

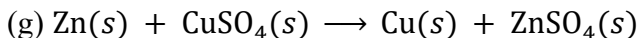
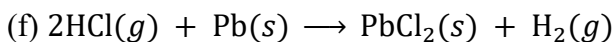
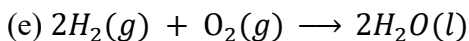
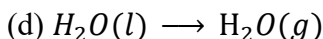
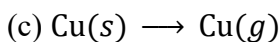
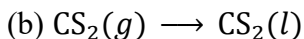
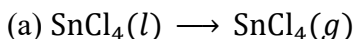
Section 73 – The Third Law of Thermodynamics

73-1. What is the difference between ΔS and ΔS° for a chemical change?

Solution

ΔS : any change in entropy under any set of conditions. ΔS° : any change in entropy with products and reactants at standard conditions (1 bar or 1 atm for gases, 1 M for solutions); if no temperature information is provided, assume the temperature is 298.15 K.

73-2. Calculate ΔS° for the following changes.



Solutions

(a)

$$\begin{aligned}\Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\ &= 1\Delta S^\circ_{\text{SnCl}_4(g)} - 1\Delta S^\circ_{\text{SnCl}_4(l)} \\ &= \left[1 \text{ mol} \left(366 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(259 \frac{\text{J}}{\text{mol K}} \right) \right] = 107 \text{ J/K}\end{aligned}$$

(b)

$$\begin{aligned}\Delta S^\circ_{298} &= \sum \nu \Delta S^\circ_{298} (\text{products}) - \sum \nu \Delta S^\circ_{298} (\text{reactants}) \\ &= 1\Delta S^\circ_{298} \text{CS}_2(l) - 1\Delta S^\circ_{298} \text{CS}_2(g) \\ &= \left[1 \text{ mol} \left(151.3 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(238.0 \frac{\text{J}}{\text{mol K}} \right) \right] = -86.7 \text{ J/K}\end{aligned}$$

(c)

$$\begin{aligned}
 \Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\
 &= 1\Delta S^\circ \text{Cu}(g) - 1\Delta S^\circ \text{Cu}(s) \\
 &= \left[1 \text{ mol} \left(166.3 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(33.15 \frac{\text{J}}{\text{mol K}} \right) \right] = 133.2 \text{ J/K}
 \end{aligned}$$

(d)

$$\begin{aligned}
 \Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\
 &= 1\Delta S^\circ \text{H}_2\text{O}(g) - 1\Delta S^\circ \text{H}_2\text{O}(l) \\
 &= \left[1 \text{ mol} \left(188.8 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(70.0 \frac{\text{J}}{\text{mol K}} \right) \right] = 118.8 \text{ J/K}
 \end{aligned}$$

(e) $\Delta S^\circ = \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants})$

$$\begin{aligned}
 &= 2\Delta S^\circ \text{H}_2\text{O}(l) - [1\Delta S^\circ \text{O}_2(g) + 2\Delta S^\circ \text{H}_2(g)] \\
 &= \left[2 \text{ mol} \left(70.0 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(205.2 \frac{\text{J}}{\text{mol K}} \right) + 2 \text{ mol} \left(130.7 \frac{\text{J}}{\text{mol K}} \right) \right] = \\
 &\quad - 326.6 \text{ J/K}
 \end{aligned}$$

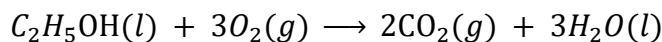
(f)

$$\begin{aligned}
 \Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\
 &= [1\Delta S^\circ \text{PbCl}_2(s) + 1\Delta S^\circ \text{H}_2(g)] - [1\Delta S^\circ \text{Pb}(s) + 2\Delta S^\circ \text{HCl}(g)] \\
 &= \left[1 \text{ mol} \left(136.0 \frac{\text{J}}{\text{mol K}} \right) + 1 \text{ mol} \left(130.7 \frac{\text{J}}{\text{mol K}} \right) \right] - \\
 &\quad \left[1 \text{ mol} \left(64.81 \frac{\text{J}}{\text{mol K}} \right) + 2 \text{ mol} \left(186.9 \frac{\text{J}}{\text{mol K}} \right) \right] = - 171.9 \text{ J/K}
 \end{aligned}$$

