

7.7 ENERGY AND EQUILIBRIUM: THE LAWS OF THERMODYNAMICS

PRACTICE

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Understanding Concepts

- (a) negative
(b) negative
(c) positive
(d) positive

Explore an Issue: Take a Stand: Can We Do Anything About Pollution?

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(There are a variety of positions that students can take as they argue the inevitability of pollution. The following argument is one possible scenario.)

At first glance, manufacturing new complex goods from simpler raw materials appears to contradict the second law of thermodynamics. However, when you consider the energy required to produce these products and the volume of waste materials the process generates, it becomes obvious that the second law remains valid. While the generation of waste materials may be inevitable, we can nevertheless control the type of waste a process generates. For example, an internal combustion engine and a hydrogen fuel cell arguably contribute a similar amount of entropy to the universe. However, the waste product of the fuel cell (steam) is much less harmful to the environment than the combustion products of gasoline.

Try This Activity: Stretching a Point

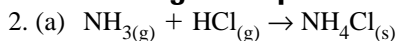
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- Forward reaction (stretching)
 $\Delta G > 0, \Delta H < 0, \Delta S < 0$
- Reverse reaction (relaxing)
 $\Delta G < 0, \Delta H > 0, \Delta S > 0$
- The rubber molecules become more ordered as the rubber band is stretched (the forward reaction). Stretching the rubber band forces the molecules to align parallel to each other, much like strands of spaghetti in a box. When the rubber band is relaxed, the long rubber molecules become more disordered since the force holding them into regular pattern has been removed.
- Bonds are forming between the polymer chains when the rubber band is being stretched. Conversely, bonds between the polymer chains are broken when the rubber band is relaxed.
- London forces are being affected during the changes.
- The spontaneous contraction of the rubber band is driven by entropy. Since ΔH is positive, the $T\Delta S$ term in the Gibbs free energy equation must be larger than ΔH in order for ΔG to be negative.
- Since $T\Delta S$ is always negative regardless of temperature, ΔG will always be negative as well. Consequently, the contraction process should be spontaneous at all temperatures.
- (Answers may vary. Sample investigation might include students testing their prediction by using rubber bands that have been warmed in a water bath or cooled in the freezer.)

PRACTICE

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Understanding Concepts



$$\begin{aligned}\Delta H^\circ &= [\Delta H^\circ_{\text{f}(\text{NH}_4\text{Cl}_{(s)})}] - [\Delta H^\circ_{\text{f}(\text{NH}_{3(g)})} + \Delta H^\circ_{\text{f}(\text{HCl}_{(g)})}] \\ &= [1 \text{ mol } (-314.4 \text{ kJ/mol})] - [1 \text{ mol } (-45.9 \text{ kJ/mol}) + 1 \text{ mol } (-92.3 \text{ kJ/mol})] \\ &= [-314.4 \text{ kJ}] - [-45.9 \text{ kJ} - 92.3 \text{ kJ}] \\ &= [-314.4 \text{ kJ}] - [-138.2 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = -176.2 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{\text{(NH}_4\text{Cl}_{(s)})}] - [S^\circ_{\text{(NH}_3\text{(g)})} + S^\circ_{\text{(HCl}_{(g)})}] \\ &= [1 \text{ mol (94.6 J/mol}\cdot\text{K)}] - [1 \text{ mol (192.78 J/mol}\cdot\text{K)} + 1 \text{ mol (186.9 J/mol}\cdot\text{K)}] \\ &= [94.6 \text{ J/K}] - [192.78 \text{ J/K} + 186.90 \text{ J/K}]\end{aligned}$$

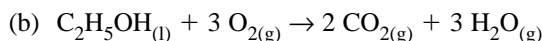
$$\begin{aligned}\Delta S^\circ &= -285.08 \text{ J/K} \\ &= -285.08 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

$$\Delta S^\circ = -0.28508 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -176.2 \text{ kJ} - (298 \text{ K})(-0.28508 \text{ kJ/K})\end{aligned}$$

$$\Delta G^\circ = -91.2 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -91.2 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 91.2 kJ of free energy is made available to do useful work for each mole of ammonia that reacts.



