


Exercises

Review Questions

1. What is the first law of thermodynamics, and how does it relate to energy use?
2. What is nature's heat tax, and how does it relate to energy use?
3. What is a perpetual motion machine? Can such a machine exist given the laws of thermodynamics?
4. Is it more efficient to heat your home with a natural gas furnace or an electric furnace? Explain.
5. What is a spontaneous process? Provide an example.
6. Explain the difference between the spontaneity of a reaction (which depends on thermodynamics) and the speed at which the reaction occurs (which depends on kinetics). Can a catalyst make a nonspontaneous reaction spontaneous?
7. What is the precise definition of entropy? What is the significance of entropy being a state function?
8. Why does the entropy of a gas increase when it expands into a vacuum?
9. Explain the difference between macrostates and microstates.
10. Based on its fundamental definition, explain why entropy is a measure of energy dispersion.
11. State the second law of thermodynamics. How does the second law explain why heat travels from a substance at higher temperature to one at lower temperature?
12. What happens to the entropy of a sample of matter when it changes state from a solid to a liquid? From a liquid to a gas?
13. Explain why water spontaneously freezes to form ice below 0 °C even though the entropy of the water decreases during the state transition. Why is the freezing of water not spontaneous above 0 °C?
14. Why do exothermic processes tend to be spontaneous at low temperatures? Why does their tendency toward spontaneity decrease with increasing temperature?
15. What is the significance of the change in Gibbs free energy (ΔG) for a reaction?
16. Predict the spontaneity of a reaction (and the temperature dependence of the spontaneity) for each possible combination of signs for ΔH and ΔS (for the system).
 - a. ΔH negative, ΔS positive
 - b. ΔH positive, ΔS negative
 - c. ΔH negative, ΔS negative
 - d. ΔH positive, ΔS positive
17. State the third law of thermodynamics and explain its significance.
18. Why is the standard entropy of a substance in the gas state greater than its standard entropy in the liquid state?
19. How does the standard entropy of a substance depend on its molar mass? On its molecular complexity?
20. How can you calculate the standard entropy change for a reaction from tables of standard entropies?
21. Describe the three different methods to calculate ΔG° for a reaction. Which method would you choose to calculate ΔG° for a reaction at a temperature other than 25 °C?
22. Why is free energy "free"?
23. Explain the difference between ΔG° and ΔG .
24. Why does water spilled on the floor evaporate even though ΔG° for the evaporation process is positive at room temperature?
25. How do you calculate the change in free energy for a reaction under nonstandard conditions?
26. How does the value of ΔG° for a reaction relate to the equilibrium constant for the reaction? What does a negative ΔG° for a reaction imply about K for the reaction? A positive ΔG° ?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in **Appendix III**  Exercises in the Problems by Topic section

Even-numbered problems can be found in Appendix A. Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

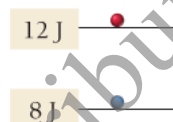
Entropy, the Second Law of Thermodynamics, and the Direction of Spontaneous Change

27. Which of these processes is spontaneous?
- the combustion of natural gas
 - the extraction of iron metal from iron ore
 - a hot drink cooling to room temperature
 - drawing heat energy from the ocean's surface to power a ship
28. Which of these processes are nonspontaneous? Are the nonspontaneous processes impossible?
- a bike going up a hill
 - a meteor falling to Earth
 - obtaining hydrogen gas from liquid water
 - a ball rolling down a hill
29. Suppose that two systems, each composed of two particles represented by circles, have 20 J of total energy. Which system, A or B, has the greater entropy? Why?

System A



System B

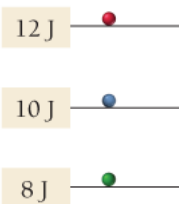


30. Suppose two systems, each composed of three particles represented by circles, have 30 J of total energy. In how many energetically equivalent ways can you distribute the particles in each system? Which system has greater entropy?

System A



System B



31. Calculate the change in entropy that occurs in the system when 1.00 mole of isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$) melts at its melting point (-89.5°C). See Table 11.9 for heats of fusion.
32. Calculate the change in entropy that occurs in the system when 1.00 mole of diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$) condenses from a gas to a liquid at its normal boiling point (34.6°C). See Table 11.7 for heats of vaporization.
33. Calculate the change in entropy that occurs in the system when 45.0 g of acetone ($\text{C}_3\text{H}_6\text{O}$) freezes at its melting point (-94.8°C). See Table 11.9 for heats of fusion.
34. Calculate the change in entropy that occurs in the system when 55.0 g of water vaporizes from a

liquid to a gas at its boiling point (100.0 °C). See **Table 11.7** for heats of vaporization.

