

Chapter 17: 2, 6, 12, 16, 34, 40, 42

17.2 Which processes are nonspontaneous? Are the nonspontaneous processes impossible?

- A bike going up a hill
Nonspontaneous – you have to pedal. But it is possible.
- A meteor falling to earth
Spontaneous
- Obtaining hydrogen gas from liquid water
Nonspontaneous – you need to supply energy – but it is possible.
- A ball rolling down a hill
Spontaneous.

17.6 Without doing any calculations, predict the sign of ΔS_{sys} for each chemical reaction:

- $\text{Mg(s)} + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{s})$
Two moles of stuff on left, one on right. Gas on left, solid on right. The products have LESS entropy than the reactants. So Products (less) – Reactants (more) = negative ΔS_{sys}
- $2 \text{H}_2\text{S}(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + 2 \text{SO}_2(\text{g})$
5 moles of gas on left, 4 on right. Negative ΔS_{sys}
- $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$
3 moles of gas on right, 2 on left. Positive ΔS_{sys}
- $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
Gases on left, solid on right. Negative ΔS_{sys}

17.12 Given the values of ΔH_{rxn}^0 , ΔS_{rxn}^0 , and T, determine ΔS_{univ} and predict whether or not the reaction will be spontaneous.

- $\Delta H_{\text{rxn}}^0 = 85 \text{ kJ}$; $\Delta S_{\text{rxn}}^0 = 147 \text{ J/K}$; $T = 298 \text{ K}$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-85 \times 10^3 \text{ J}}{298 \text{ K}} = -285 \text{ J/K}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 147 \frac{\text{J}}{\text{K}} + \left(-285 \frac{\text{J}}{\text{K}}\right) = -138 \frac{\text{J}}{\text{K}}$$

Since $\Delta S_{\text{universe}}$ is negative, the reaction can't be spontaneous.

- $\Delta H_{\text{rxn}}^0 = 85 \text{ kJ}$; $\Delta S_{\text{rxn}}^0 = 147 \text{ J/K}$; $T = 755 \text{ K}$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-85 \times 10^3 \text{ J}}{755 \text{ K}} = -113 \text{ J/K}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 147 \frac{\text{J}}{\text{K}} + \left(-113 \frac{\text{J}}{\text{K}}\right) = +34 \frac{\text{J}}{\text{K}}$$

Since $\Delta S_{\text{universe}}$ is positive, the reaction is spontaneous.

$$\text{c. } \Delta H_{\text{rxn}}^0 = 85 \text{ kJ}; \Delta S_{\text{rxn}}^0 = -147 \text{ J/K}; T = 298 \text{ K}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-85 \times 10^3 \text{ J}}{298 \text{ K}} = -285 \text{ J/K}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -147 \frac{\text{J}}{\text{K}} + \left(-285 \frac{\text{J}}{\text{K}}\right) = -432 \frac{\text{J}}{\text{K}}$$

Since $\Delta S_{\text{universe}}$ is negative, the reaction can't be spontaneous.

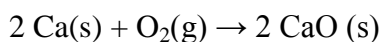
$$\text{d. } \Delta H_{\text{rxn}}^0 = -85 \text{ kJ}; \Delta S_{\text{rxn}}^0 = 147 \text{ J/K}; T = 398 \text{ K}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-(-85 \times 10^3 \text{ J})}{398 \text{ K}} = +214 \text{ J/K}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 147 \frac{\text{J}}{\text{K}} + \left(+214 \frac{\text{J}}{\text{K}}\right) = 361 \frac{\text{J}}{\text{K}}$$

Since $\Delta S_{\text{universe}}$ is positive, the reaction is spontaneous.

17.16 Calculate the free energy change for the reaction at 25 °C. Is the reaction spontaneous?



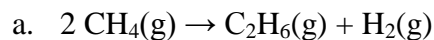
$$\Delta H_{\text{rxn}}^0 = -1269.8 \text{ kJ}; \Delta S_{\text{rxn}}^0 = -364.6 \text{ J/K}$$

SOLUTION:

$$\Delta G = \Delta H - T\Delta S = -1269.8 \times 10^3 \text{ J} - (298 \text{ K}) \left(-364.6 \frac{\text{J}}{\text{K}}\right) = -1.16 \times 10^6 \text{ J}$$

Negative ΔG means spontaneous reaction.

