5. (E) (a) Increase in entropy because a gas has been created from a liquid, a condensed phase.

(b) Decrease in entropy as a condensed phase, a solid, is created from a solid and a gas.

(c) For this reaction we cannot be certain of the entropy change. Even though the number of moles of gas produced is the same as the number that reacted, we cannot conclude that the entropy change is zero because not all gases have the same molar entropy.

(d) \[2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)\] Decrease in entropy since five moles of gas with high entropy become only four moles of gas, with about the same quantity of entropy per mole.

10. (M) In this problem we are given standard enthalpies of the formation \(\Delta H_f^o\) of liquid and gas pentane at 298.15 K and asked to estimate the normal boiling point of pentane, \(\Delta G_{\text{vap}}^o\) and furthermore comment on the significance of the sign of \(\Delta G_{\text{vap}}^o\).

The general strategy in solving this problem is to first determine \(\Delta H_{\text{vap}}^o\) from the known enthalpies of formation. Trouton’s rule can then be used to determine the normal boiling point of pentane. Lastly, \(\Delta G_{\text{vap}}^{\circ,298K}\) can be calculated using

\[\Delta G_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} - T\Delta S_{\text{vap}}^{\circ}.\]

**Stepwise approach:**

Calculate \(\Delta H_{\text{vap}}^{\circ}\) from the known values of \(\Delta H_f^o\) (part a):

\[
\begin{align*}
C_5H_{12}(l) & \rightleftharpoons C_5H_{12}(g) \\
\Delta H_f^o & = -173.5 \text{ kJmol}^{-1} \quad -146.9 \text{ kJmol}^{-1} \\
\Delta H_{\text{vap}}^{\circ} & = -146.9 - (-173.5) \text{kJmol}^{-1} = 26.6 \text{kJmol}^{-1}
\end{align*}
\]

Determine normal boiling point using Trouton’s rule (part a):

\[
\Delta S_{\text{vap}}^{\circ} = \frac{\Delta H_{\text{vap}}^{\circ}}{T_{\text{vap}}} = \frac{26.6 \text{kJmol}^{-1}}{87 \text{kJmol}^{-1} \text{K}^{-1}} = 0.306 \text{K}
\]

\[T_{\text{vap}} = \frac{\Delta H_{\text{vap}}^{\circ}}{\Delta S_{\text{vap}}^{\circ}} = \frac{26.6 \text{kJmol}^{-1}}{87 \text{kJmol}^{-1} \text{K}^{-1}} \times \frac{1000}{1000} = 306 \text{K}
\]

\[T_{\text{vap}} = 32.9^\circ C\]

Use \(\Delta G_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} - T\Delta S_{\text{vap}}^{\circ}\) to calculate \(\Delta G_{\text{vap}}^{\circ,298K}\) (part b):

\[
\Delta G_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} - T\Delta S_{\text{vap}}^{\circ}
\]

\[
\Delta G_{\text{vap}}^{\circ,298K} = 26.6 \text{kJmol}^{-1} - 298.15 \times \frac{87 \text{kJmol}^{-1} \text{K}^{-1}}{1000} = 0.66 \text{kJmol}^{-1}
\]
Comment on the value of \( \Delta G^*_{\text{vap},298K} \) (part c):
The positive value of \( \Delta G^*_{\text{vap}} \) indicates that normal boiling (having a vapor pressure of 1.00 atm) for pentane should be non-spontaneous (will not occur) at 298. The vapor pressure of pentane at 298 K should be less than 1.00 atm.

**Conversion pathway approach:**

\[
C_3H_{12}(l) \rightleftharpoons C_3H_{12}(g)
\]

\[
\Delta H^o_\text{vap} = -173.5 \text{ kJmol}^{-1} - 146.9 \text{ kJmol}^{-1}
\]

\[
\Delta S^o_\text{vap} = \frac{\Delta H^o_\text{vap}}{T_{\text{nbp}}} = \frac{87 \text{ Jmol}^{-1}\text{K}^{-1}}{1000} = 0.087 \text{ kJmol}^{-1}\text{K}^{-1}
\]

\[
\Delta G^*_{\text{vap}} = \Delta G^o_{\text{vap}} - T \Delta S^o_{\text{vap}} = 26.6 \text{ kJmol}^{-1} - 298.15 \times \frac{87 \text{ kJmol}^{-1}\text{K}^{-1}}{1000} = 0.66 \text{ kJmol}^{-1}
\]