35. Without doing any calculations, determine the sign of ΔS_{sys} for each chemical reaction.

- $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$
- $\text{CH}_2 = \text{CH}_2(g) + \text{H}_2(g) \rightarrow \text{CH}_3\text{CH}_3(g)$
- $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s)$
- $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$

36. Without doing any calculations, determine the sign of ΔS_{sys} for each chemical reaction.

- $\text{Mg}(s) + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s)$
- $2\text{H}_2\text{S}(g) + 3\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 2\text{SO}_2(g)$
- $2\text{O}_3(g) \rightarrow 3\text{O}_2(g)$
- $\text{HCl}(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Cl}(s)$

37. Without doing any calculations, determine the sign of ΔS_{sys} and ΔS_{surr} for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

- $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$ $\Delta H_{\text{rxn}}^\circ = -2044 \text{ kJ}$
- $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$ $\Delta H_{\text{rxn}}^\circ = +182.6 \text{ kJ}$
- $2\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{N}_2\text{O}(g)$ $\Delta H_{\text{rxn}}^\circ = +163.2 \text{ kJ}$
- $4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$ $\Delta H_{\text{rxn}}^\circ = -906 \text{ kJ}$

38. Without doing any calculations, determine the sign of ΔS_{sys} and ΔS_{surr} for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

- $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$ $\Delta H_{\text{rxn}}^\circ = -566.0 \text{ kJ}$
- $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2$ $\Delta H_{\text{rxn}}^\circ = +113.1 \text{ kJ}$
- $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$ $\Delta H_{\text{rxn}}^\circ = -483.6 \text{ kJ}$
- $\text{CO}_2(g) \rightarrow \text{C}(s) + \text{O}_2(g)$ $\Delta H_{\text{rxn}}^\circ = +393.5 \text{ kJ}$

39. Calculate ΔS_{surr} at the indicated temperature for each reaction.

- $\Delta H_{\text{rxn}}^\circ = -385 \text{ kJ}; 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -385 \text{ kJ}; 77 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = +114 \text{ kJ}; 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = +114 \text{ kJ}; 77 \text{ K}$

40. A reaction has $\Delta H_{\text{rxn}}^\circ = -112 \text{ kJ}$ and $\Delta H_{\text{rxn}}^\circ = 354 \text{ J/K}$. At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?

41. Given the values of $\Delta H_{\text{rxn}}^\circ$, $\Delta S_{\text{rxn}}^\circ$, and T , determine ΔS_{univ} and predict whether each reaction is spontaneous. (Assume that all reactants and products are in their standard states.)

- $\Delta H_{\text{rxn}}^\circ = +115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = +263 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 615 \text{ K}$

42. Given the values of $\Delta H_{\text{rxn}}^\circ$, $\Delta S_{\text{rxn}}^\circ$, and T , determine ΔS_{univ} and predict whether each reaction is spontaneous. (Assume that all reactants and products are in their standard states.)

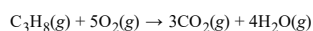
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 855 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = +157 \text{ J/K}; T = 398 \text{ K}$

Standard Entropy Changes and Gibbs Free Energy

43. Calculate the change in Gibbs free energy for each set of $\Delta H_{\text{rxn}}^\circ$, $\Delta S_{\text{rxn}}^\circ$, and T given in **Problem 41**. Predict whether each reaction is spontaneous at the temperature indicated. (Assume that all reactants and products are in their standard states.)

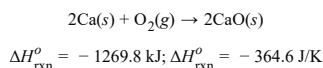
44. Calculate the change in Gibbs free energy for each set of $\Delta H_{\text{rxn}}^\circ$, $\Delta S_{\text{rxn}}^\circ$, and T given in **Problem 42**. Predict whether each reaction is spontaneous at the temperature indicated. (Assume that all reactants and products are in their standard states.)

45. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous?



$$\Delta H_{\text{rxn}}^{\circ} = -2217 \text{ kJ}; \quad \Delta S_{\text{rxn}}^{\circ} = 101.1 \text{ J/K};$$

46. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous? (Assume that all reactants and products are in their standard states.)



47. Fill in the blanks in the table. Both ΔH and ΔS refer to the system.

ΔH	ΔS	ΔG	Low Temperature	High Temperature
—	+	—	Spontaneous	_____
—	—	Temperature dependent	_____	_____
+	+	_____	_____	Spontaneous
_____	—	_____	Nonspontaneous	Nonspontaneous

48. Predict the conditions (high temperature, low temperature, all temperatures, or no temperatures) under which each reaction is spontaneous.

- $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$
- $\text{CO}_2\text{(s)} \rightarrow \text{CO}_2\text{(g)}$
- $\text{H}_2\text{(g)} \rightarrow 2\text{H(g)}$
- $2\text{NO}_2\text{(g)} \rightarrow 2\text{NO(g)} + \text{O}_2\text{(g)}$ (endothermic)

49. How does the molar entropy of a substance change with increasing temperature?

50. What is the molar entropy of a pure crystal at 0 K? What is the significance of the answer to this question?

51. For each pair of substances, choose the one that you expect to have the higher standard molar entropy

(S°) at 25 °C. Explain the reasons for your choices.

- $\text{CO(g)}; \text{CO}_2\text{(g)}$
- $\text{CH}_3\text{OH(l)}; \text{CH}_3\text{OH(g)}$
- $\text{Ar(g)}; \text{CO}_2\text{(g)}$
- $\text{CH}_4\text{(g)}; \text{SiH}_4\text{(g)}$
- $\text{NO}_2\text{(g)}; \text{CH}_3\text{CH}_2\text{CH}_3\text{(g)}$
- $\text{NaBr(s)}; \text{NaBr(aq)}$

52. For each pair of substances, choose the one that you expect to have the higher standard molar entropy (S°) at 25 °C. Explain the reasons for your choices.

