Unit 70 – Spontaneity

70-1. What is a spontaneous reaction?

Solution

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

70-2. What is a nonspontaneous reaction?

Solution

A reaction that has no natural tendency to occur and takes place only with the continual input of energy from an external source.

70-3. Indicate whether the following processes are spontaneous or nonspontaneous.

(a) Liquid water freezing at a temperature below its freezing point
(b) Liquid water freezing at a temperature above its freezing point
(c) The combustion of gasoline
(d) A ball thrown into the air
(e) A raindrop falling to the ground
(f) Iron rusting in a moist atmosphere

Solution

(a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

70-4. A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

Solution

The process involves a greater dispersal of matter as the He atoms transfer from a relatively small initial volume (the balloon) to a much larger final volume (the room, or house, or ultimately earth's atmosphere).

70-5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

Solution

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

Unit 71 – Entropy

71-1. Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $H_2(g)$, $HBrO_4(g)$, $HBr(g)$
(b) $H_2O(l)$, $H_2O(g)$, $H_2O(s)$
(c) $He(g)$, $Cl_2(g)$, $P_4(g)$

Solution

(a) $H_2(g) < HBr(g) < HBrO_4(g)$, due to increasing complexity and mass of molecules;
(b) $H_2O(s) < H_2O(l) < H_2O(g)$ due to increasing dispersal of matter;
(c) $He(g) < Cl_2(g) < P_4(g)$ due to increasing complexity and mass of species

71-2. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

Solution

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

71-3. Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$I_2(s) \rightarrow I_2(g)$
$I_2(s) \rightarrow I_2(l)$

Is ΔS positive or negative in the processes? In which of the processes will the magnitude of the entropy change be greater?

Solution

The change of entropy will be positive in the both cases, as a relatively ordered solid is converted into less ordered liquid or gas. The sublimation will lead to a greater change in S since the final state (gas) is more disordered and dispersed than liquid.

71-4. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $C_2H_5OH(l)$ or $C_3H_7OH(l)$
(b) $C_2H_5OH(l)$ or $C_2H_5OH(g)$
(c) $2H(g)$ or $H(g)$

Solution

(a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature.
(b) $C_2H_5OH(g)$ as it is in the gaseous state.

(c) $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

71-5. Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.
(b) Exhaled breath forms fog on a cold morning.
(c) Snow melts.

Solution

(a) $\Delta S > 0$; entropy increases since water molecules in the solid possess greater freedom of motion at the higher temperature.

(b) $\Delta S < 0$; the fog is comprised of tiny water droplets formed by condensation of water vapor in the exhaled breath, and entropy decreases as the water first cools from body temperature to colder ambient temperature and then transitions from the gaseous to the liquid state.

(c) $\Delta S > 0$; entropy increases as the water molecules in the solid snowflakes gain greater freedom of motion upon melting to yield liquid water.

71-6. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $\text{Na}^+(aq) + \text{Cl}^-(aq) \longrightarrow \text{NaCl}(s)$

(b) $2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_2(s)$

(c) $2C_6H_{14}(l) + 19O_2(g) \longrightarrow 14H_2O(g) + 12\text{CO}_2(g)$

Solution

(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution.

(b) Negative. There is a net loss of three moles of gas from reactants to products.

(c) Positive. There is a net increase of seven moles of gas from reactants to products.

71-7. The balanced chemical equation for the combustion of methane, $CH_4(g)$ is as follows:

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

Solution: With three moles of gaseous reactants and three moles of gaseous products, it is not clear if the products or reactants have the greater entropy.

71-8. The balanced chemical equation for the combustion of benzene, $C_6H_6(l)$ is as follows:

$$C_6H_6(l) + 7.5\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(g).$$

Would you expect ΔS to be positive or negative in this process?

Solution: There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

Unit 72 – The Second Law of Thermodynamics

72-1. HI has a normal boiling point of –35.4°C, and its ΔH_{vap} is 21.16 kJ mol^{-1}. Calculate the molar entropy of vaporization (ΔS_{vap}).