$$\begin{aligned}\Delta H^\circ &= [2\Delta H^\circ_{f(\text{CO}_{2(g)})} + 3\Delta H^\circ_{f(\text{H}_2\text{O}_{(g)})}] - [\Delta H^\circ_{f(\text{C}_2\text{H}_5\text{OH}_{(l)})} + 3\Delta H^\circ_{f(\text{O}_{2(g)})}] \\ &= [2 \text{ mol} \times (-393.5 \text{ kJ/mol}) + 3 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [(-235.2 \text{ kJ/mol}) + 3 \text{ mol} \times (0)] \\ &= [-1512.4 \text{ kJ}] - [-235.2 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = -1277.2 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [2S^\circ_{\text{(CO}_{2(g)})} + 3S^\circ_{\text{(H}_2\text{O}_{(g)})}] - [S^\circ_{\text{(C}_2\text{H}_5\text{OH}_{(l)})} + 3S^\circ_{\text{(O}_{2(g)})}] \\ &= [2 \text{ mol} \times (213.78 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [(161.0 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol} \times (205.14 \text{ J/mol}\cdot\text{K})] \\ &= [994.08 \text{ J/K}] - [776.42 \text{ J/K}]\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 217.66 \text{ J/K} \\ &= 217.66 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

$$\Delta S^\circ = 0.21766 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -1277.2 \text{ kJ} - (298 \text{ K})(0.21766 \text{ kJ/K})\end{aligned}$$

$$\Delta G^\circ = -1342.1 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -1342.1 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 1342.1 kJ of free energy is made available to do useful work for each mole of ethanol that burns.

(c) $\Delta H^\circ = [2\Delta H^\circ_{f(\text{HCN}_{(g)})} + 6\Delta H^\circ_{f(\text{H}_2\text{O}_{(g)})}] - [2\Delta H^\circ_{f(\text{NH}_3\text{(g)})} + 3\Delta H^\circ_{f(\text{O}_{2(g)})} + 2\Delta H^\circ_{f(\text{CH}_4\text{(g)})}]$

$$\begin{aligned}&= [2 \text{ mol} \times (+135.1 \text{ kJ/mol}) + 6 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [2 \text{ mol} \times (-45.9 \text{ kJ/mol}) + 3 \text{ mol} \times (0 \text{ kJ/mol}) \\ &\quad + 2 \text{ mol} \times (-74.4 \text{ kJ/mol})] \\ &= [-1180.6 \text{ kJ}] - [-240.6 \text{ kJ}] \\ &= -940.0 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= [2S^\circ_{\text{(HCN}_{(g)})} + 6S^\circ_{\text{(H}_2\text{O}_{(g)})}] - [2S^\circ_{\text{(NH}_3\text{(g)})} + 3S^\circ_{\text{(O}_{2(g)})} + 2S^\circ_{\text{(CH}_4\text{(g)})}] \\ &= [2 \text{ mol} \times (201.81 \text{ J/mol}\cdot\text{K}) + 6 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol} \times (+192.78 \text{ J/mol}\cdot\text{K}) \\ &\quad + 3 \text{ mol} \times (+205 \text{ J/mol}\cdot\text{K})] \\ &= [1536.66 \text{ J/K}] - [1373.58 \text{ J/K}]\end{aligned}$$

$$\Delta S^\circ = 163.08 \text{ J/K}$$

$$\begin{aligned}
 &= 163.08 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta S^\circ &= 0.16308 \text{ kJ/K} \\
 \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
 &= -940.0 \text{ kJ} - (298 \text{ K})(0.16308 \text{ kJ/K}) \\
 &= -940.0 \text{ kJ} - 48.6 \text{ kJ} \\
 \Delta G^\circ &= -988.6 \text{ kJ}
 \end{aligned}$$

The standard Gibbs free energy change associated with this reaction is -988.6 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 988.6 kJ of free energy is made available to do useful work for each mole of ethanol that burns.

PRACTICE

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Understanding Concepts

$$\begin{aligned}
 3. \text{Br}_{2(l)} &\rightleftharpoons \text{Br}_{2(g)} \\
 T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
 &= [\Delta H^\circ_{f(\text{Br}_{2(g)})} - \Delta H^\circ_{f(\text{Br}_{2(l)})}] \\
 &= 1 \text{ mol} \times (+30.9 \text{ kJ/mol}) - 1 \text{ mol} \times (0) \\
 T &= +30.9 \text{ kJ} \\
 \Delta S^\circ &= [S^\circ_{(\text{Br}_{2(g)})} - S^\circ_{(\text{Br}_{2(l)})}] \\
 &= 1 \text{ mol} \times (+245.47 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+152.2 \text{ J/mol}\cdot\text{K}) \\
 &= 245.47 \text{ J/mol}\cdot\text{K} - 152.2 \text{ J/mol}\cdot\text{K} \\
 \Delta S^\circ &= 93.3 \text{ J/mol}\cdot\text{K} \\
 &= 93.3 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta S^\circ &= 0.0933 \text{ kJ/K} \\
 T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
 &= \frac{30.9 \text{ kJ}}{0.0933 \text{ kJ/K}} \\
 T &= 331 \text{ K} \\
 t &= (T - 273^\circ\text{C}) \\
 &= (331 \text{ K} - 273^\circ\text{C}) \\
 t &= 58^\circ\text{C}
 \end{aligned}$$

