the negative value of ΔG° , this reaction is spontaneous at standard conditions. There are more molecules of reactant gases than product gases, so ΔS° will be negative (unfavorable). Therefore, this reaction must be exothermic ($\Delta H^\circ < 0$). When ΔH° and ΔS° are both negative, the reaction will be spontaneous at relatively low temperatures where the favorable ΔH° term dominates.

82. From Appendix 4, $S^\circ = 198 \text{ J/K} \cdot \text{mol}$ for $\text{CO}(\text{g})$ and $S^\circ = 27 \text{ J/K} \cdot \text{mol}$ for $\text{Fe}(\text{s})$.

Let $S_1^\circ = S^\circ$ for $\text{Fe}(\text{CO})_5(\text{l})$ and $S_g^\circ = S^\circ$ for $\text{Fe}(\text{CO})_5(\text{g})$.

$$\Delta S^\circ = -677 \text{ J/K} = 1 \text{ mol}(S_1^\circ) - [1 \text{ mol} (27 \text{ J/K} \cdot \text{mol}) + 5 \text{ mol}(198 \text{ J/K} \cdot \text{mol})]$$

$$S_1^\circ = 340. \text{ J/K} \cdot \text{mol}$$

$$\Delta S^\circ = 107 \text{ J/K} = 1 \text{ mol} (S_g^\circ) - 1 \text{ mol} (340. \text{ J/K} \cdot \text{mol})$$

$$S_g^\circ = S^\circ \text{ for } \text{Fe}(\text{CO})_5(\text{g}) = 447 \text{ J/K} \cdot \text{mol}$$