17.34 Use standard free energies of formation to calculate ΔG^0 at 25 °C for each of the reactions in Problem 32. How well do the values of ΔG^0 calculated this way compare to those calculated from ΔH^0 and ΔS^0 ? Which of the two methods could be used to determine how ΔG^0 changes with temperature?



$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants})$$

$$\Delta G^0 = [\Delta G_f^0(\text{H}_2(\text{g})) + \Delta G_f^0(\text{C}_2\text{H}_6(\text{g}))] - [2 \times \Delta G_f^0(\text{CH}_4(\text{g}))]$$

$$\Delta G^0 = \left[0 + \left(-32.0 \frac{\text{kJ}}{\text{mol}}\right)\right] - \left[2 \times \left(-50.5 \frac{\text{kJ}}{\text{mol}}\right)\right] = 69 \text{ kJ}$$

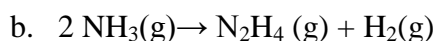
$$\Delta H^0 = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants})$$

$$\Delta H^0 = [\Delta H_f^0(\text{H}_2(\text{g})) + \Delta H_f^0(\text{C}_2\text{H}_6(\text{g}))] - [2 \times \Delta H_f^0(\text{CH}_4(\text{g}))]$$

$$\Delta H^0 = \left[0 + \left(-84.68 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2 \times \left(-74.6 \frac{\text{kJ}}{\text{mol}} \right) \right] = 64.5 \text{ kJ}$$

$$\begin{aligned} \Delta S^0 &= \sum S_f^0(\text{products}) - \sum S_f^0(\text{reactants}) \\ \Delta S^0 &= [S_f^0(\text{H}_2(\text{g})) + S_f^0(\text{C}_2\text{H}_6(\text{g}))] - [2 \times S_f^0(\text{CH}_4(\text{g}))] \\ \Delta S^0 &= \left[130.7 \frac{\text{J}}{\text{K}} + 229.2 \frac{\text{J}}{\text{K}} \right] - \left[2 \times \frac{186.3 \text{J}}{\text{K}} \right] = -12.7 \text{ J/K} \end{aligned}$$

$$\Delta G = \Delta H - T\Delta S = 64.5 \times 10^3 \text{ J} - (298 \text{ K}) \left(-\frac{12.7 \text{ J}}{\text{K}} \right) = 6.83 \times 10^4 \text{ J} = 68.3 \text{ kJ}$$



$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants})$$

$$\Delta G^0 = [\Delta G_f^0(\text{H}_2(\text{g})) + \Delta G_f^0(\text{N}_2\text{H}_4(\text{g}))] - [2 \times \Delta G_f^0(\text{NH}_3(\text{g}))]$$

$$\Delta G^0 = \left[0 + \left(159.4 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2 \times \left(-16.4 \frac{\text{kJ}}{\text{mol}} \right) \right] = 192.2 \text{ kJ}$$

$$\Delta H^0 = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants})$$

$$\Delta H^0 = [\Delta H_f^0(\text{H}_2(\text{g})) + \Delta H_f^0(\text{N}_2\text{H}_4(\text{g}))] - [2 \times \Delta H_f^0(\text{NH}_3(\text{g}))]$$

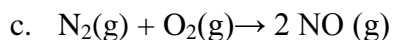
$$\Delta H^0 = \left[0 + \left(95.4 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2 \times \left(-45.9 \frac{\text{kJ}}{\text{mol}} \right) \right] = 187.2 \text{ kJ}$$

$$\Delta S^0 = \sum S_f^0(\text{products}) - \sum S_f^0(\text{reactants})$$

$$\Delta S^0 = [S_f^0(\text{H}_2(\text{g})) + S_f^0(\text{N}_2\text{H}_4(\text{g}))] - [2 \times S_f^0(\text{NH}_3(\text{g}))]$$

$$\Delta S^0 = \left[130.7 \frac{\text{J}}{\text{K}} + 238.5 \frac{\text{J}}{\text{K}} \right] - \left[2 \times 192.8 \frac{\text{J}}{\text{K}} \right] = -16.4 \text{ J/K}$$

$$\begin{aligned} \Delta G = \Delta H - T\Delta S &= 187.2 \times 10^3 \text{ J} - (298 \text{ K}) \left(-16.4 \frac{\text{J}}{\text{K}} \right) = 1.921 \times 10^5 \text{ J} \\ &= 192.1 \text{ kJ} \end{aligned}$$