The boiling point of bromine is 58°C .

$$\begin{aligned}
 4. \text{Hg}_{(l)} &\rightleftharpoons \text{Hg}_{(g)} \\
 T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
 &= [\Delta H^\circ_{f(\text{Hg}_{(g)})} - \Delta H^\circ_{f(\text{Hg}_{(l)})}] \\
 &= 1 \text{ mol} \times (+61.38 \text{ kJ/mol}) - 1 \text{ mol} \times (0) \\
 T &= +61.38 \text{ kJ} \\
 \Delta S^\circ &= [S^\circ_{(\text{Hg}_{(g)})} - S^\circ_{(\text{Hg}_{(l)})}] \\
 &= 1 \text{ mol} \times (+174.97 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+75.90 \text{ J/mol}\cdot\text{K})
 \end{aligned}$$

$$\begin{aligned}
&= 174.97 \text{ J/mol}\cdot\text{K} - 75.90 \text{ J/mol}\cdot\text{K} \\
\Delta S^\circ &= 99.07 \text{ J/mol}\cdot\text{K} \\
&= 99.07 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
\Delta S^\circ &= 0.09907 \text{ kJ/K} \\
T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
&= \frac{61.38 \text{ kJ}}{0.09907 \text{ kJ/K}} \\
T &= 620 \text{ K} \\
t &= (T - 273^\circ\text{C}) \\
&= (620 \text{ K} - 273^\circ\text{C}) \\
t &= 347^\circ\text{C}
\end{aligned}$$

The boiling point of mercury is 347°C .

SECTION 7.7 QUESTIONS

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Understanding Concepts

- Given the necessary activation energy to begin, a spontaneous change occurs without outside assistance. A change in entropy measures the change in disorder or randomness of a system while a change in enthalpy measures a change in the energy that flows in or out of a system.
- Change in enthalpy refers to the difference between the enthalpies of products and reactants while a change in entropy measures the difference in randomness or disorder between products and reactants.
- positive
 - negative
 - positive
- All changes either directly or indirectly increase the entropy of the universe.
 - The likelihood or probability of dropping the puzzle parts onto the floor and having them land in a random state is far greater than having them land assembled.
 - Although school can be considered a highly structured environment, the operation of the school still obeys the second law of thermodynamics. For example, a considerable amount of energy is used to transport students to the school. Furthermore, a great deal of energy is involved in the manufacture of all the materials that are used in school – everything from the paper this text is printed on to the food in the cafeteria. The heat released from these processes, as well as the waste generated, increases entropy.
- $\Delta H < 0$, $\Delta S > 0$
 - $\Delta H > 0$, $\Delta S < 0$
- $\Delta H < 0$, $\Delta S > 0$
 - Given that

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

$$= (-) - (+)(+)$$
This combination of negative ΔH° and positive ΔS° will always result in a negative value for ΔG° , implying that the reaction is spontaneous.
- $$\text{NH}_4\text{NO}_{3(s)} \rightarrow \text{NH}_{4(aq)}^+ + \text{NO}_{3(aq)}^-$$
For this reaction,
 $\Delta H^\circ > 0$, since the dissolving of ammonium nitrate is endothermic.
 $\Delta S^\circ > 0$, since the entropy of the system increases as the reaction proceeds.
Therefore,

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

$$= (+) - (T)(+)$$
If the reaction is spontaneous at room temperature, $\Delta G^\circ < 0$. Consequently, T must be sufficiently large so that $T\Delta S^\circ > \Delta H^\circ$.

8. The rate of a chemical reaction cannot be inferred from the standard free energy of the reaction. The rate of a reaction can only be determined experimentally.
9. The decomposition of a compound into its elements is an endothermic process ($\Delta H > 0$), resulting in an increase in entropy, $\Delta S > 0$.