- $\text{NaNO}_3\text{(s)}; \text{NaNO}_3\text{(aq)}$
- $\text{CH}_4\text{(g)}; \text{CH}_3\text{CH}_3\text{(g)}$
- $\text{Br}_2\text{(l)}; \text{Br}_2\text{(g)}$
- $\text{Br}_2\text{(g)}; \text{F}_2\text{(g)}$
- $\text{PCl(g)}; \text{PCl}_5\text{(g)}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{(g)}; \text{SO}_2\text{(g)}$

53. Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning.

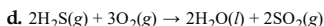
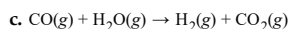
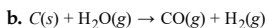
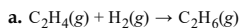
- $\text{NH}_3\text{(g)}; \text{Ne(g)}; \text{SO}_2\text{(g)}; \text{CH}_3\text{CH}_2\text{OH(g)}; \text{He(g)}$
- $\text{H}_2\text{O(s)}; \text{H}_2\text{O(l)}; \text{H}_2\text{O(g)}$
- $\text{CH}_4\text{(g)}; \text{CF}_4\text{(g)}; \text{CCl}_4\text{(g)}$

54. Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning.

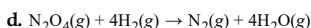
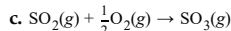
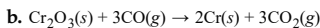
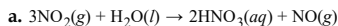
- $\text{I}_2\text{(s)}; \text{F}_2\text{(g)}; \text{Br}_2\text{(g)}; \text{Cl}_2\text{(g)}$
- $\text{H}_2\text{O(g)}; \text{H}_2\text{O}_2\text{(g)}; \text{H}_2\text{S(g)}$

c. $C(s, \text{graphite})$; $C(s, \text{diamond})$; $C(s, \text{amorphous})$

55. Use data from Appendix IIB to calculate $\Delta S_{\text{rxn}}^{\circ}$ for each of the reactions. In each case, try to rationalize the sign of $\Delta S_{\text{rxn}}^{\circ}$.



56. Use data from Appendix IIB to calculate $\Delta S_{\text{rxn}}^{\circ}$ for each of the reactions. In each case, try to rationalize the sign of $\Delta H_{\text{rxn}}^{\circ}$.



57. Find ΔS° for the formation of $CH_2Cl_2(g)$ from its gaseous elements in their standard states.

Rationalize the sign of ΔS° .

58. Find ΔS° for the reaction between nitrogen gas and fluorine gas to form nitrogen trifluoride gas.

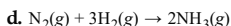
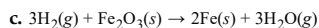
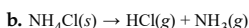
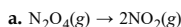
Rationalize the sign of ΔS° .

59. Methanol burns in oxygen to form carbon dioxide and water. Write a balanced equation for the combustion of liquid methanol and calculate $\Delta H_{\text{rxn}}^{\circ}$, $\Delta S_{\text{rxn}}^{\circ}$, and $\Delta G_{\text{rxn}}^{\circ}$ at 25 °C. Is the combustion of methanol spontaneous?

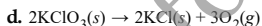
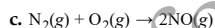
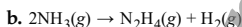
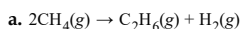
60. In photosynthesis, plants form glucose ($C_6H_{12}O_6$) and oxygen from carbon dioxide and water.

Write a balanced equation for photosynthesis and calculate $\Delta H_{\text{rxn}}^{\circ}$, $\Delta S_{\text{rxn}}^{\circ}$, and $\Delta G_{\text{rxn}}^{\circ}$ at 25 °C. Is photosynthesis spontaneous?

61. For each reaction, calculate $\Delta H_{\text{rxn}}^{\circ}$, $\Delta S_{\text{rxn}}^{\circ}$, and $\Delta G_{\text{rxn}}^{\circ}$ at 25 °C and state whether the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C?



62. For each reaction, calculate $\Delta H_{\text{rxn}}^{\circ}$, $\Delta S_{\text{rxn}}^{\circ}$, and $\Delta G_{\text{rxn}}^{\circ}$ at 25 °C and state whether the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C?



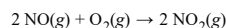
63. Use standard free energies of formation to calculate ΔG° at 25 °C for each reaction in **Problem**

61. How do the values of ΔG° calculated this way compare to those calculated from ΔH° and ΔS° ? Which of the two methods could be used to determine how ΔG° changes with temperature?

64. Use standard free energies of formation to calculate ΔG° at 25 °C for each reaction in **Problem**

62. How well do the values of ΔG° calculated this way compare to those calculated from ΔH° and ΔS° ? Which of the two methods could be used to determine how ΔG° changes with temperature?

65. Consider the reaction:



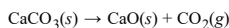
Estimate ΔG° for this reaction at each temperature and predict whether the reaction is spontaneous. (Assume that ΔH° and ΔS° do not change too much within the given temperature range.)

a. 298 K

b. 715 K

c. 855 K

66. Consider the reaction:

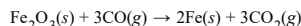


Estimate ΔG° for this reaction at each temperature and predict whether the reaction is spontaneous.

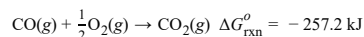
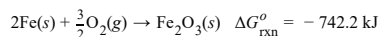
(Assume that ΔH° and ΔS° do not change too much within the given temperature range.)