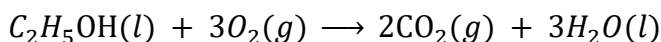
(g)

$$\begin{aligned}
 \Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\
 &= [1\Delta S^\circ \text{Cu}(s) + 1\Delta S^\circ \text{ZnSO}_4(s)] - [1\Delta S^\circ \text{Zn}(s) + 1\Delta S^\circ \text{CuSO}_4(s)] \\
 &= \left[1 \text{ mol} \left(33.15 \frac{\text{J}}{\text{mol K}} \right) + 1 \text{ mol} \left(110.5 \frac{\text{J}}{\text{mol K}} \right) \right] - \\
 &\quad \left[1 \text{ mol} \left(41.6 \frac{\text{J}}{\text{mol K}} \right) + 1 \text{ mol} \left(109.2 \frac{\text{J}}{\text{mol K}} \right) \right] = - 7.2 \text{ J/K}
 \end{aligned}$$

- 73-3. Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH , under the standard conditions to give gaseous carbon dioxide and liquid water. The balanced reaction for the combustion of liquid ethanol is as follows:



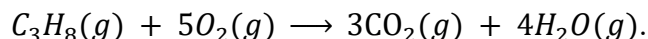
Solution: The reaction for the combustion of liquid ethanol is as follows:



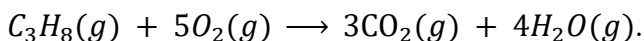
Thus the ΔS° can be calculated as follows:

$$\begin{aligned}\Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\ &= [2\Delta S^\circ CO_2(g) + 3\Delta S^\circ H_2O(l)] - [1\Delta S^\circ C_2H_5OH(l) + 3\Delta S^\circ O_2(g)] \\ &= \left[2 \text{ mol} \left(213.6 \frac{J}{\text{mol K}} \right) + 3 \text{ mol} \left(69.91 \frac{J}{\text{mol K}} \right) \right] - \\ &\quad \left[1 \text{ mol} \left(161 \frac{J}{\text{mol K}} \right) + 3 \text{ mol} \left(205.03 \frac{J}{\text{mol K}} \right) \right] = -139 \text{ J/K}\end{aligned}$$

- 73-4. Determine the entropy change for the combustion of gaseous propane, C_3H_8 , under the standard conditions to give gaseous carbon dioxide and water. The balanced reaction for the combustion of propane is as follows:



Solution: The reaction is



and so the ΔS° can be calculated as follows:

$$\begin{aligned}\Delta S^\circ &= \sum \nu \Delta S^\circ (\text{products}) - \sum \nu \Delta S^\circ (\text{reactants}) \\ &= [3\Delta S^\circ CO_2(g) + 4\Delta S^\circ H_2O(g)] - [1\Delta S^\circ C_3H_8(g) + 5\Delta S^\circ O_2(g)] \\ &= \left[3 \text{ mol} \left(213.8 \frac{J}{\text{mol K}} \right) + 4 \text{ mol} \left(188.8 \frac{J}{\text{mol K}} \right) \right] - \\ &\quad \left[1 \text{ mol} \left(270.3 \frac{J}{\text{mol K}} \right) + 5 \text{ mol} \left(205.02 \frac{J}{\text{mol K}} \right) \right] = 100.3 \text{ J/K}\end{aligned}$$

- 73-5. “Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$. Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

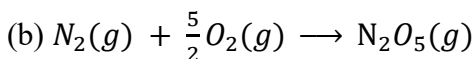
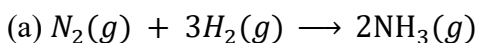
Solution

Calculating ΔS_{univ} is necessary to answer the question:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ \Delta S_{\text{sys}}^{\circ} &= \sum \nu \Delta S^{\circ} (\text{products}) - \sum \nu \Delta S^{\circ} (\text{reactants}) \\ \Delta S_{\text{sys}}^{\circ} &= (\Delta S^{\circ} \text{Fe} + \Delta S^{\circ} \text{Al}_2\text{O}_3) - (1\Delta S^{\circ} \text{Fe}_2\text{O}_3 + 2\Delta S^{\circ} \text{Al}) \\ \Delta S_{\text{sys}}^{\circ} &= \left[2 \text{ mol} \left(27.3 \frac{\text{J}}{\text{mol K}} \right) + 1 \text{ mol} \left(50.92 \frac{\text{J}}{\text{mol K}} \right) \right] - \\ &\quad \left[1 \text{ mol} \left(87.40 \frac{\text{J}}{\text{mol K}} \right) + 2 \text{ mol} \left(28.3 \frac{\text{J}}{\text{mol K}} \right) \right] = -38.48 \text{ J/K} \\ \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} = -38.48 \frac{\text{J}}{\text{mol} \cdot \text{K}} - \frac{-851.8 \frac{\text{kJ}}{\text{mol}} \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{298.15} = 2820 \text{ J/K}\end{aligned}$$

As $\Delta S_{\text{univ}} > 0$, the reaction is spontaneous.