15. **(E)** Answer (b) is correct. Br—Br bonds are broken in this reaction, meaning that it is endothermic, with \( \Delta H > 0 \). Since the number of moles of gas increases during the reaction, \( \Delta S > 0 \). And, because \( \Delta G = \Delta H - T \Delta S \), this reaction is non-spontaneous (\( \Delta G > 0 \)) at low temperatures where the \( \Delta H \) term predominates and spontaneous (\( \Delta G < 0 \)) at high temperatures where the \( T \Delta S \) term predominates.

23. **(M)** \( \Delta H^o = \Delta H^o_f [\text{NH}_4\text{Cl}(s)] - \Delta H^o_f [\text{NH}_3(g)] - \Delta H^o_f [\text{HCl}(g)] \)

\[
= -314.4 \text{ kJmol}^{-1} - (-46.11 \text{ kJmol}^{-1} - 92.31 \text{ kJmol}^{-1}) = -176.0 \text{ kJmol}^{-1}
\]

\( \Delta G^o = \Delta G^o_f [\text{NH}_4\text{Cl}(s)] - \Delta G^o_f [\text{NH}_3(g)] - \Delta G^o_f [\text{HCl}(g)] \)

\[
= -202.9 \text{ kJmol}^{-1} - (-16.48 \text{ kJmol}^{-1} - 95.30 \text{ kJmol}^{-1}) = -91.1 \text{ kJmol}^{-1}
\]

\( \Delta G^o = \Delta H^o - T \Delta S^o \)

\[
\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-176.0 \text{ kJmol}^{-1} + 91.1 \text{ kJmol}^{-1}}{298 \text{ K}} = -285 \text{ Jmol}^{-1}
\]

25. **(M) (a)** \( \Delta S^o = 2S^o [\text{POCl}_3(1)] - 2S^o [\text{PCl}_3(g)] - S^o [\text{O}_2(g)] \)

\[
= 2(222.4 \text{ J/K}) - 2(311.7 \text{ J/K}) - 205.1 \text{ J/K} = -383.7 \text{ J/K}
\]

\( \Delta G^o = \Delta H^o - T \Delta S^o = -620.2 \times 10^3 \text{ J} - (298 \text{ K})(-383.7 \text{ J/K}) = -506 \times 10^3 \text{ J} = -506 \text{ kJ} \)

(b) The reaction proceeds spontaneously in the forward direction when reactants and products are in their standard states, because the value of \( \Delta G^o \) is less than zero.
32. **(D)** In this problem we are asked to find $\Delta G^\circ$ at 298 K for the decomposition of ammonium nitrate to yield dinitrogen oxide gas and liquid water. Furthermore, we are asked to determine whether the decomposition will be favored at temperatures above or below 298 K. In order to answer these questions, we first need the balanced chemical equation for the process. From the data in Appendix D, we can determine $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$. Both quantities will be required to determine $\Delta G^\circ_{\text{rxn}} (\Delta G^\circ_{\text{rxn}}=\Delta H^\circ_{\text{rxn}}-T\Delta S^\circ_{\text{rxn}})$. Finally the magnitude of $\Delta G^\circ_{\text{rxn}}$ as a function of temperature can be judged depending on the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$.

**Stepwise approach:**

First we need the balanced chemical equation for the process:

$$\text{NH}_4\text{NO}_3(\text{s}) \xrightarrow{\Delta} \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$

Now we can determine $\Delta H^\circ_{\text{rxn}}$ by utilizing $\Delta H_f^\circ$ values provided in Appendix D:

$$\Delta H_f^\circ -365.6 \text{ kJ mol}^{-1} \quad 82.05 \text{ kJ mol}^{-1} \quad -285.6 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{rxn}}=\Sigma \Delta H_f^\circ_{\text{products}} - \Sigma \Delta H_f^\circ_{\text{reactants}}$$

$$\Delta H^\circ_{\text{rxn}}=[2 \text{ mol}(-285.8 \text{ kJ mol}^{-1}) + 1 \text{ mol}(82.05 \text{ kJ mol}^{-1})] -[1 \text{ mol}(-365.6 \text{ kJ mol}^{-1})]$$