- a. 298 K
- b. 1055 K
- c. 1455 K

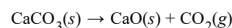
67. Determine ΔG° for the reaction:



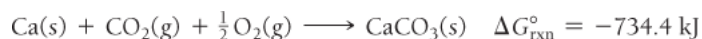
Use the following reactions with known $\Delta G^\circ_{\text{rxn}}$ values:



68. Calculate $\Delta G^\circ_{\text{rxn}}$ for the reaction:



Use the following reactions and given $\Delta G^\circ_{\text{rxn}}$ values:

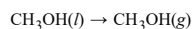


Free Energy Changes, Nonstandard Conditions, and the Equilibrium Constant

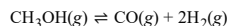
69. Consider the sublimation of iodine at 25.0 °C:



- a. Find $\Delta G^\circ_{\text{rxn}}$ at 25.0 °C.
 - b. Find ΔG_{rxn} at 25.0 °C under the following nonstandard conditions:
 - i. $P_{\text{I}_2} = 1.00 \text{ mmHg}$
 - ii. $P_{\text{I}_2} = 0.100 \text{ mmHg}$
 - c. Explain why iodine spontaneously sublimates in open air at 25 °C.
70. Consider the evaporation of methanol at 25.0 °C.



- a. Find $\Delta G^\circ_{\text{rxn}}$ at 25.0 °C.
 - b. Find ΔG_{rxn} at 25.0 °C under the following nonstandard conditions:
 - i. $P_{\text{CH}_3\text{OH}} = 150.0 \text{ mmHg}$
 - ii. $P_{\text{CH}_3\text{OH}} = 100.0 \text{ mmHg}$
 - iii. $P_{\text{CH}_3\text{OH}} = 10.0 \text{ mmHg}$
 - c. Explain why methanol spontaneously evaporates in open air at 25.0 °C.
71. Consider the reaction:



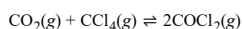
Calculate ΔG for this reaction at 25 °C under the following conditions:

$$P_{\text{CH}_3\text{OH}} = 0.855 \text{ atm}$$

$$P_{\text{CO}} = 0.125 \text{ atm}$$

$$P_{\text{H}_2} = 0.183 \text{ atm}$$

72. Consider the reaction:



Calculate ΔG for this reaction at 25 °C under the following conditions:

$$\begin{aligned}P_{\text{CO}_2} &= 0.112\text{atm} \\P_{\text{CCl}_4} &= 0.174\text{atm} \\P_{\text{COCl}_2} &= 0.744\text{atm}\end{aligned}$$

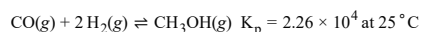
73. Use data from Appendix IIB to calculate the equilibrium constant at 25 °C for each reaction.

- a. $2\text{CO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{CO}_2\text{(g)}$
b. $2\text{H}_2\text{S(g)} \rightleftharpoons 2\text{H}_2\text{(g)} + \text{S}_2\text{(g)}$

74. Use data from Appendix IIB to calculate the equilibrium constant at 25 °C for each reaction. ΔG_f° for BrCl(g) is -1.0 kJ/mol .

- a. $2\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$
b. $\text{Br}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{BrCl(g)}$

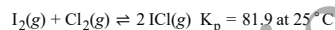
75. Consider the reaction:



Calculate ΔG_{rxn} for the reaction at 25 °C under the following conditions:

- a. standard conditions
b. at equilibrium
c. $P_{\text{CH}_3\text{OH}} = 1.0\text{ atm}$; $P_{\text{CO}} = P_{\text{H}_2} = 0.010\text{ atm}$

76. Consider the reaction:



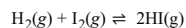
Calculate ΔG_{rxn} for the reaction at 25 °C under the following conditions:

- a. standard conditions
b. at equilibrium
c. $P_{\text{ICl}} = 2.55\text{atm}$; $P_{\text{I}_2} = 0.325\text{atm}$; $P_{\text{Cl}_2} = 0.221\text{ atm}$

77. Estimate the value of the equilibrium constant at 525 K for each reaction in **Problem 73**.

78. Estimate the value of the equilibrium constant at 655 K for each reaction in **Problem 74**. (ΔH_f° for BrCl is 14.6 KJ/mol .)

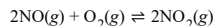
79. Consider the reaction:



The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for the reaction.

Temperature	K_p
150 K	1.4×10^{-6}
175 K	4.6×10^{-4}
200 K	3.6×10^{-2}
225 K	1.1
250 K	15.5

80. Consider the reaction:



The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for the reaction.

Temperature	K
-------------	-----

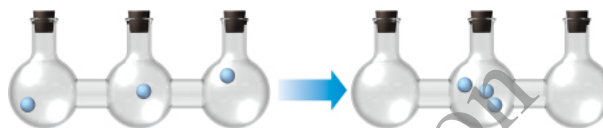
Temperature	K_p
170 K	3.8×10^{-3}
180 K	0.34
190 K	18.4
200 K	681

81. The change in enthalpy ($\Delta H_{\text{rxn}}^\circ$) for a reaction is -25.8 kJ/mol . The equilibrium constant for the reaction is 1.4×10^3 at 298 K. What is the equilibrium constant for the reaction at 655 K?
82. A reaction has an equilibrium constant of 8.5×10^3 at 298 K. At 755 K, the equilibrium constant is 0.65. Find $\Delta H_{\text{rxn}}^\circ$ for the reaction.

Cumulative Problems

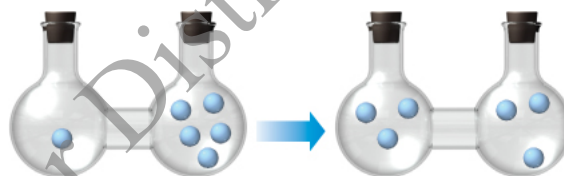
83. Determine the sign of ΔS_{sys} for each process.