73-6. Using the relevant S° values listed in Appendix G, calculate the S° at 298K for the following changes:



Solution:

(a) $\Delta S_{\text{sys}}^{\circ} = \sum \nu \Delta S^{\circ} (\text{products}) - \sum \nu \Delta S^{\circ} (\text{reactants})$

$$\begin{aligned}\Delta S_{\text{sys}}^{\circ} &= (2\Delta S^{\circ} \text{NH}_3) - (1\Delta S^{\circ} \text{N}_2 + 3\Delta S^{\circ} \text{H}_2) \\ \Delta S_{\text{sys}}^{\circ} &= \left[2 \text{ mol} \left(192.8 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(191.6 \frac{\text{J}}{\text{mol K}} \right) + 3 \text{ mol} \left(130.7 \frac{\text{J}}{\text{mol K}} \right) \right] \\ &= -198.1 \text{ J/K} \quad ;\end{aligned}$$

(b) $\Delta S_{\text{sys}}^{\circ} = \sum \nu \Delta S^{\circ} (\text{products}) - \sum \nu \Delta S^{\circ} (\text{reactants})$

$$\begin{aligned}\Delta S_{\text{sys}}^{\circ} &= (2\Delta S^{\circ} \text{N}_2\text{O}_5) - \left(1\Delta S^{\circ} \text{N}_2 + \frac{5}{2} \times \Delta S^{\circ} \text{O}_2 \right) \\ \Delta S_{\text{sys}}^{\circ} &= \left[1 \text{ mol} \left(355.7 \frac{\text{J}}{\text{mol K}} \right) \right] - \left[1 \text{ mol} \left(191.6 \frac{\text{J}}{\text{mol K}} \right) + \frac{5}{2} \text{ mol} \left(205.2 \frac{\text{J}}{\text{mol K}} \right) \right] \\ &= -348.9 \text{ J/K}\end{aligned}$$

73-7. Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed below. All the processes occur at the standard conditions and 25 °C.

- (a) $\text{MnO}_2(s) \rightarrow \text{Mn}(s) + \text{O}_2(g)$
(b) $\text{H}_2(g) + \text{Br}_2(l) \rightarrow 2\text{HBr}(g)$
(c) $\text{Cu}(s) + \text{S}(g) \rightarrow \text{CuS}(s)$
(d) $2\text{LiOH}(s) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$
(e) $\text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{C}(s, \text{graphite}) + 2\text{H}_2\text{O}(g)$
(f) $\text{CS}_2(g) + 3\text{Cl}_2(g) \rightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$

Solution:

(a) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$
$$\Delta S^\circ = \left[1 \text{ mol} \left(3.20 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(205.2 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(53.05 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = 184.2 \text{ J/K}$$

(b) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$
$$\Delta S^\circ = \left[2 \text{ mol} \left(198.7 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(152.23 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(130.7 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = 114.5 \text{ J/K}$$

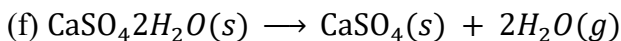
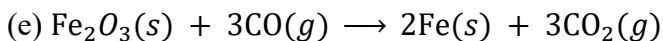
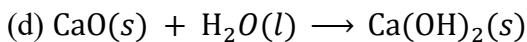
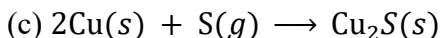
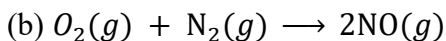
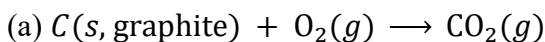
(c) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$
$$\Delta S^\circ = \left[1 \text{ mol} \left(66.5 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(33.15 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(167.82 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = -134.5 \text{ J/K}$$