Solution:

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\Delta S_{\text{vap}} = \frac{(21.16\ \text{kJ mol}^{-1})}{(-35.4 + 273.15)\text{K}}$$

$$\Delta S_{\text{vap}} = \frac{(21.16\ \text{kJ mol}^{-1})}{237.8\ \text{K}}$$

$$\Delta S_{vap} = 0.08898\ \text{kJ mol}^{-1}\ \text{K}^{-1}$$

Normally molar entropies of vaporization are in units of J mol^{-1} K^{-1}, but the answer can be readily converted to these units if needed:

$$\Delta S_{\text{vap}} = 0.08898\ \text{kJ mol}^{-1}\text{K}^{-1} \times \frac{(1000\ \text{J}\ )}{1\ \text{kJ}}$$

$$\Delta S_{vap} = 88.98\ \text{J mol}^{-1}\ \text{K}^{-1}$$

72-2. What is the total entropy change (i.e., system plus surroundings) when 17.9 g of water (ΔH_{fus} =6.01 kJ mol^{-1}) freezes at 0.0°C in a freezer compartment whose temperature is held at -29.0 °C? Is this process spontaneous?

Solution:

Approach: we know that $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$. Thus we need to calculate both the entropy change of the water as it freezes at 0.00 °C (the ΔS_{sys}) and the entropy change of the freezer compartment (held at -29.0 °C) as it absorbs the heat lost by the water (the ΔS_{surr}), and then add them together. From experience, we know that water will freeze in a freezer, so we know that the process is spontaneous (and so our answer for ΔS_{total} ought to be positive).

Note that we are provided with the value for ΔH_{fus}, which is the heat change that occurs when water changes from solid to liquid. However, since in this problem we are asked about the water is changing from liquid to solid we need ΔH_{sol}, which is equal in magnitude but opposite in sign ($\Delta H_{sol} = -\Delta H_{fus}$).

The heat change of the system can be calculated as follows:

$$\Delta H_{sys} = -6.01\ \text{kJ mol}^{-1} \times \left(17.9\ \text{g} \times \frac{1\ \text{mol H}_2\text{O}}{18.015\ \text{g H}_2\text{O}}\right) \times \frac{1000\ \text{J}}{1\ \text{kJ}}$$

$$\Delta H_{sys} = -6.01\ \text{kJ mol}^{-1} \times (0.9936\ \text{mol H}_2\text{O}) \times \frac{1000\ \text{J}}{1\ \text{kJ}}$$

$$\Delta H_{sys} = -5.97 \text{ x } 10^3\ \text{J}$$

Thus,

$$\Delta S_{sys} = \frac{\Delta H_{sys}}{T} = \frac{-5.97 \times 10^3\ \text{J}}{(273.15\ \text{K})} = -21.9\ \text{J K}^{-1}$$

The sign of ΔS_{sys} is negative, as we would expect since the water is undergoing a phase change from liquid to solid.

The heat change of the surroundings would be equal in magnitude but opposite in sign to the heat change of the system, and so we can calculate ΔS_{surr} as follows:

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-(-5.97 \times 10^3\ \text{J})}{(273.15 - 29.0)\ \text{K}} = \frac{5.97 \times 10^3\ \text{J}}{(244.2)\ \text{K}} = 24.4\ \text{J K}^{-1}$$

Now we can calculate the total entropy change:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{total} = -21.9\ \text{J K}^{-1} + 24.4\ \text{J K}^{-1} = 2.5\ \text{J K}^{-1}.$$

The total entropy change is positive, which indicates that this is a spontaneous process. This answer "makes sense" since, from experience, we know that water will freeze in a freezer, so we know that the process is spontaneous.

72-3. What is the total entropy change (i.e. system plus surroundings) when 68.2 g of ice (ΔH_{fus} = 6.01 kJ mol^{-1}) melts at 0.0 ºC on a counter in the kitchen whose temperature is 20.0 ºC? Is this process spontaneous?

Solution:

The approach is the same as the previous question.