- water boiling
- water freezing
-

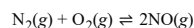


84. Determine the sign of ΔS_{sys} for each process.

- dry ice subliming
- dew forming
-

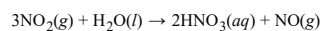


85. Our atmosphere is composed primarily of nitrogen and oxygen, which coexist at 25 °C without reacting to any significant extent. However, the two gases can react to form nitrogen monoxide according to the reaction:

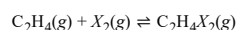


- Calculate ΔG° and K_p for this reaction at 298 K. Is the reaction spontaneous?
- Estimate ΔG° at 2000 K. Does the reaction become more spontaneous as temperature increases?

86. Nitrogen dioxide, a pollutant in the atmosphere, can combine with water to form nitric acid. One of the possible reactions is shown here. Calculate ΔG° and K_p for this reaction at 25 °C and comment on the spontaneity of the reaction.



87. Ethene (C_2H_4) can be halogenated by the reaction:

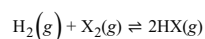


where X_2 can be Cl_2 , Br_2 , or I_2 . Use the thermodynamic data given to calculate ΔH° , ΔS° , ΔG° and K_p for the halogenation reaction by each of the three halogens at 25 °C. Which reaction is most spontaneous?

Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

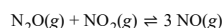
Compound	ΔH_f° (kJ/mol)	S° (J/mol · K)
$C_2H_4Cl_2(g)$	-129.7	308.0
$C_2H_4Br_2(g)$	+38.3	330.6
$C_2H_4I_2(g)$	+66.5	347.8

88. H_2 reacts with the halogens (X_2) according to the reaction:



where X_2 can be Cl_2 , Br_2 or I_2 . Use the thermodynamic data in Appendix IIB to calculate ΔH° , ΔS° , ΔG° , and K_p for the reaction between hydrogen and each of the three halogens. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

89. Consider this reaction occurring at 298 K:



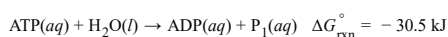
- Show that the reaction is not spontaneous under standard conditions by calculating ΔG_{rxn}° .
- If a reaction mixture contains only N_2O and NO_2 at partial pressures of 1.0 atm each, the reaction will be spontaneous until some NO forms in the mixture. What maximum partial pressure of NO builds up before the reaction ceases to be spontaneous?
- Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, what temperature is required to make the reaction spontaneous under standard conditions?

90. Consider this reaction occurring at 298 K:



- Show that the reaction is not spontaneous under standard conditions by calculating ΔG_{rxn}° .
- If $BaCO_3$ is placed in an evacuated flask, what is the partial pressure of CO_2 when the reaction reaches equilibrium?
- Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, at what temperature is the partial pressure of carbon dioxide 1.0 atm?

91. Living organisms use energy from the metabolism of food to create an energy-rich molecule called adenosine triphosphate (ATP). The ATP then acts as an energy source for a variety of reactions that the living organism must carry out to survive. ATP provides energy through its hydrolysis, which can be symbolized as follows:



where ADP represents adenosine diphosphate and P_i represents an inorganic phosphate group (such as HPO_4^{2-}).

- Calculate the equilibrium constant, K , for the given reaction at 298 K.
- The free energy obtained from the oxidation (reaction with oxygen) of glucose ($C_6H_{12}O_6$) to form carbon dioxide and water can be used to re-form ATP by driving the given reaction in reverse. Calculate the standard free energy change for the oxidation of glucose and estimate the maximum number of moles of ATP that can be formed by the oxidation of one mole of glucose.
- The standard free energy change for the hydrolysis of ATP was given in Problem 91. In a particular cell, the concentrations of ATP, ADP, and P_i are 0.0031 M, 0.0014 M, and 0.0048 M, respectively. Calculate the free energy change for the hydrolysis of ATP under these conditions. (Assume a temperature of 298 K.)

93. These reactions are important in catalytic converters in automobiles. Calculate ΔG° for each at 298

K. Predict the effect of increasing temperature on the magnitude of ΔG° .

- $2 \text{CO(g)} + 2 \text{NO(g)} \rightarrow \text{N}_2\text{(g)} + 2 \text{CO}_2\text{(g)}$
- $5 \text{H}_2\text{(g)} + 2 \text{NO(g)} \rightarrow 2 \text{NH}_3\text{(g)} + 2 \text{H}_2\text{O(g)}$
- $2 \text{H}_2\text{(g)} + 2 \text{NO(g)} \rightarrow \text{N}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$
- $2 \text{NH}_3\text{(g)} + 2 \text{O}_2\text{(g)} \rightarrow \text{N}_2\text{O(g)} + 3 \text{H}_2\text{O(g)}$

94. Calculate ΔG° at 298 K for these reactions and predict the effect on ΔG° of lowering the temperature.

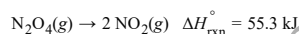
- $\text{NH}_3\text{(g)} + \text{HBr(g)} \rightarrow \text{NH}_4\text{Br(s)}$
- $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$
 $\text{CH}_4\text{(g)} + 3 \text{Cl}_2\text{(g)} \rightarrow \text{CHCl}_3\text{(g)} + 3 \text{HCl(g)}$
- $\left(\Delta G_f^\circ \text{ for } \text{CHCl}_3\text{(g)} \text{ is } -70.4 \text{ kJ/mol.} \right)$

95. All the oxides of nitrogen have positive values of ΔG_f° at 298 K, but only one common oxide of nitrogen has a positive ΔS_f° . Identify that oxide of nitrogen without reference to thermodynamic data and explain.

