

- (c) Assume the reactant is P(g), not P(s).

$$\Delta H^\circ = 2(-1594.4) + 5(0) - 2(316.4) - 10(-268.61) = -1135.5 \text{ kJ}$$

$$\Delta S^\circ = 2(300.8) + 5(130.58) - 2(163.2) - 10(173.51) = -807.0 \text{ J/K}$$

$$\Delta G^\circ = 2(-1520.7) + 5(0) - 2(280.0) - 10(-270.70) = -894.4 \text{ kJ}$$

$$\Delta G^\circ = -1135.5 \text{ kJ} - 298 \text{ K}(-0.8070 \text{ kJ/K}) = -895.014 = -895.0 \text{ kJ}$$

(The small discrepancy in ΔG° values is because of experimental uncertainties in tabulated thermodynamic data.)

- (d)
- $\Delta H^\circ = -284.5 - (0) - (0) = -284.5 \text{ kJ}$

$$\Delta S^\circ = 122.5 - 64.67 - 205.0 = -147.2 \text{ J/K}$$

$$\Delta G^\circ = -240.6 - (0) - (0) = -240.6 \text{ kJ}$$

$$\Delta G^\circ = -284.5 \text{ kJ} - 298 \text{ K}(-0.1472 \text{ kJ/K}) = -240.634 = -240.6 \text{ kJ}$$

- 19.59
- Analyze/Plan.*
- Follow the logic in Sample Exercise 19.7.
- Solve.*

$$\begin{aligned} \text{(a)} \quad \Delta G^\circ &= 2\Delta G^\circ \text{SO}_3(\text{g}) - [2\Delta G^\circ \text{SO}_2(\text{g}) + \Delta G^\circ \text{O}_2(\text{g})] \\ &= 2(-370.4) - [2(-300.4) + 0] = -140.0 \text{ kJ, spontaneous} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta G^\circ &= 3\Delta G^\circ \text{NO}(\text{g}) - [\Delta G^\circ \text{NO}_2(\text{g}) + \Delta G^\circ \text{N}_2\text{O}(\text{g})] \\ &= 3(86.71) - [51.84 + 103.59] = +104.70 \text{ kJ, nonspontaneous} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta G^\circ &= 4\Delta G^\circ \text{FeCl}_3(\text{s}) + 3\Delta G^\circ \text{O}_2(\text{g}) - [6\Delta G^\circ \text{Cl}_2(\text{g}) + 2\Delta G^\circ \text{Fe}_2\text{O}_3(\text{s})] \\ &= 4(-334) + 3(0) - [6(0) + 2(-740.98)] = +146 \text{ kJ, nonspontaneous} \end{aligned}$$

$$\begin{aligned} \text{(d)} \quad \Delta G^\circ &= \Delta G^\circ \text{S}(\text{s}) + 2\Delta G^\circ \text{H}_2\text{O}(\text{g}) - [\Delta G^\circ \text{SO}_2(\text{g}) + 2\Delta G^\circ \text{H}_2(\text{g})] \\ &= 0 + 2(-228.57) - [(-300.4) + 2(0)] = -156.7 \text{ kJ, spontaneous} \end{aligned}$$

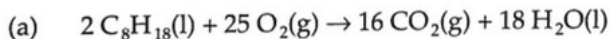
$$\begin{aligned} \text{19.60 (a)} \quad \Delta G^\circ &= 2\Delta G^\circ \text{AgCl}(\text{s}) - [2\Delta G^\circ \text{Ag}(\text{s}) + \Delta G^\circ \text{Cl}_2(\text{g})] \\ &= 2(-109.7) - 2(0) - 0 = -219.4 \text{ kJ, spontaneous} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad &\text{P}_4\text{O}_{10}(\text{s}) + 16 \text{H}_2(\text{g}) \rightarrow 4 \text{PH}_3(\text{g}) + 10 \text{H}_2\text{O}(\text{g}) \\ \Delta G^\circ &= 4\Delta G^\circ \text{PH}_3(\text{g}) + 10\Delta G^\circ \text{H}_2\text{O}(\text{g}) - [\Delta G^\circ \text{P}_4\text{O}_{10}(\text{s}) + 16\Delta G^\circ \text{H}_2(\text{g})] \\ &= 4(13.4) + 10(-228.57) - [-2675.2] - 16(0) = 443.1 \text{ kJ, nonspontaneous} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta G^\circ &= \Delta G^\circ \text{CF}_4(\text{g}) + 4\Delta G^\circ \text{HF}(\text{g}) - [\Delta G^\circ \text{CH}_4(\text{g}) + 4\Delta G^\circ \text{F}_2(\text{g})] \\ &= -635.1 + 4(-270.70) - (-50.8) - 4(0) = -1667.1 \text{ kJ, spontaneous} \end{aligned}$$