$$\Delta H^\circ_{\text{rxn}}=-124.0 \text{ kJ}$$

Similarly, $\Delta S^\circ_{\text{rxn}}$ can be calculated utilizing $S^\circ$ values provided in Appendix D:

$$\text{NH}_4\text{NO}_3(\text{s}) \xrightarrow{\Delta} \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$

$$S^\circ = 15.1 \text{ J mol}^{-1} \text{ K}^{-1} \quad 219.9 \text{ J mol}^{-1} \text{ K}^{-1} \quad 69.91 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S^\circ_{\text{rxn}}=\Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{rxn}}=[2 \text{ mol} \times 69.91 \text{ J K}^{-1} \text{ mol}^{-1} + 1 \text{ mol} \times 219.9 \text{ J K}^{-1} \text{ mol}^{-1}] -[1 \text{ mol} \times 151.1 \text{ J K}^{-1} \text{ mol}^{-1}]$$

$$\Delta S^\circ_{\text{rxn}}=208.6 \text{ J K}^{-1} = 0.2086 \text{ kJ K}^{-1}$$

To find $\Delta G^\circ_{\text{rxn}}$ we can either utilize $\Delta G_f^\circ$ values provided in Appendix D or $\Delta G^\circ_{\text{rxn}}=\Delta H^\circ_{\text{rxn}}-T\Delta S^\circ_{\text{rxn}}$.

$$\Delta G^\circ_{\text{rxn}}=\Delta H^\circ_{\text{rxn}}-T\Delta S^\circ_{\text{rxn}}=-124.0 \text{ kJ} - 298.15 \text{ K} \times 0.2086 \text{ kJ K}^{-1}$$

$$\Delta G^\circ_{\text{rxn}}=-186.1 \text{ kJ}$$

Magnitude of $\Delta G^\circ_{\text{rxn}}$ as a function of temperature can be judged depending on the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$.

Since $\Delta H^\circ_{\text{rxn}}$ is negative and $\Delta S^\circ_{\text{rxn}}$ is positive, the decomposition of ammonium nitrate is spontaneous at all temperatures. However, as the temperature increases, the $T\Delta S$ term gets larger and as a result, the decomposition reaction shift towards producing more products. Consequently, we can say that the reaction is more highly favored above 298 K (it will also be faster at higher temperatures).

**Conversion pathway approach:**

From the balanced chemical equation for the process

$$\text{NH}_4\text{NO}_3(\text{s}) \xrightarrow{\Delta} \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$

we can determine $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ by utilizing $\Delta H_f^\circ$ and $S^\circ$ values provided in Appendix D:

$$\Delta H^\circ_{\text{rxn}}=[2 \text{ mol}(-285.8 \text{ kJ mol}^{-1}) + 1 \text{ mol}(82.05 \text{ kJ mol}^{-1})] -[1 \text{ mol}(-365.6 \text{ kJ mol}^{-1})]$$

$$\Delta S^\circ_{\text{rxn}}=[2 \text{ mol} \times 69.91 \text{ J K}^{-1} \text{ mol}^{-1} + 1 \text{ mol} \times 219.9 \text{ J K}^{-1} \text{ mol}^{-1}] -[1 \text{ mol} \times 151.1 \text{ J K}^{-1} \text{ mol}^{-1}]$$
Δ\(H^\circ\)_{rxn} = -124.0 kJ

\[\Delta S^\circ_{rxn} = [2 \text{ mol } \times 69.91 \text{ J K}^{-1}\text{mol}^{-1} + 1 \text{ mol } \times 219.9 \text{ J K}^{-1}\text{mol}^{-1}] - [1 \text{ mol } \times 151.1 \text{ J K}^{-1}\text{mol}^{-1}]
\]

\[\Delta G^\circ_{rxn} = 208.6 \text{ J K}^{-1} = 0.2086 \text{ kJ K}^{-1}\]

\[\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = -124.0 \text{ kJ} - 298.15 \text{ K} \times 0.2086 \text{ kJ K}^{-1}\]

\[\Delta G^\circ_{rxn} = -186.1 \text{ kJ}\]

Since \(\Delta H^\circ_{rxn}\) is negative and \(\Delta S^\circ_{rxn}\) is positive, the decomposition of ammonium nitrate is spontaneous at all temperatures. However, as the temperature increases, the \(T\Delta S\) term gets larger and as a result, the decomposition reaction shift towards producing more products. The reaction is highly favored above 298 K (it will also be faster).