96. The values of ΔG_f° for the hydrogen halides become less negative with increasing atomic number. The ΔG_f° of HI is slightly positive. On the other hand, the trend in ΔS_f° is to become more positive with increasing atomic number. Explain.

97. Consider the reaction $\text{X}_2\text{(g)} \rightarrow 2 \text{X(g)}$. When a vessel initially containing 755 torr of X_2 comes to equilibrium at 298 K, the equilibrium partial pressure of X is 103 torr. The same reaction is repeated with an initial partial pressure of 748 torr of X_2 at 755 K; the equilibrium partial pressure of X is 532 torr. Find ΔH° for the reaction.

98. Dinitrogen tetroxide decomposes to nitrogen dioxide:



At 298 K, a reaction vessel initially contains 0.100 atm of N_2O_4 . When equilibrium is reached, 58% of the N_2O_4 has decomposed to NO_2 . What percentage of N_2O_4 decomposes at 388 K? Assume that the initial pressure of N_2O_4 is the same (0.100 atm).

99. Indicate and explain the sign of ΔS_{univ} for each process.

- $2 \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(l)}$ at 298 K
- the electrolysis of $\text{H}_2\text{O(l)}$ to $\text{H}_2\text{(g)}$ and $\text{O}_2\text{(g)}$ at 298 K
- the growth of an oak tree from an acorn

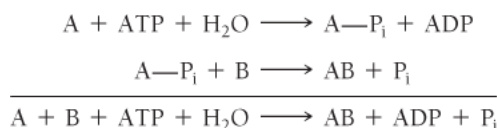
100. The Haber process is very important for agriculture because it converts $\text{N}_2\text{(g)}$ from the atmosphere into bound nitrogen, which can be taken up and used by plants. The Haber process reaction is $\text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)} \rightleftharpoons 2 \text{NH}_3\text{(g)}$. The reaction is exothermic but is carried out at relatively high temperatures. Why?

101. A metal salt with the formula MCl_2 crystallizes from water to form a solid with the composition $\text{MCl}_2 \cdot 6 \text{H}_2\text{O}$. The equilibrium vapor pressure of water above this solid at 298 K is 18.3 mmHg. What is the value of ΔG for the reaction $\text{MCl}_2 \cdot 6 \text{H}_2\text{O(s)} \rightleftharpoons \text{MCl}_2\text{(s)} + 6 \text{H}_2\text{O(g)}$ when the pressure of water vapor is 18.3 mmHg? When the pressure of water vapor is 760.0 mmHg?

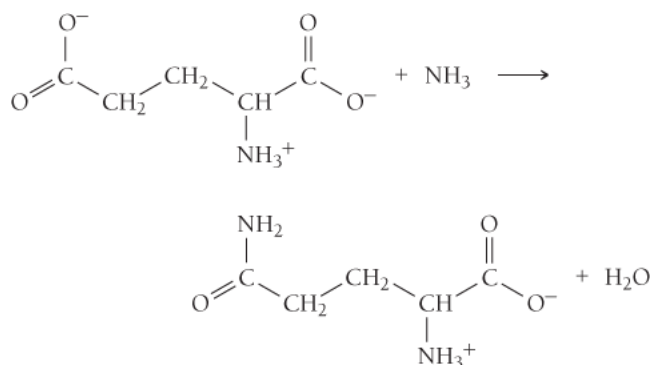
102. The solubility of AgCl(s) in water at 25 °C is $1.33 \times 10^{-5} \text{ mol/L}$, and its ΔH° of solution is 65.7 k/mol. What is its solubility at 50.0 °C?

Challenge Problems

103. Review the subsection in this chapter entitled *Making a Nonspontaneous Process Spontaneous in Section 18.8*. The hydrolysis of ATP, shown in **Problem 91**, is often used to drive nonspontaneous processes—such as muscle contraction and protein synthesis—in living organisms. The nonspontaneous process to be driven must be coupled to the ATP hydrolysis reaction. For example, suppose the nonspontaneous process is $\text{A} + \text{B} \rightarrow \text{AB}$ (ΔG° positive). The coupling of a nonspontaneous reaction such as this one to the hydrolysis of ATP is often accomplished by the mechanism:

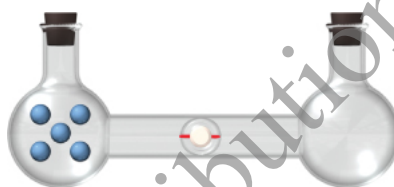


As long as ΔG_{rxn} for the nonspontaneous reaction is less than 30.5 kJ, the reaction can be made spontaneous by coupling in this way to the hydrolysis of ATP. Suppose that ATP is to drive the reaction between glutamate and ammonia to form glutamine:

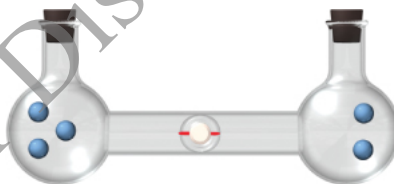


- a. Calculate K for the reaction between glutamate and ammonia. (The standard free energy change for the reaction is +14.2 kJ/mol. Assume a temperature of 298 K.)
- b. Write a set of reactions such as those given showing how the glutamate and ammonia reaction can couple with the hydrolysis of ATP. What is $\Delta G_{\text{rxn}}^\circ$ and K for the coupled reaction?
104. Calculate the entropy of each state and rank the states in order of increasing entropy.