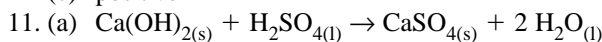
Given that

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

$$= (+) - (T)(+)$$

Since T is always positive, there must exist a temperature at which $T\Delta S > \Delta H$, resulting in the spontaneous decomposition of the compound.

10. (a) negative
(b) negative
(c) positive



$$\begin{aligned}\Delta H^\circ &= [\Delta H^\circ_{\text{f(CaSO}_{4(s)})} + 2\Delta H^\circ_{\text{f(H}_2\text{O}_{(l)})}] - [\Delta H^\circ_{\text{f(Ca(OH)}_{2(s)})} + \Delta H^\circ_{\text{f(H}_2\text{SO}_{4(l)})}] \\ &= [1 \text{ mol} \times (-1434.1 \text{ kJ/mol}) + 2 \text{ mol} \times (-285.8 \text{ kJ/mol})] - [1 \text{ mol} \times (-986.1 \text{ kJ/mol}) + 1 \text{ mol} \times (-814.0 \text{ kJ/mol})] \\ &= [-2005.7 \text{ kJ}] - [-1800.1 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = -205.6 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{\text{(CaSO}_{4(s)})} + 2S^\circ_{\text{(H}_2\text{O}_{(l)})}] - [S^\circ_{\text{(Ca(OH)}_{2(s)})} + S^\circ_{\text{(H}_2\text{SO}_{4(l)})}] \\ &= [1 \text{ mol} \times (+108.4 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (+69.95 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} \times (+83.4 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} \times (+156.90 \text{ J/mol}\cdot\text{K})] \\ &= [248.3 \text{ J/K}] - [240.3 \text{ J/K}]\end{aligned}$$

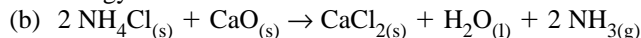
$$\begin{aligned}\Delta S^\circ &= 8.0 \text{ J/K} \\ &= 8.0 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

$$\Delta S^\circ = 0.0080 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -205.6 \text{ kJ} - (298 \text{ K})(0.0080 \text{ kJ/K}) \\ &= -205.6 \text{ kJ} - 2.4 \text{ kJ}\end{aligned}$$

$$\Delta G^\circ = -208.0 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -208.0 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 208.0 kJ of free energy is made available to do useful work for each mole of calcium hydroxide that reacts.



$$\begin{aligned}\Delta H^\circ &= [\Delta H^\circ_{\text{f(CaCl}_{2(aq)})} + \Delta H^\circ_{\text{f(H}_2\text{O}_{(l)})} + 2\Delta H^\circ_{\text{f(NH}_3(g)})] - [2\Delta H^\circ_{\text{f(NH}_4\text{Cl}_{(s)})} + \Delta H^\circ_{\text{f(CaO}_{(s)})}] \\ &= [1 \text{ mol} \times (-795.8 \text{ kJ/mol}) + 1 \text{ mol} \times (-285.8 \text{ kJ/mol}) + 2 \text{ mol} \times (-45.9 \text{ kJ/mol})] - [2 \text{ mol} \times (-314.1 \text{ kJ/mol})] \\ &= [-1173.4 \text{ kJ}] - [-1263.7 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = +90.3 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{\text{(CaCl}_{2(aq)})} + S^\circ_{\text{(H}_2\text{O}_{(l)})} + 2S^\circ_{\text{(NH}_3(g)})] - [2S^\circ_{\text{(NH}_4\text{Cl}_{(s)})} + S^\circ_{\text{(CaO}_{(s)})}] \\ &= [1 \text{ mol} \times (+104.6 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} \times (+69.95 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (+192.78 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol} \times (+83.4 \text{ J/mol}\cdot\text{K})] \\ &= [560.11 \text{ J/K}] - [227.3 \text{ J/K}]\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 332.8 \text{ J/K} \\ &= 332.8 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

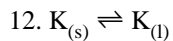
$$\Delta S^\circ = 0.3328 \text{ kJ/K}$$

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

$$= +90.3 \text{ kJ} - (298 \text{ K})(0.3328 \text{ kJ/K})$$

$$\Delta G^\circ = +803.8 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is +803.8 kJ. Since ΔG° is positive, the reaction is not spontaneous under standard conditions. A total of 803.8 kJ of free energy must be provided per mole of calcium oxide to make the reaction proceed according to the balanced equation.