$$\begin{aligned} \text{(d)} \quad \Delta G^\circ &= 2\Delta G^\circ \text{H}_2\text{O}(\text{l}) + \Delta G^\circ \text{O}_2(\text{g}) - 2\Delta G^\circ \text{H}_2\text{O}_2(\text{l}) \\ &= 2(-237.13) + 0 - 2(-120.4) = -233.5 \text{ kJ, spontaneous} \end{aligned}$$

- 19.61
- Analyze/Plan.*
- Follow the logic in Sample Exercise 19.8(a).
- Solve.*



- (b) Because there are more moles of gas in the reactants, ΔS° is negative, which makes $-T\Delta S$ positive. ΔG° is less negative than ΔH° . (This argument is true for the reaction as written. If the products are all in the gas phase, there are more moles of gas in the products and ΔG° is more negative than ΔH° .)

- 19.62 (a) ΔG° should be less negative than ΔH° . Products contain fewer moles of gas, so ΔS° is negative. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; $-T\Delta S^\circ$ is positive, so ΔG° is less negative than ΔH° .
- (b) We can estimate ΔS° using a similar reaction and then use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (estimate) to get a ballpark figure. There are no sulfite salts listed in Appendix C, so use a reaction such as $\text{CO}_2(\text{g}) + \text{CaO}(\text{s}) \rightarrow \text{CaCO}_3(\text{s})$ or $\text{CO}_2(\text{g}) + \text{BaO}(\text{s}) \rightarrow \text{BaCO}_3(\text{s})$. Or, calculate both ΔS° values and use the average as your estimate.

19.63 *Analyze/Plan.* Based on the signs of ΔH and ΔS for a particular reaction, assign a category from Table 19.3 to each reaction. *Solve.*

- (a) (iii) ΔG is negative at low temperatures, positive at high temperatures. That is, the forward reaction is spontaneous at lower temperatures but not spontaneous at higher temperatures.
- (b) (ii) ΔG is positive at all temperatures. The forward reaction is nonspontaneous at all temperatures.
- (c) (iv) ΔG is positive at low temperatures, negative at high temperatures. That is, the forward reaction will proceed spontaneously at high temperature, but not at low temperature.

19.64 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

(a) $\Delta G^\circ = -844 \text{ kJ} - 298 \text{ K}(-0.165 \text{ kJ/K}) = -795 \text{ kJ}$, spontaneous

(b) $\Delta G^\circ = +572 \text{ kJ} - 298 \text{ K}(0.179 \text{ kJ/K}) = +519 \text{ kJ}$, nonspontaneous

To be spontaneous, ΔG must be negative ($\Delta G < 0$).

$$\text{Thus, } \Delta H^\circ - T\Delta S^\circ < 0; \Delta H^\circ < T\Delta S^\circ; T > \Delta H^\circ/\Delta S^\circ; T > \frac{572 \text{ kJ}}{0.179 \text{ kJ/K}} = 3.20 \times 10^3 \text{ K}$$

19.65 *Analyze/Plan.* We are told that the reaction is barely spontaneous and endothermic, and asked to estimate the sign and magnitude of ΔS . If a reaction is spontaneous, $\Delta G < 0$. Use this information with Equation 19.11 to solve the problem. *Solve.*

At 390 K, $\Delta G < 0$; $\Delta G = \Delta H - T\Delta S < 0$

$23.7 \text{ kJ} - 390 \text{ K}(\Delta S) < 0$; $23.7 \text{ kJ} < 390 \text{ K}(\Delta S)$; $\Delta S > 23.7 \text{ kJ}/390 \text{ K}$

$\Delta S > 0.06077 \text{ kJ/K}$ or $\Delta S > 60.8 \text{ J/K}$

The reaction is spontaneous and endothermic, so the sign of ΔS must be positive. Because the reaction is "barely" spontaneous, the magnitude will not be much greater than 61 J/K.

19.66 At 45 °C or 318 K, $\Delta G > 0$. $\Delta G = \Delta H - T\Delta S > 0$

$\Delta H - 318 \text{ K}(72 \text{ J/K}) > 0$; $\Delta H > +2.3 \times 10^4 \text{ J}$; $\Delta H > +23 \text{ kJ}$

The reaction is nonspontaneous and has a positive ΔS , so it must be endothermic. Because it is "barely" nonspontaneous, the magnitude will not be much greater than 23 kJ.

