Section 73 – The Third Law of Thermodynamics

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

Solution

ΔS: any change in entropy under any set of conditions. $\Delta S°$: 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^o for the following changes.

(a) $SnCl_4(l) \longrightarrow SnCl_4(g)$

(b) $CS_2(g) \longrightarrow CS_2(l)$

(c) $Cu(s) \longrightarrow Cu(g)$

(d) $H_2O(l) \longrightarrow H_2O(g)$

(e) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(f) $2HCl(g) + Pb(s) \longrightarrow PbCl_2(s) + H_2(g)$

(g) $Zn(s) + CuSO_4(s) \longrightarrow Cu(s) + ZnSO_4(s)$

Solutions

(a)

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

$$= 1\Delta S^\circ\, SnCl_4(g) - 1\Delta S^\circ\, SnCl_4(l)$$

$$= \left[1 \text{ mol}\left(366 \frac{J}{\text{mol K}}\right)\right] - \left[1 \text{ mol}\left(259 \frac{J}{\text{mol K}}\right)\right] = 107 \text{ J/K}$$

(b)

$$\Delta S^o_{298} = \sum \nu \Delta S^o_{298}(\text{products}) - \sum \nu \Delta S^o_{298}(\text{reactants})$$

$$= 1\Delta S^\circ_{298} Cs_2(l) - 1\Delta S^\circ_{298} Cs_2(g)$$

$$= \left[1 \text{ mol}\left(151.3 \frac{J}{\text{mol K}}\right)\right] - \left[1 \text{ mol}\left(238.0 \frac{J}{\text{mol K}}\right)\right] = -86.7 \text{ J/K}$$

(c)

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

(d)

$$\Delta S^o = \sum \nu \Delta S^o \text{ (products)} - \sum \nu \Delta S^o \text{ (reactants)}$$
$$= 1\Delta S^\circ H_2O(g) - 1\Delta S^\circ H_2O(l)$$
$$= \left[1 \text{ mol} \left(188.8 \frac{J}{\text{mol K}}\right)\right] - \left[1 \text{ mol} \left(70.0 \frac{J}{\text{mol K}}\right)\right] = 118.8 \text{ J/K}$$

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

$$= 2\Delta S^\circ H_2O(l) - \left[1\Delta S^\circ O_2(g) + 2\Delta S^\circ H_2(g)\right]$$
$$= \left[2 \text{ mol} \left(70.0 \frac{J}{\text{mol K}}\right)\right] - \left[1 \text{ mol} \left(205.2 \frac{J}{\text{mol K}}\right) + 2 \text{ mol} \left(130.7 \frac{J}{\text{mol K}}\right)\right] =$$
$$-326.6 \text{ J/K}$$

(f)

$$\Delta S^o = \sum \nu \Delta S^o \text{ (products)} - \sum \nu \Delta S^o \text{ (reactants)}$$
$$= \left[1\Delta S^\circ \text{PbCl}_2(s) + 1\Delta S^\circ H_2(g)\right] - \left[1\Delta S^\circ \text{Pb}(s) + 2\Delta S^\circ \text{HCl}(g)\right]$$
$$= \left[1 \text{ mol} \left(136.0 \frac{J}{\text{mol K}}\right) + 1 \text{ mol} \left(130.7 \frac{J}{\text{mol K}}\right)\right] -$$
$$\left[1 \text{ mol} \left(64.81 \frac{J}{\text{mol K}}\right) + 2 \text{ mol} \left(186.9 \frac{J}{\text{mol K}}\right)\right] = -171.9 \text{ J/K}$$

(g)