The heat change of the system can be calculated as follows:

$$\Delta H_{sys} = 6.01\ \text{kJ mol}^{-1} \times \left(68.2\ \text{g} \times \frac{1\ \text{mol H}_2\text{O}}{18.015\ \text{g H}_2\text{O}}\right) \times \frac{1000\ \text{J}}{1\ \text{kJ}}$$

$$\Delta\mathrm{H_{sys}} = 6.01\ \mathrm{kJ\ mol^{-1}} \times (3.79\ \mathrm{mol\ H_2O}) \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}}$$

$$\Delta\mathrm{H_{sys}} = 2.28 \times 10^4\ \mathrm{J}$$

Thus,

$$\Delta\mathrm{S_{sys}} = \frac{\Delta H_{sys}}{T} = \frac{2.28 \times 10^4\ \mathrm{J}}{(273.15\ \mathrm{K})} = 83.5\ \mathrm{J\ K^{-1}}$$

The heat change of the surroundings would be equal in magnitude but opposite in sign to the heat change of the system, and so we can calculate ΔS_{surr} as follows:

$$\Delta\mathrm{S_{surr}} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-(2.28 \times 10^4\ \mathrm{J})}{(273.15 + 20.0)\ \mathrm{K}} = \frac{-2.28 \times 10^4\ \mathrm{J}}{(293.2)\ \mathrm{K}} = -77.8\ \mathrm{J\ K^{-1}}$$

Now we can calculate the total entropy change:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{total} = 83.5\ \mathrm{J\ K^{-1}} - 77.8\ \mathrm{J\ K^{-1}} = 5.7\ \mathrm{J\ K^{-1}}.$$

The total entropy change is positive, which indicates that this is a spontaneous process. This answer "makes sense" since, from experience, we know that ice will melt on a counter top in a kitchen (at room temperature), so we know that the process is spontaneous.

72-4. What is the total entropy change when 1.76 mol of water ($\Delta H_{fus} = 6.01\ \mathrm{kJ\ mol^{-1}}$) melts at 0.0 °C outside in Winnipeg when it is -35.0 °C outside? Is this process spontaneous?

Solution:

The approach is the same as the previous questions.

The heat change of the system can be calculated as follows:

$$\Delta\mathrm{H_{sys}} = 6.01\ \mathrm{kJ\ mol^{-1}} \times (1.76\ \mathrm{mol}) \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}}$$

$$\Delta\mathrm{H_{sys}} = 1.06 \times 10^4\ \mathrm{J}$$

Thus,

$$\Delta\mathrm{S_{sys}} = \frac{\Delta H_{sys}}{T} = \frac{1.06 \times 10^4\ \mathrm{J}}{(273.15\ \mathrm{K})} = 38.8\ \mathrm{J\ K^{-1}}$$

The heat change of the surroundings would be equal in magnitude but opposite in sign to the heat change of the system, and so we can calculate ΔS_{surr} as follows:

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-(1.06 \times 10^4 \text{ J})}{(273.15 - 35.0)\text{ K}} = \frac{-1.06 \times 10^4 \text{ J}}{238.2 \text{ K}} = -44.5 \text{ J K}^{-1}$$

Now we can calculate the total entropy change:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{total} = 38.8 \text{ J K}^{-1} - 44.5 \text{ J K}^{-1} = -5.7 \text{ J K}^{-1}.$$

The total entropy change is negative, which indicates that this is a NOT spontaneous process. This answer "makes sense" since, from experience, we know that ice will NOT melt outside when it is that cold out, and so the process is not spontaneous.

Unit 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 $\Delta S°$ 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)

$$\begin{aligned}\mathit{\Delta S^o} &= \sum \nu \mathit{\Delta S^o}\,(\text{products}) - \sum \nu \mathit{\Delta S^o}\,(\text{reactants})\\ &= 1\Delta S^\circ\ \mathrm{SnCl_4}(g)\ -\ 1\Delta S^\circ\ \mathrm{SnCl_4}(l)\\ &= \left[1\ \text{mol}\left(366\ \frac{J}{\text{mol K}}\right)\right] - \left[1\ \text{mol}\left(259\ \frac{J}{\text{mol K}}\right)\right] = 107\ \text{J/K}\end{aligned}$$