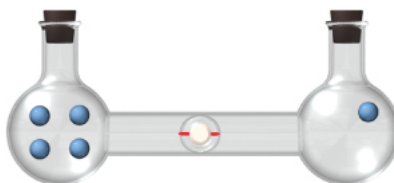
a.



b.



c.



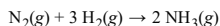
105. Suppose we redefine the standard state as $P = 2$ atm. Find the new standard ΔG_f° values of each substance.

- a. HCl(g)
 b. $\text{N}_2\text{O(g)}$
 c. H(g)

Explain the results in terms of the relative entropies of reactants and products of each reaction.

106. The ΔG for the freezing of $\text{H}_2\text{O(l)}$ at -10°C is -210 J/mol, and the heat of fusion of ice at this temperature is 5610 J/mol. Find the entropy change of the universe when 1 mol of water freezes at -10°C .

107. Consider the reaction that occurs during the Haber process:



The equilibrium constant is 3.9×10^5 at 300 K and 1.2×10^{-1} at 500 K. Calculate $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for this reaction.

108. The salt ammonium nitrate can follow three modes of decomposition: (a) to $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$, (b) to $\text{N}_2\text{O}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, and (c) to $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$. Calculate $\Delta G_{\text{rxn}}^\circ$ for each mode of decomposition at 298 K. Explain in light of these results how it is still possible to use ammonium nitrate as a fertilizer and the precautions that should be taken when it is used.

109. Given the tabulated data, calculate ΔS_{vap} for each of the first four liquids.

($\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$, where T is in K)

Compound	Name	bp (°C)	ΔH_{vap} (kJ/mol) at bp
$\text{C}_4\text{H}_{10}\text{O}$	Diethyl ether	34.6	26.5
C_3H_6	Acetone	56.1	29.1
C_6H_6	Benzene	79.8	30.8
CHCl_3	Chloroform	60.8	29.4
$\text{C}_2\text{H}_5\text{OH}$	Ethanol	77.8	38.6
H_2O	Water	100.0	40.7

All four values should be close to each other. Predict whether the last two liquids in the table have ΔS_{vap} in this same range. If not, predict whether it is larger or smaller and explain. Verify your prediction.

Conceptual Problems

110. Which statement is true?

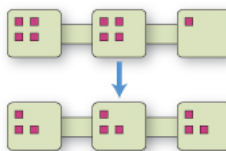
- A spontaneous reaction is always a fast reaction.
- A spontaneous reaction is always a slow reaction.
- The spontaneity of a reaction is not necessarily related to the speed of a reaction.

111. Which process is necessarily driven by an increase in the entropy of the surroundings?

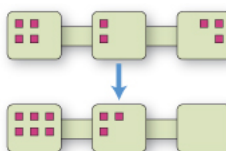
- the condensation of water
- the sublimation of dry ice
- the freezing of water

112. Consider the changes in the distribution of nine particles into three interconnected boxes shown here. Which has the most negative ΔS ?

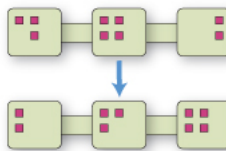
a.



b.



c.



113. Which statement is true?

- a. A reaction in which the entropy of the system increases can be spontaneous only if it is exothermic.
- b. A reaction in which the entropy of the system increases can be spontaneous only if it is endothermic.
- c. A reaction in which the entropy of the system decreases can be spontaneous only if it is exothermic.

114. Which process is spontaneous at 298 K?

- a. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g, 1 \text{ atm})$
- b. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g, 0.10 \text{ atm})$
- c. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g, 0.010 \text{ atm})$

115. The free energy change of the reaction $\text{A}(g) \rightarrow \text{B}(g)$ is zero under certain conditions. The *standard* free energy change of the reaction is -42.5 kJ . Which statement must be true about the reaction?

- a. The concentration of the product is greater than the concentration of the reactant.
- b. The reaction is at equilibrium.
- c. The concentration of the reactant is greater than the concentration of the product.

116. The reaction $\text{A}(g) \rightleftharpoons \text{B}(g)$ has an equilibrium constant of 5.8 and under certain conditions has $Q = 336$. What can you conclude about the sign of $\Delta G_{\text{rxn}}^\circ$ and ΔG_{rxn} for this reaction under these conditions?

Questions for Group Work

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

117. Imagine that you roll two dice. Write down all the possible rolls that sum to 2. Write all the possible rolls that sum to 12. Write all the possible rolls that sum to 7. Which configuration has the greatest entropy: 2, 12, or 7?

118. If you roll one million dice, what will be the average of all the dice? If there is a room with one million dice and they all have a 1 on the top face, and there is an earthquake strong enough to roll dice around, what is the likelihood that after the earthquake all the top faces will sum to one million? To six million? How does this thought experiment illustrate the second law of thermodynamics?

119. Not all processes in which the system increases in entropy are spontaneous. How can this observation be consistent with the second law? Provide an example and explain your answer in complete sentences.