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

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:

$$C_2H_5\mathrm{OH}(l) + 3O_2(g) \longrightarrow 2\mathrm{CO}_2(g) + 3H_2O(l)$$

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

$$C_2H_5\mathrm{OH}(l) + 3O_2(g) \longrightarrow 2\mathrm{CO}_2(g) + 3H_2O(l)$$

Thus the ΔS^o can be calculated as follows:

$$\Delta S^o = \sum \nu \Delta S^o\,(\text{products}) - \sum \nu \Delta S^o\,(\text{reactants})$$
$$= \left[2\Delta S^\circ\,\mathrm{CO}_2(g) + 3\Delta S^\circ\,H_2O(l)\right] - \left[1\Delta S^\circ\,C_2H_5\mathrm{OH}(l) + 3\Delta S^\circ\,O_2(g)\right]$$
$$= \left[2\text{ mol}\left(213.6\ \frac{J}{\text{mol K}}\right) + 3\text{ mol}\left(69.91\ \frac{J}{\text{mol K}}\right)\right] -$$
$$\left[1\text{ mol}\left(161\ \frac{J}{\text{mol K}}\right) + 3\text{ mol}\left(205.03\ \frac{J}{\text{mol K}}\right)\right] = -139\text{ J/K}$$

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:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3\mathrm{CO}_2(g) + 4H_2O(g).$$

Solution: The reaction is

$C_3H_8(g) + 5O_2(g) \longrightarrow 3\mathrm{CO}_2(g) + 4H_2O(g).$
and so the ΔS^o can be calculated as follows:

$$\Delta S^o = \sum \nu \Delta S^o\,(\text{products}) - \sum \nu \Delta S^o\,(\text{reactants})$$
$$= \left[3\Delta S^\circ\,\mathrm{CO}_2(g) + 4\Delta S^\circ\,H_2O(g)\right] - \left[1\Delta S^\circ\,C_3H_8(g) + 5\Delta S^\circ\,O_2(g)\right]$$
$$= \left[3\text{ mol}\left(213.8\ \frac{J}{\text{mol K}}\right) + 4\text{ mol}\left(188.8\ \frac{J}{\text{mol K}}\right)\right] -$$
$$\left[1\text{ mol}\left(270.3\ \frac{J}{\text{mol K}}\right) + 5\text{ mol}\left(205.02\ \frac{J}{\text{mol K}}\right)\right] = 100.3\text{ J/K}$$

73-5. "Thermite" reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $Fe_2O_3(s) + 2\mathrm{Al}(s) \longrightarrow Al_2O_3(s) + 2\mathrm{Fe}(s)$. 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

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

$$\Delta S^{\circ}_{\text{sys}} = \left(\Delta S^{\circ}\,\text{Fe} + \Delta S^{\circ}\,Al_2O_3\right) - \left(1\Delta S^{\circ}\,Fe_2O_3 + 2\Delta S^{\circ}\,\text{Al}\right)$$

$$\Delta S^{\circ}_{\text{sys}} = \left[2\text{ mol}\left(27.3\frac{J}{\text{mol K}}\right) + 1\text{ mol}\left(50.92\frac{J}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(87.40\frac{J}{\text{mol K}}\right) + 2\text{ mol}\left(28.3\frac{J}{\text{mol K}}\right)\right] = -38.48\text{ J/K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} = -38.48\frac{J}{\text{mol}\cdot K} - \frac{-851.8\frac{\text{kJ}}{\text{mol}}\left(\frac{1000\text{ J}}{1\text{ kJ}}\right)}{298.15} = 2820\text{ J/K}$$

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:

(a) $N_2(g) + 3H_2(g) \longrightarrow 2\text{NH}_3(g)$

(b) $N_2(g) + \frac{5}{2}O_2(g) \longrightarrow \text{N}_2O_5(g)$

Solution:

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

$$\Delta S^{\circ}_{\text{sys}} = \left(2\Delta S^{\circ}\,\text{NH}_3\right) - \left(1\Delta S^{\circ}\,N_2 + 3\Delta S^{\circ}\,H_2\right)$$

$$\Delta S^{\circ}_{\text{sys}} = \left[2\text{ mol}\left(192.8\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(191.6\frac{\text{J}}{\text{mol K}}\right) + 3\text{ mol}\left(130.7\frac{\text{J}}{\text{mol K}}\right)\right] = -198.1\text{ J/K}$$

;