(b)

$$\begin{aligned}\mathit{\Delta S^o_{298}} &= \sum \nu \mathit{\Delta S^o_{298}}(\text{products}) - \sum \nu \mathit{\Delta S^o_{298}}(\text{reactants})\\ &= 1\Delta S^\circ_{298}\mathrm{Cs_2}(l)\ -\ 1\Delta S^\circ_{298}\mathrm{Cs_2}(g)\\ &= \left[1\ \text{mol}\left(151.3\ \frac{J}{\text{mol K}}\right)\right] - \left[1\ \text{mol}\left(238.0\ \frac{J}{\text{mol K}}\right)\right] = -\,86.7\ \text{J/K}\end{aligned}$$

(c)

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

(d)

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

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

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

(f)

$$\begin{aligned}\mathit{\Delta S^o} &= \sum \nu \mathit{\Delta S^o}\,(\text{products}) - \sum \nu \mathit{\Delta S^o}\,(\text{reactants})\\ &= \left[1\mathit{\Delta S^\circ}\ \mathrm{PbCl_2}(s) + 1\Delta S^\circ\ H_2(g)\right]\ -\ \left[1\mathit{\Delta S^\circ}\ \mathrm{Pb}(s)\ +\ 2\Delta S^\circ\ \mathrm{HCl}(g)\right]\end{aligned}$$

$$= \left[1\text{ mol}\left(136.0\ \frac{J}{\text{mol K}}\right) + 1\text{ mol}\left(130.7\ \frac{J}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(64.81\ \frac{J}{\text{mol K}}\right) + 2\text{ mol}\left(186.9\ \frac{J}{\text{mol K}}\right)\right] = -\,171.9\text{ J/K}$$

(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:

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

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

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

Thus the ΔS^o can be calculated as follows:

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

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:

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

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:

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

73-5. "Thermite" reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $\mathrm{Fe}_2O_3(s) + 2\mathrm{Al}(s) \longrightarrow \mathrm{Al}_2O_3(s) + 2\mathrm{Fe}(s)$. 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:

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

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

$$\Delta S^\circ_{\text{sys}} = \left(\Delta S^\circ\,\mathrm{Fe} + \Delta S^\circ\,\mathrm{Al}_2O_3\right) - \left(1\Delta S^\circ\,\mathrm{Fe}_2O_3 + 2\Delta S^\circ\,\mathrm{Al}\right)$$

$$\Delta S^\circ_{\text{sys}} = \left[2\text{ mol}\left(27.3\frac{J}{\text{mol K}}\right) + 1\text{ mol}\left(50.92\frac{J}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(87.40\frac{J}{\text{mol K}}\right) + 2\text{ mol}\left(28.3\frac{J}{\text{mol K}}\right)\right] = -38.48\text{ J/K}$$

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

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

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

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

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

Solution:

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

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

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

;

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

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

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

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) $\text{MnO}_2(s) \longrightarrow \text{Mn}(s) + \text{O}_2(g)$

(b) $H_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$

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

(d) $2\text{LiOH}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2O(g)$

(e) $\text{CH}_4(g) + \text{O}_2(g) \longrightarrow \text{C}(s, \text{graphite}) + 2H_2O(g)$

(f) $\text{CS}_2(g) + 3\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$

Solution:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

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

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: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{J}{\text{mol}K} + \frac{-27.95 \times 10^3 \frac{J}{\text{mol}}}{500 + 273.15} = -13.2\frac{J}{\text{mol}K}$

At 700 °C, the following is true: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{J}{\text{mol}\cdot K} + \frac{-27.95 \times 10^3 \frac{J}{\text{mol}}}{700 + 273.15} = -5.8\frac{J}{\text{mol}\cdot K}$

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.

Unit 74 – Free Energy

74-1. What is the difference between ΔG and $\Delta G°$ for a chemical change?

Solution

ΔG: the (Gibbs) free energy change for any reaction under any set of conditions. $\Delta G°$: the (Gibbs) free energy change for a reaction in which the reagents and products are in their standard states (1 bar or 1 atm for gases, 1 M for solutions) at a specified temperature.