35. (M) In this problem we are asked to determine the equilibrium constant and the change in Gibbs free energy for the reaction between carbon monoxide and hydrogen to yield methanol. The equilibrium concentrations of each reagent at 483K were provided. We proceed by first determining the equilibrium constant. Gibbs free energy can be calculated using \(\Delta G^\circ = -RT \ln K\).

*Stepwise approach:*

First determine the equilibrium constant for the reaction at 483K:

\[
K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911 \times 0.0822^2} = 14.5
\]

Now use \(\Delta G^\circ = -RT \ln K\) to calculate the change in Gibbs free energy at 483 K:

\[
\Delta G^\circ = -RT \ln K
\]

\[
\Delta G^\circ = -8.314 \times 483 \times \ln(14.5) \text{Jmol}^{-1} = -1.1 \times 10^4 \text{Jmol}^{-1}
\]

\[
\Delta G^\circ = -11 \text{kJmol}^{-1}
\]

*Conversion pathway approach:*

\[
K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911 \times 0.0822^2} = 14.5
\]

\[
\Delta G^\circ = -RT \ln K = -8.314 \times 483 \times \ln(14.5) \text{Jmol}^{-1} = -1.1 \times 10^4 \text{Jmol}^{-1}
\]

\[
\Delta G^\circ = -11 \text{kJmol}^{-1}
\]

38. (M) (a) \(\Delta G^\circ = 2\Delta G^\circ_1\left[N_2O_5\left(g\right)\right] - 2\Delta G^\circ_1\left[N_2O_4\left(g\right)\right] - \Delta G^\circ_1\left[O_2\left(g\right)\right]\)

\[
= 2\left(115.1 \text{ kJ/mol}\right) - 2\left(97.89 \text{ kJ/mol}\right) - \left(0.00 \text{ kJ/mol}\right) = 34.4 \text{ kJ/mol}
\]

(b) \(\Delta G^\circ = -RT \ln K_p\)

\[
\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{34.4 \times 10^3 \text{ Jmol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{K}^{-1} \times 298 \text{ K}} = -13.9
\]

\[
K_p = e^{-13.9} = 9 \times 10^{-7}
\]

44. (M) As was the case for exercise 39, we need to calculate the non-standard free energy change for the reaction. Once again, we will employ the equation \(\Delta G = \Delta G^\circ + RT \ln Q\), but this time
Chapter 19: Spontaneous Change: Entropy and Gibbs Energy

\[ Q_c = \frac{[\text{NH}_4^+ \text{aq}][\text{OH}^- \text{aq}]}{[\text{NH}_3 \text{aq}]} ; \quad Q_c = \left( \frac{1.0 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \right)^2 = 1.0 \times 10^{-5} \]

\[ \Delta G = 29.05 \text{ kJ} + (8.3145 \times 10^{-3} \text{ kJ/Kmol})(298 \text{ K})\ln(1.0 \times 10^{-5}) \]

\[ \Delta G = 29.05 \text{ kJ} + (-28.53 \text{ kJ}) = 0.52 \text{ kJ}. \]

Since \( \Delta G \) is positive, the reaction is spontaneous in the reverse direction.

51. (E) \( \Delta G^o = -RT \ln K_p = -\left(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1}\right)(298 \text{ K})\ln\left(6.5 \times 10^{11}\right) = -67.4 \text{ kJ/mol} \)

\( \text{CO} (g) + \text{Cl}_2 (g) \rightarrow \text{COCl}_2 (g) \quad \Delta G^o = -67.4 \text{ kJ/mol} \)

\( \text{C} \text{(graphite)} + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{CO} (g) \quad \Delta G^o_r = -137.2 \text{ kJ/mol} \)

\( \Delta G^o_r \) of \( \text{COCl}_2 (g) \) given in Appendix D is \(-204.6 \text{ kJ/mol} \), thus the agreement is excellent.