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

$$\Delta S^{\circ}_{\text{sys}} = \left(2\Delta S^{\circ}\,N_2O_5\right) - \left(1\Delta S^{\circ}\,N_2 + \frac{5}{2}\times \Delta S^{\circ}\,O_2\right)$$

$$\Delta S^{\circ}_{\text{sys}} = \left[1\text{ mol}\left(355.7\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(191.6\frac{\text{J}}{\text{mol K}}\right) + \frac{5}{2}\text{ mol}\left(205.2\frac{\text{J}}{\text{mol K}}\right)\right] = -348.9\text{ J/K}$$

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) $\mathrm{MnO_2}(s) \longrightarrow \mathrm{Mn}(s) + \mathrm{O_2}(g)$

(b) $H_2(g) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{HBr}(g)$

(c) $\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{CuS}(s)$

(d) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2}O(g)$

(e) $\mathrm{CH_4}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{C}(s, \text{graphite}) + 2H_2O(g)$

(f) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

Solution:

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

$\Delta S^\circ = \left[1 \text{ mol}\left(3.20 \frac{J}{\text{mol}\cdot K}\right) + 1 \text{ mol}\left(205.2 \frac{J}{\text{mol}\cdot K}\right)\right] -$

$\left[1 \text{ mol}\left(53.05 \frac{J}{\text{mol}\cdot K}\right)\right] = 184.2 \text{ J/K}$

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

$\Delta S^\circ = \left[2 \text{ mol}\left(198.7 \frac{J}{\text{mol}\cdot K}\right)\right] -$

$\left[1 \text{ mol}\left(152.23 \frac{J}{\text{mol}\cdot K}\right) + 1 \text{ mol}\left(130.7 \frac{J}{\text{mol}\cdot K}\right)\right] = 114.5 \text{ J/K}$

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

$\Delta S^\circ = \left[1 \text{ mol}\left(66.5 \frac{J}{\text{mol}\cdot K}\right)\right] - \left[1 \text{ mol}\left(33.15 \frac{J}{\text{mol}\cdot K}\right) + 1 \text{ mol}\left(167.82 \frac{J}{\text{mol}\cdot K}\right)\right] =$

-134.5 J/K

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

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

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

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

(f) $\Delta S^\circ = \sum v\Delta S°(\text{products}) - \sum v\Delta S°(\text{reactants})$

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

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.

(a) $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$

(b) $O_2(g) + N_2(g) \longrightarrow 2NO(g)$

(c) $2Cu(s) + S(g) \longrightarrow Cu_2S(s)$

(d) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$

(e) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

(f) $CaSO_4 2H_2O(s) \longrightarrow CaSO_4(s) + 2H_2O(g)$

Solution:

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

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

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

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

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

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

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

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

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

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

(f) $\Delta S^\circ = \sum v\Delta S°(\text{products}) - \sum v\Delta S°(\text{reactants})$

$$\Delta S^\circ = \left[1\text{ mol}\left(106.5\ \frac{J}{\text{mol}\cdot K}\right) + 2\text{ mol}\left(188.8\ \frac{J}{\text{mol}\cdot K}\right)\right] - \left[1\text{ mol}\left(194.14\ \frac{J}{\text{mol}\cdot K}\right)\right]$$
$$= 290.0\text{ J/K}$$

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

$S^\circ_{\text{NaCl}(s)} = 72.11\frac{J}{\text{mol}K}$ $S^\circ_{\text{NaCl}(l)} = 95.06\frac{J}{\text{mol}K}$ $\Delta H^\circ_{\text{fusion}} = 27.95\text{ kJ/mol}$

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

Solution:

The process is NaCl *(s)* → NaCl *(l)*. At 500 °C, the following is true: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{J}{\text{mol}K} + \frac{-2\ .95\times10^3\frac{J}{\text{mol}}}{500+273.15} = -13.2\frac{J}{\text{mol}K}$

At 700 °C, the following is true: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{J}{\text{mol}\cdot K} + \frac{-27.95\times10^3\frac{J}{\text{mol}}}{700+273.15} = -5.8\frac{J}{\text{mol}\cdot K}$

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.