74-2. A reaction has $\Delta H° = 100$ kJ/mol and $\Delta S° = 100$ J/molK. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Solution

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta G^{\circ} = 100 - 298.15 \times 1000 \frac{J}{\text{mol} \cdot K}\left(\frac{1\text{ kJ}}{1000\text{ J}}\right) = 70.2\text{ kJ/mol}$$

The $\Delta G^{\circ} > 0$, so the reaction is nonspontaneous at room temperature.

$\Delta G = \Delta H - T\Delta S$

$$0 = 100 - T\left[100 \frac{J}{\text{mol} \cdot K}\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)\right]$$

$T = 1000$ K

Above 1000 K, ΔG will become negative, and the reaction will become spontaneous.

74-3. Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Solution

The reaction starts with $Q < K$ as the reaction proceeds, and Q increases until equilibrium is reached (where $Q = K$).

74-4. Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $\text{MnO}_2(s) \longrightarrow \text{Mn}(s) + \text{O}_2(g)$

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

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

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

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

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

Solution

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

$\Delta G^\circ = [1\text{ mol}(0\text{ kJ/mol}) + 1\text{ mol}(0\text{ kJ/mol})] - [1\text{ mol}(-465.1\text{ kJ/mol})] = 465.1$
nonspontaneous

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

$\Delta G^\circ = [2\text{ mol}(-53.43\text{ kJ/mol})] - [1\text{ mol}(0\text{ kJ/mol}) + 1\text{ mol}(0\text{ kJ/mol})] = -106.86\text{ kJ}$
spontaneous

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

$\Delta G^\circ = [1\text{ mol}(-53.6\text{ kJ/mol})] - [1\text{ mol}(0\text{ kJ/mol}) + 1\text{ mol}(238.25\text{ kJ/mol})] = -291.9\text{ kJ}$ spontaneous

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

$$\Delta G^\circ = [1\text{ mol}(-1132.19\text{ kJ/mol}) + 1\text{ mol}(-228.59\text{ kJ/mol})] - [2\text{ mol}(-441.5\text{ kJ/mol}) + 1\text{ mol}(-394.36\text{ kJ/mol})] = -83.4\text{ kJ}$$

spontaneous

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

$$\Delta G^\circ = [1\text{ mol}(0\text{ kJ/mol}) + 2\text{ mol}(-228.59\text{ kJ/mol})] - [1\text{ mol}(-50.5\text{ kJ/mol}) + 1\text{ mol}(0\text{ kJ/mol})] = -406.7\text{ kJ}$$

spontaneous

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

$$\Delta G^\circ = [1\text{ mol}(-58.2\text{ kJ/mol}) + 1\text{ mol}(-29.25\text{ kJ/mol})] - [1\text{ mol}(66.8\text{ kJ/mol}) + 3\text{ mol}(0\text{ kJ/mol})] = -154.3\text{ kJ}$$

spontaneous

74-5. Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $C(s, \text{graphite}) + \mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g)$

(b) $O_2(g) + \mathrm{N}_2(g) \longrightarrow 2\mathrm{NO}(g)$

(c) $2\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{Cu}_2S(s)$

(d) $\mathrm{CaO}(s) + \mathrm{H}_2O(l) \longrightarrow \mathrm{Ca(OH)}_2(s)$

(e) $\mathrm{Fe}_2O_3(s) + 3\mathrm{CO}(g) \longrightarrow 2\mathrm{Fe}(s) + 3\mathrm{CO}_2(g)$

(f) $\mathrm{CaSO}_4 2H_2O(s) \longrightarrow \mathrm{CaSO}_4(s) + 2H_2O(g)$

Solution

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

$\Delta G^\circ = [1\text{ mol}(-394.36\text{ kJ/mol})] - [1\text{ mol}(0\text{ kJ/mol}) + 1\text{ mol}(0\text{ kJ/mol})] =$
-394.36 kJ spontaneous

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

$\Delta G^\circ = [2\text{ mol}(87.6\text{ kJ/mol})] - [1\text{ mol}(0\text{ kJ/mol}) + 1\text{ mol}(0\text{ kJ/mol})] = 175.2\text{ kJ}$
nonspontaneous