$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= [\Delta H^\circ_{f(\text{K}_{(l)})} - \Delta H^\circ_{f(\text{K}_{(s)})}]$$

$$= 1 \text{ mol} \times (+2.284 \text{ kJ/mol}) - 1 \text{ mol} \times (0)$$

$$T = +2.284 \text{ kJ}$$

$$\Delta S^\circ = [S^\circ_{(\text{K}_{(l)})} - S^\circ_{(\text{K}_{(s)})}]$$

$$= 1 \text{ mol} \times (+71.46 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+64.68 \text{ J/mol}\cdot\text{K})$$

$$= 71.46 \text{ J/mol}\cdot\text{K} - 64.68 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ = 6.78 \text{ J/mol}\cdot\text{K}$$

$$= 6.78 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.00678 \text{ kJ/K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= \frac{2.284 \text{ kJ}}{0.00678 \text{ kJ/K}}$$

$$T = 337 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (337 \text{ K} - 273^\circ\text{C})$$

$$t = 64^\circ\text{C}$$

The melting point of potassium is 64°C .

13. (a) $\Delta H^\circ > 0$. Reactions involving bond formation tend to be endothermic.

$\Delta S^\circ > 0$. Solid ammonium is far more ordered than the gaseous reactants.

$\Delta G^\circ < 0$. The picture provides evidence that the reaction occurs spontaneously. Therefore, $\Delta G^\circ < 0$.



$$\Delta H^\circ = [\Delta H^\circ_{f(\text{NH}_4\text{Cl}_{(s)})}] - [\Delta H^\circ_{f(\text{NH}_{3(g)})} + \Delta H^\circ_{f(\text{HCl}_{(g)})}]$$

$$= [1 \text{ mol} (-314.4 \text{ kJ/mol})] - [1 \text{ mol} (-45.9 \text{ kJ/mol}) + 1 \text{ mol} (-92.3 \text{ kJ/mol})]$$

$$= [-314.4 \text{ kJ}] - [-45.9 \text{ kJ} - 92.3 \text{ kJ}]$$

$$= [-314.4 \text{ kJ}] - [-138.2 \text{ kJ}]$$

$$\Delta H^\circ = -176.2 \text{ kJ}$$

$$\Delta S^\circ = [S^\circ_{(\text{NH}_4\text{Cl}_{(s)})}] - [S^\circ_{(\text{NH}_{3(g)})} + S^\circ_{(\text{HCl}_{(g)})}]$$

$$= [1 \text{ mol} (94.6 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} (192.78 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} (186.9 \text{ J/mol}\cdot\text{K})]$$

$$= [94.6 \text{ J/K}] - [192.78 \text{ J/K} + 186.90 \text{ J/K}]$$

$$\Delta S^\circ = -285.08 \text{ J/K}$$

$$= -285.08 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = -0.28508 \text{ kJ/K}$$

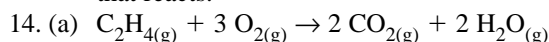
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -176.2 \text{ kJ} - (298 \text{ K})(-0.28508 \text{ kJ/K})$$

$$\Delta G^\circ = -91.2 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -91.2 kJ .

- (c) All the calculated values agreed with the predicted values except ΔH° . The enthalpy change for this reaction is negative. Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 91.2 kJ of free energy is made available to do useful work for each mole of ammonia that reacts.



$$\begin{aligned}\Delta H^\circ &= [2\Delta H^\circ_{f(\text{CO}_{2(g)})} + 2\Delta H^\circ_{f(\text{H}_2\text{O}_{(g)})}] - [\Delta H^\circ_{f(\text{C}_2\text{H}_{4(g)})} + 3\Delta H^\circ_{f(\text{O}_{2(g)})}] \\ &= [2 \text{ mol} \times (-393.5 \text{ kJ/mol}) + 2 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [(+52.5 \text{ kJ/mol}) + 3 \text{ mol} \times (0)] \\ &= [-1270.6 \text{ kJ}] - [+52.5 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = -1323.1 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [2S^\circ_{(\text{CO}_{2(g)})} + 2S^\circ_{(\text{H}_2\text{O}_{(g)})}] - [S^\circ_{(\text{C}_2\text{H}_{4(g)})} + 3S^\circ_{(\text{O}_{2(g)})}] \\ &= [2 \text{ mol} \times (213.78 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [(219.3 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol} \times (+205.14 \text{ J/mol}\cdot\text{K})] \\ &= [+805.24 \text{ J/K}] - [+834.42 \text{ J/K}]\end{aligned}$$

$$\Delta S^\circ = 29.18 \text{ J/K}$$

$$= -29.18 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = -0.02918 \text{ kJ/K}$$

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

$$= -1323.1 \text{ kJ} - (298 \text{ K})(-0.02918 \text{ kJ/K})$$

$$\Delta G^\circ = -1314.4 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -1314.4 kJ .