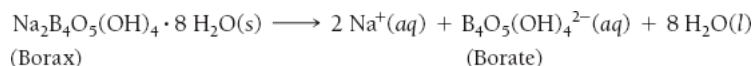
120. Have each group member look up ΔH_f° and S° for one substance in the reaction:

$3 \text{ O}_2(g) + 6 \text{ H}_2(g) + 6 \text{ C}(s, \text{ graphite}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s, \text{ glucose})$. What is ΔH° for this reaction? What is ΔS° ? When is ΔH_f° for a substance equal to zero? When is S° for a substance equal to zero?

121. Calculate ΔG° at 25°C for the reaction in the previous question. Is this reaction spontaneous under standard conditions? How do you know? What is the determining factor: the change in energy or the change in entropy or both? Explain.

Data Interpretation and Analysis

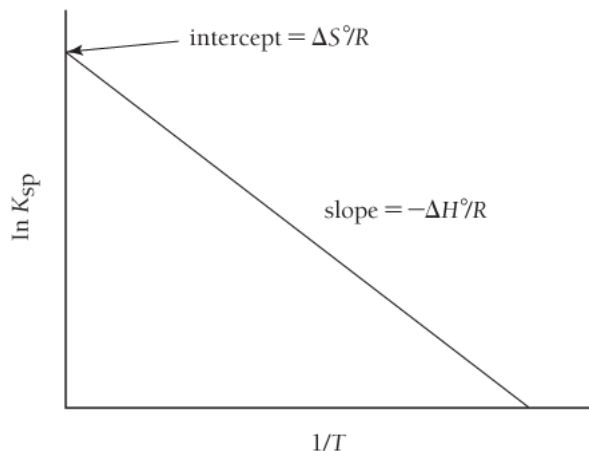
122. Borax, sodium tetraborate decahydrate, is an important mineral found in dry lakebeds in California. It is used to make soap and glass, and used as a preservative. You can use the values of K_{sp} of borax at different temperatures to determine ΔH° , ΔS° , and ΔG° for the dissolution of borax:



The relationship:

$$\ln(K_{sp}) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

has the form of a linear equation $y = mx + b$, where y is the $\ln K_{sp}$ and x is $1/T$. The slope is equal to $(\Delta H^\circ/R)$, and the y intercept is $\Delta S^\circ/R$, where R is the gas constant, 8.314 J/K mol. If you measure K_{sp} at several different temperatures, you can plot the $\ln K$ versus $1/T$ (T in kelvin) as shown here.



A Plot of K_{sp} versus $1/T$ where the Units of Temperature Are in Kelvin.

Knowing the values of ΔH° and ΔS° at a specific temperature allows the calculation of the change in Gibbs free energy for the reaction: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The following table lists K_{sp} values for the dissolution of borax at several temperatures ($^\circ\text{C}$).

K_{sp} Values for the Dissolution of Borax at Several Temperatures ($^\circ\text{C}$).

Temperature ($^\circ\text{C}$)	K_{sp}
40.0	0.041
45.0	0.083
50.0	0.264
55.0	0.486
60.0	0.552

- Plot a graph of $\ln K_{sp}$ versus $1/T$ (T in kelvin) and find the best-fitting line.
- Determine ΔH° . Is this process endothermic or exothermic?
- Determine ΔS° .
- Determine ΔH° at 298 K.
- Sketch a graph of $\ln K$ versus $1/T$ for an exothermic process.

Answers to Conceptual Connections

Cc 18.1 (a) The more spread out the particles are between the three boxes, the greater the entropy.

Therefore, the entropy change is positive only in scheme (a).

Cc 18.2 Biological systems do not violate the second law of thermodynamics. The key to understanding this concept is realizing that entropy changes in the system can be negative as long as the entropy change of the universe is positive. Biological systems can decrease their own entropy, but only at the expense of creating more entropy in the surroundings (which they do primarily by emitting the heat they generate by their metabolic processes). Thus, for any biological process, ΔS_{univ} is positive.

Cc 18.3 (a) Sublimation is endothermic (it requires energy to overcome the intermolecular forces that hold solid carbon dioxide together), so ΔH is positive. The number of moles of gas increases when the solid turns into a gas, so the entropy of the carbon dioxide increases and ΔS is positive. Since $\Delta G = \Delta H - T\Delta S$, ΔG is positive at low temperature and negative at high temperature.

Cc 18.4 $\text{Kr} < \text{Cl}_2 < \text{SO}_3$. Because krypton is a monoatomic gas, it has the least entropy. Because SO_3 is the most complex molecule, it has the most entropy. The molar masses of the three gases vary slightly, but not enough to overcome the differences in molecular complexity.

Cc 18.5 (a) A high concentration of reactants relative to products will lead to $Q < 1$, making the term $RT \ln Q$ in

Equation 18.14 negative. ΔG_{rxn} is more negative than $\Delta G_{\text{rxn}}^\circ$ and the reaction is more spontaneous.

Cc 18.6 (c) Since the equilibrium constant is less than 1, the reaction proceeds toward reactants under standard conditions (when $Q = 1$). Therefore, $\Delta G_{\text{rxn}}^\circ$ is positive.

Cc 18.7 $\Delta G_{\text{rxn}} < 0, Q < K$

Not for Distribution

Not for Distribution

Not for Distribution

Not for Distribution

Processing math: 100%

Not for Distribution