19.67 *Analyze/Plan.* Use Equation 19.11 to calculate T when $\Delta G = 0$. This is similar to calculating the temperature of a phase transition in Sample Exercise 19.10. Use Table 19.3 to determine whether the reaction is spontaneous or nonspontaneous above this temperature. *Solve.*

$$(a) \quad \Delta G = \Delta H - T\Delta S; 0 = -32 \text{ kJ} - T(-98 \text{ J/K}); 32 \times 10^3 \text{ J} = T(98 \text{ J/K})$$

$$T = 32 \times 10^3 \text{ J} / (98 \text{ J/K}) = 326.5 = 330 \text{ K}$$

(b) Nonspontaneous. The sign of ΔS is negative, so as T increases, ΔG becomes more positive.

19.68 ΔG is negative when $T\Delta S > \Delta H$ or $T > \Delta H/\Delta S$.

$$\Delta H^\circ = \Delta H^\circ \text{CH}_3\text{OH} + \Delta H^\circ \text{CO(g)} - \Delta H^\circ \text{CH}_3\text{COOH(l)}$$

$$= -201.2 - 110.5 - (-487.0) = 175.3 \text{ kJ}$$

$$\Delta S^\circ = S^\circ \text{CH}_3\text{OH} + S^\circ \text{CO(g)} - S^\circ \text{CH}_3\text{COOH(l)} = 237.6 + 197.9 - 159.8 = 275.7 \text{ J/K}$$

$$T > \frac{175.3 \text{ kJ}}{0.2757 \text{ kJ/K}} = 635.8 \text{ K}$$

The reaction is spontaneous above 635.8 K (363 °C).

19.69 *Analyze/Plan.* Given a chemical equation and thermodynamic data (values of ΔH_f° , ΔG_f° , and S°) for reactants and products, predict the variation of ΔG° with temperature and calculate ΔG° at 800 K and 1000 K. Use Equations 5.31 and 19.8 to calculate ΔH° and ΔS° , respectively; use these values to calculate ΔG° at various temperatures, using Equation 19.12. The signs of ΔH° and ΔS° determine the variation of ΔG° with temperature. *Solve.*

(a) Calculate ΔH° and ΔS° to determine the sign of $T\Delta S^\circ$.

$$\Delta H^\circ = 3\Delta H^\circ \text{NO(g)} - \Delta H^\circ \text{NO}_2\text{(g)} - \Delta H^\circ \text{N}_2\text{O(g)}$$

$$= 3(90.37) - 33.84 - 81.6 = 155.7 \text{ kJ}$$

$$\Delta S^\circ = 3S^\circ \text{NO(g)} - S^\circ \text{NO}_2\text{(g)} - S^\circ \text{N}_2\text{O(g)}$$

$$= 3(210.62) - 240.45 - 220.0 = 171.4 \text{ J/K}$$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Because ΔS° is positive, $-T\Delta S^\circ$ becomes more negative as T increases and ΔG° becomes more negative.

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 155.7 \text{ kJ} - (800 \text{ K})(0.1714 \text{ kJ/K})$

$$\Delta G^\circ = 155.7 \text{ kJ} - 137 \text{ kJ} = 19 \text{ kJ}$$

Because ΔG° is positive at 800 K, the reaction is not spontaneous at this temperature.

(c) $\Delta G^\circ = 155.7 \text{ kJ} - (1000 \text{ K})(0.1714 \text{ kJ/K}) = 155.7 \text{ kJ} - 171.4 \text{ kJ} = -15.7 \text{ kJ}$

ΔG° is negative at 1000 K and the reaction is spontaneous at this temperature.

19.70 (a) $\Delta H^\circ = \Delta H_f^\circ \text{CH}_3\text{OH(g)} - \Delta H_f^\circ \text{CH}_4\text{(g)} - 1/2 \Delta H_f^\circ \text{O}_2\text{(g)}$

$$= -201.2 - (-74.8) - (1/2)(0) = -126.4 \text{ kJ}$$

$$\Delta S^\circ = S^\circ \text{CH}_3\text{OH(g)} - S^\circ \text{CH}_4\text{(g)} - 1/2 S^\circ \text{O}_2\text{(g)}$$

$$= 237.6 - 186.3 - 1/2(205.0) = -51.2 \text{ J/K} = -0.0512 \text{ kJ/K}$$

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. $-T\Delta S^\circ$ is positive, so ΔG° will increase (becomes more positive) as temperature increases.