$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants})$$

$$\Delta G^0 = [2 \times \Delta G_f^0(\text{NO}(\text{g}))] - [\Delta G_f^0(\text{O}_2(\text{g})) + \Delta G_f^0(\text{N}_2(\text{g}))]$$

$$\Delta G^0 = \left[2 \times \left(87.6 \frac{\text{kJ}}{\text{mol}} \right) \right] - [0 + 0] = 175.2 \text{ kJ}$$

$$\Delta H^0 = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants})$$

$$\Delta H^0 = [2 \times \Delta H_f^0(\text{NO}(g))] - [\Delta H_f^0(\text{O}_2(g)) + \Delta H_f^0(\text{N}_2(g))]$$

$$\Delta H^0 = \left[2 \times \left(91.3 \frac{\text{kJ}}{\text{mol}} \right) \right] - [0 + 0] = 182.6 \text{ kJ}$$

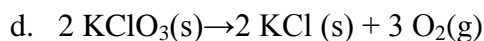
$$\Delta S^0 = \sum S_f^0(\text{products}) - \sum S_f^0(\text{reactants})$$

$$\Delta S^0 = [2 \times \Delta S_f^0(\text{NO}(g))] - [S_f^0(\text{O}_2(g)) + S_f^0(\text{N}_2(g))]$$

$$\Delta S^0 = \left[2 \times 210.8 \frac{\text{J}}{\text{K}} \right] - \left[205.2 \frac{\text{J}}{\text{K}} + 191.6 \frac{\text{J}}{\text{K}} \right] = 24.8 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S = 182.6 \times 10^3 \text{ J} - (298 \text{ K}) \left(-\frac{24.8 \text{ J}}{\text{K}} \right) = 1.752 \times 10^5 \text{ J}$$

$$= 175.2 \text{ kJ}$$



$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants})$$

$$\Delta G^0 = [3 \times \Delta G_f^0(\text{O}_2(g)) + 2 \times \Delta G_f^0(\text{KCl}(s))] - [2 \times \Delta G_f^0(\text{KClO}_3(s))]$$

$$\Delta G^0 = \left[0 + 2 \times \left(-408.5 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2 \times \left(-296.3 \frac{\text{kJ}}{\text{mol}} \right) \right] = -224.4 \text{ kJ}$$

$$\Delta H^0 = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants})$$

$$\Delta H^0 = [3 \times \Delta H_f^0(\text{O}_2(g)) + 2 \times \Delta H_f^0(\text{KCl}(s))] - [2 \times \Delta H_f^0(\text{KClO}_3(s))]$$

$$\Delta H^0 = \left[0 + 2 \times \left(-436.5 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2 \times \left(-397.7 \frac{\text{kJ}}{\text{mol}} \right) \right] = -77.6 \text{ kJ}$$

$$\Delta S^0 = \sum S_f^0(\text{products}) - \sum S_f^0(\text{reactants})$$

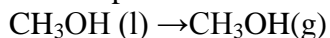
$$\Delta S^0 = [3 \times S_f^0(\text{O}_2(g)) + 2 \times S_f^0(\text{KCl}(s))] - [2 \times S_f^0(\text{KClO}_3(s))]$$

$$\Delta S^0 = \left[3 \times 205.2 \frac{\text{J}}{\text{K}} + 2 \times 82.6 \frac{\text{J}}{\text{K}} \right] - \left[2 \times \frac{143.1 \text{ J}}{\text{K}} \right] = 494.6 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S = -77.6 \times 10^3 \text{ J} - (298 \text{ K}) \left(\frac{494.6 \text{ J}}{\text{K}} \right) = -2.25 \times 10^5 \text{ J}$$

$$= -225 \text{ kJ}$$

17.40 Consider the evaporation of methanol at 25.0 C:



- Find ΔG^0 at 25.0 C
- Find ΔG^0 at 25.0 C under these nonstandard conditions:
 - $P_{\text{CH}_3\text{OH}} = 150.0 \text{ mmHg}$
 - $P_{\text{CH}_3\text{OH}} = 100.0 \text{ mmHg}$