56. (M) (a) \( \Delta S^o = S^o \left[ \text{CH}_3\text{CH}_2\text{OH}(g) \right] + S^o \left[ \text{H}_2\text{O}(g) \right] - S^o \left[ \text{CO}(g) \right] - 2S^o \left[ \text{H}_2(g) \right] - S^o \left[ \text{CH}_3\text{OH}(g) \right] \)

\[ \Delta S^o = 282.7 \left( \frac{\text{J}}{\text{Kmol}} \right) + 188.8 \left( \frac{\text{J}}{\text{Kmol}} \right) - 197.7 \left( \frac{\text{J}}{\text{Kmol}} \right) - 2\left( 130.7 \left( \frac{\text{J}}{\text{Kmol}} \right) \right) - 239.8 \left( \frac{\text{J}}{\text{Kmol}} \right) \]

\[ \Delta S^o = -227.4 \left( \frac{\text{J}}{\text{Kmol}} \right) \]

\( \Delta H^o = \Delta H^o_r \left[ \text{CH}_3\text{CH}_2\text{OH}(g) \right] + \Delta H^o_r \left[ \text{H}_2\text{O}(g) \right] - \Delta H^o_r \left[ \text{CO}(g) \right] - 2\Delta H^o_r \left[ \text{H}_2(g) \right] - \Delta H^o_r \left[ \text{CH}_3\text{OH}(g) \right] \)

\[ \Delta H^o = -235.1 \left( \frac{\text{kJ}}{\text{mol}} \right) - 241.8 \left( \frac{\text{kJ}}{\text{mol}} \right) - 110.5 \left( \frac{\text{kJ}}{\text{mol}} \right) - 2\left( 0.00 \left( \frac{\text{kJ}}{\text{mol}} \right) \right) - \left( -200.7 \left( \frac{\text{kJ}}{\text{mol}} \right) \right) \]

\[ \Delta H^o = -165.7 \left( \frac{\text{kJ}}{\text{mol}} \right) \]

\[ \Delta G^o = -165.7 \left( \frac{\text{kJ}}{\text{mol}} \right) - (298 \text{ K})\left( -227.4 \times 10^{-3} \frac{\text{kJ}}{\text{Kmol}} \right) = -165.4 \left( \frac{\text{kJ}}{\text{mol}} \right) + 67.8 \left( \frac{\text{kJ}}{\text{mol}} \right) = -97.9 \left( \frac{\text{kJ}}{\text{mol}} \right) \]

(b) \( \Delta H^o < 0 \) for this reaction. Thus it is favored at low temperatures. Also, because \( \Delta n_{\text{gas}} = +2 - 4 = -2 \), which is less than zero, the reaction is favored at high pressures.

(c) First we assume that neither \( \Delta S^o \) nor \( \Delta H^o \) varies significantly with temperature. Then we compute a value for \( \Delta G^o \) at 750 K. From this value of \( \Delta G^o \), we compute a value for \( K_p \).

\[ \Delta G^o = \Delta H^o - T\Delta S^o = -165.7 \text{ kJ/mol} - \left(750 \text{ K}\right)\left( -227.4 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \right) \]

\[ = -165.7 \text{ kJ/mol} + 170.6 \text{ kJ/mol} = +4.9 \text{ kJ/mol} = -RT \ln K_p \]

\[ \ln K_p = \frac{-\Delta G^o}{RT} = \frac{-4.9 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 750 \text{ K}} = -0.79 \]

\[ K_p = e^{-0.79} = 0.5 \]
63. (M) (a) \[ \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{57.2 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{273 \text{ K}} \right) = -2.11 \]

\[ \frac{K_2}{K_1} = e^{-2.11} = 0.121 \quad K_2 = 0.121 \times 0.113 = 0.014 \text{ at } 273 \text{ K} \]

(b) \[ \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{57.2 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{T_1} - \frac{1}{298 \text{ K}} \right) = \ln \frac{0.113}{1.00} = -2.180 \]

\[ \left( \frac{1}{T_1} - \frac{1}{298 \text{ K}} \right) = \frac{-2.180 \times 8.3145}{57.2 \times 10^3} \text{ K}^{-1} = -3.17 \times 10^{-4} \text{ K}^{-1} \]

\[ \frac{1}{T_1} = \frac{1}{298} - 3.17 \times 10^{-4} = 3.36 \times 10^{-3} - 3.17 \times 10^{-4} = 3.04 \times 10^{-3} \text{ K}^{-1}; \quad T_1 = 329 \text{ K} \]