(d) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$
$$\Delta S^\circ = \left[1 \text{ mol} \left(90.71 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(188.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[2 \text{ mol} \left(42.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(213.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = -20.4 \text{ J/K}$$

(e) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$
$$\Delta S^\circ = \left[1 \text{ mol} \left(5.740 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 2 \text{ mol} \left(188.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(186.3 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(205.2 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = -8.16 \text{ J/K}$$

(f) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$
$$\Delta S^\circ = \left[1 \text{ mol} \left(309.7 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 1 \text{ mol} \left(319.45 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(238.0 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 3 \text{ mol} \left(223.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] = -278.2 \text{ J/K}$$

73-8. Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed below. All the processes occur at the standard conditions and 25 °C.



Solution:

(a) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1 \text{ mol} \left(213.8 \frac{J}{\text{mol} \cdot K} \right) \right] - \left[1 \text{ mol} \left(5.740 \frac{J}{\text{mol} \cdot K} \right) + 1 \text{ mol} \left(205.2 \frac{J}{\text{mol} \cdot K} \right) \right] = 2.86 \text{ J/K}$$

(b) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[2 \text{ mol} \left(210.8 \frac{J}{\text{mol} \cdot K} \right) \right] - \left[1 \text{ mol} \left(191.6 \frac{J}{\text{mol} \cdot K} \right) + 1 \text{ mol} \left(205.2 \frac{J}{\text{mol} \cdot K} \right) \right] = 24.8 \text{ J/K}$$

(c) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1 \text{ mol} \left(120.9 \frac{J}{\text{mol} \cdot K} \right) \right] - \left[2 \text{ mol} \left(33.15 \frac{J}{\text{mol} \cdot K} \right) + 1 \text{ mol} \left(167.82 \frac{J}{\text{mol} \cdot K} \right) \right] = -113.2 \text{ J/K}$$

(d) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1 \text{ mol} \left(83.4 \frac{J}{\text{mol} \cdot K} \right) \right] - \left[1 \text{ mol} \left(38.1 \frac{J}{\text{mol} \cdot K} \right) + 1 \text{ mol} \left(70.0 \frac{J}{\text{mol} \cdot K} \right) \right] = -24.7 \text{ J/K}$$

(e) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[2 \text{ mol} \left(27.3 \frac{J}{\text{mol} \cdot K} \right) + 3 \text{ mol} \left(213.8 \frac{J}{\text{mol} \cdot K} \right) \right] - \left[1 \text{ mol} \left(81.40 \frac{J}{\text{mol} \cdot K} \right) + 3 \text{ mol} \left(197.7 \frac{J}{\text{mol} \cdot K} \right) \right] = 15.5 \text{ J/K}$$

$$\begin{aligned}
 \text{(f) } \Delta S^\circ &= \sum v \Delta S^\circ(\text{products}) - \sum v \Delta S^\circ(\text{reactants}) \\
 \Delta S^\circ &= \left[1 \text{ mol} \left(106.5 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + 2 \text{ mol} \left(188.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - \left[1 \text{ mol} \left(194.14 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] \\
 &= 290.0 \text{ J/K}
 \end{aligned}$$

73-9. By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of $\text{NaCl}(s)$ is spontaneous at 500 °C and at 700 °C.

$$S_{\text{NaCl}(s)}^\circ = 72.11 \frac{\text{J}}{\text{molK}} \quad S_{\text{NaCl}(l)}^\circ = 95.06 \frac{\text{J}}{\text{molK}} \quad \Delta H_{\text{fusion}}^\circ = 27.95 \text{ kJ/mol}$$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

Solution:

The process is $\text{NaCl}(s) \rightarrow \text{NaCl}(l)$. At 500 °C, the following is true: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} +$

$$\frac{q_{\text{surr}}}{T} = (95.06 - 72.11) \frac{\text{J}}{\text{molK}} + \frac{-27.95 \times 10^3 \frac{\text{J}}{\text{mol}}}{500 + 273.15} = -13.2 \frac{\text{J}}{\text{molK}}$$

At 700 °C, the following is true: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11) \frac{\text{J}}{\text{molK}} +$

$$\frac{-27.95 \times 10^3 \frac{\text{J}}{\text{mol}}}{700 + 273.15} = -5.8 \frac{\text{J}}{\text{molK}}$$

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.