- c. $P_{\text{CH}_3\text{OH}} = 10.0 \text{ mmHg}$
 c. Explain why methanol spontaneously evaporates in open air at 25.0 C.

SOLUTION:

$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants})$$

$$\begin{aligned} \Delta G^0 &= [\Delta G_f^0(\text{CH}_3\text{OH}(g))] - [\Delta G_f^0(\text{CH}_3\text{OH}(l))] \\ &= -162.3 \frac{\text{kJ}}{\text{mol}} - \left(-166.6 \frac{\text{kJ}}{\text{mol}}\right) = 4.3 \text{ kJ/mol} \end{aligned}$$

$$\Delta G = \Delta G^0 + RT \ln Q = \Delta G^0 + RT \ln P_{\text{CH}_3\text{OH}}$$

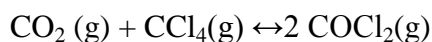
$$\begin{aligned} \Delta G &= \Delta G^0 + RT \ln P_{\text{CH}_3\text{OH}} \\ &= 4.3 \times 10^3 \frac{\text{J}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}}\right) (298 \text{ K}) \ln \left(\frac{150}{760} \text{ atm}\right) \\ &= 2.8 \times 10^2 \text{ J/mol} \end{aligned}$$

$$\begin{aligned} \Delta G &= \Delta G^0 + RT \ln P_{\text{CH}_3\text{OH}} = \\ 4.3 \times 10^3 \frac{\text{J}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}}\right) (298 \text{ K}) \ln \left(\frac{100}{760} \text{ atm}\right) &= -72.5 \text{ J/mol} \end{aligned}$$

$$\begin{aligned} \Delta G &= \Delta G^0 + RT \ln P_{\text{CH}_3\text{OH}} \\ &= 4.3 \times 10^3 \frac{\text{J}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}}\right) (298 \text{ K}) \ln \left(\frac{10}{760} \text{ atm}\right) \\ &= -6429 \text{ J/mol} \end{aligned}$$

At low pressures of methanol, the phase transition is spontaneous. So as long as the beaker is open to the air so that the pressure of methanol can't increase, the methanol evaporates.

17.42 Consider the reaction:



Calculate ΔG for this reaction at 25°C under these conditions:

$$P_{\text{CO}_2} = 0.112 \text{ atm}$$

$$P_{\text{CCl}_4} = 0.174 \text{ atm}$$

$$P_{\text{COCl}_2} = 0.744 \text{ atm}$$

$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants})$$

$$\begin{aligned} \Delta G^0 &= [2 \times \Delta G_f^0(\text{COCl}_2(\text{g}))] - [\Delta G_f^0(\text{CO}_2(\text{g})) + \Delta G_f^0(\text{CCl}_4(\text{g}))] \\ &= \left[2 \times \left(-204.9 \frac{\text{kJ}}{\text{mol}}\right)\right] - \left[-394.4 \frac{\text{kJ}}{\text{mol}} + \left(-62.3 \frac{\text{kJ}}{\text{mol}}\right)\right] \\ &= 46.9 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned}\Delta G &= \Delta G^0 + RT \ln Q = \Delta G^0 + RT \ln \frac{P_{COCl_2}^2}{P_{CO_2} P_{CCl_4}} \\ \Delta G &= 46.9 \times \frac{10^3 J}{mol} + \left(8.314 \frac{J}{mol K} \right) (298 K) \ln \frac{0.744^2}{(0.112)(0.174)} \\ &= 46.9 \times 10^3 \frac{J}{mol} + 8.29 \times \frac{10^3 J}{mol} = 5.52 \times 10^4 J/mol\end{aligned}$$