- (b) Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 1314.4 kJ of free energy is made available to do useful work for each mole of ethene that burns.

15. Once a system reaches equilibrium in a closed system, $\Delta G = 0$.

Making Connections

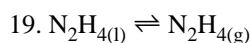
16. (a) (Sample answers) dissolving sugar, burning a candle, melting ice, making a sandwich, charging a battery, pumping water

17. There are a number of processes involved in the operation of a car that increase the entropy of the universe. For example:

- The combustion of fuel takes the large ordered molecules in gasoline and converts them into many smaller molecules with considerable kinetic energy.
- After an oil change, clean oil gradually becomes dirty as it accumulates engine residue.
- Left unprotected, the metallic components of a car rust.
- There are many different types of fluids pumped throughout a network of hoses in the car. Leaks are inevitable.

18. Chemical reactions used in the home include:

- The combustion of natural gas: $\text{CH}_{4(g)} + 2 \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2 \text{H}_2\text{O}_{(g)}$. Free energy from this reaction is used to increase the kinetic energy of air molecules drawn into the furnace. The warm air is then blown throughout the house.
- The dissolving of cleaning products such as lye (sodium hydroxide): $\text{NaOH}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$. Free energy released from this reaction is used to help dissolve organic matter that accumulates in plumbing.



$$\begin{aligned} T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= [\Delta H^\circ_{f(\text{N}_2\text{H}_{4(g)})} - \Delta H^\circ_{f(\text{N}_2\text{H}_{4(l)})}] \\ &= 1 \text{ mol} \times (+50.6 \text{ kJ/mol}) - 1 \text{ mol} \times (+95.4 \text{ kJ/mol}) \end{aligned}$$

$$T = -44.8 \text{ kJ}$$

$$\begin{aligned} \Delta S^\circ &= [S^\circ_{(\text{N}_2\text{H}_{4(g)})} - S^\circ_{(\text{N}_2\text{H}_{4(l)})}] \\ &= 1 \text{ mol} \times (+237.11 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+121.21 \text{ J/mol}\cdot\text{K}) \\ &= 237.11 \text{ J/mol}\cdot\text{K} - 121.21 \text{ J/mol}\cdot\text{K} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= 115.9 \text{ J/mol}\cdot\text{K} \\ &= 115.9 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \end{aligned}$$

$$\Delta S^\circ = 0.1159 \text{ kJ/K}$$

$$\begin{aligned} T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= \frac{-44.8 \text{ kJ}}{0.1159 \text{ kJ/K}} \end{aligned}$$

$$T = 387 \text{ K}$$

$$\begin{aligned} t &= (T - 273^\circ\text{C}) \\ &= (387 \text{ K} - 273^\circ\text{C}) \end{aligned}$$

$$t = 114^\circ\text{C}$$

The boiling point of hydrazine is 114°C .

- (b) Hydrazine is used mainly as a chemical intermediate in the production of agricultural chemicals, and spandex fibres. It is also a rocket fuel. Hydrazine is also used for plating metals on glass and plastics and as a component of photographic developers.

CHAPTER 7 LAB ACTIVITIES

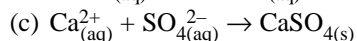
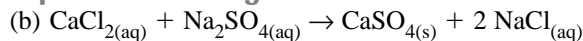
INVESTIGATION 7.1.1 DISCOVERING THE EXTENT OF A CHEMICAL REACTION

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Prediction

- (a) The reaction is quantitative since equimolar amounts of both reactants are combined.

Experimental Design



Procedure

- (d)
1. Measure 10 mL (or 5 mL) of $\text{CaCl}_{2(aq)}$ in a clean graduated cylinder.
 2. Pour the solution into a clean 50-mL or 100-mL beaker.
 3. Measure 5 mL (or 10 mL) of $\text{Na}_2\text{SO}_{4(aq)}$ in a clean graduated cylinder.
 4. Slowly add this quantity of $\text{Na}_2\text{SO}_{4(aq)}$ to the $\text{CaCl}_{2(aq)}$ while stirring.
 5. Filter the precipitate from the mixture.
 6. Collect about 5 mL of the filtrate into a small clean test tube.
 7. Test the filtrate by adding a few drops of $\text{Na}_2\text{CO}_{3(aq)}$.