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

$\Delta G^\circ = [1\text{ mol}(-86.2\text{ kJ/mol})] - [2\text{ mol}(0\text{ kJ/mol}) + 1\text{ mol}(238.25\text{ kJ/mol})]$
$= -324.4\text{ kJ}$

spontaneous

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

$\Delta G^\circ = [1\text{ mol}(-897.5\text{ kJ/mol})] -$
$[1\text{ mol}(-603.3\text{ kJ/mol}) + 1\text{ mol}(-237.1\text{ kJ/mol})] = -57.1\text{ kJ}$

spontaneous

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

$\Delta G^\circ = [2\text{ mol}(0\text{ kJ/mol}) + 3\text{ mol}(-394.36\text{ kJ/mol})] -$
$[1\text{ mol}(-742.2\text{ kJ/mol}) + 3\text{ mol}(-137.15\text{ kJ/mol})] = -29.4\text{ kJ}$

spontaneous

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

$\Delta G^\circ = [1\text{ mol}(-1322.0\text{ kJ/mol}) + 2\text{ mol}(-228.59\text{ kJ/mol})] -$

$$[1\ \text{mol}(-1797.45\ \text{kJ/mol})]\ =\ 18.3\ \text{kJ}$$

Nonspontaneous

74-6. Given:

$$P_4(s)\ +5O_2(g) \longrightarrow \text{P}_4O_{10}(s) \qquad \Delta G^{\circ}\ =\ -2697.0\ \text{kJ/mol}$$

$$2H_2(g)\ +\ \text{O}_2(g) \longrightarrow 2H_2O(g) \qquad \Delta G^{\circ}\ =\ -457.18\ \text{kJ/mol}$$

$$6H_2O(g)\ +\ \text{P}_4O_{10}(s) \longrightarrow 4H_3\text{PO}_4(l) \qquad \Delta G^{\circ}\ =\ -428.66\ \text{kJ/mol}$$

(a) Determine the standard free energy of formation, ΔG_f°, for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

Solution

(a) The standard free energy of formation is the standard free energy change for $\frac{1}{4}P_4(s)\ +\ \frac{3}{2}H_2(g)\ +\ 2O_2(g) \longrightarrow \text{H}_3\text{PO}_4(l)$. We can use a Hess's law-like approach. Note that adding the first reaction plus three times the second reaction plus the third reaction gives, after cancelling terms

$$P_4(s)\ +\ 6H_2(g)\ +\ 8O_2(g) \longrightarrow 4H_3\text{PO}_4(l)$$

$$\Delta G_{\text{rxn}}^{\circ}\ =\ [(-2697.0)\ +\ 3(-457.18)\ +\ (-428.66)]\ \text{kJ/mol}\ =\ -4497.2\ \text{kJ/mol}$$

Dividing this result by four gives the equation of interest. The standard free energy of formation is –1124.3kJ/mol. (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

74-7. Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

Solution

$$3O_2(g) \longrightarrow 2O_3(g)$$

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

$$\Delta G^{\circ}\ =\ [2\ \text{mol}(163.2\ \text{kJ/mol})]\ -\ [1\ \text{mol}(0\ \text{kJ/mol})]\ =\ 326.4\ \text{kJ};$$

Nonspontaneous

74-8. Consider the decomposition of red mercury(II) oxide under standard state conditions.

$$2\text{HgO}(s, \text{red}) \longrightarrow 2\text{Hg}(l)\ +\ \text{O}_2(g)$$

(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

Solution

(a) Using the data in Appendix G, determine ΔG°_{298}:

$$\begin{aligned}\Delta G^\circ &= 2\Delta G^\circ_f(\mathrm{Hg}(l)) + \Delta G^\circ_f(\mathrm{O_2}(g)) - 2\Delta G^\circ_f(\mathrm{HgO}(s,\ \mathrm{red}))\\ &= \{2(0) + 0 - 2(-58.5)\}\ \mathrm{kJ/mol} = 117.0\ \mathrm{kJ/mol}\end{aligned}$$

From its value at 298.15 K, the reaction is nonspontaneous; (b) requires the ratio of the standard enthalpy change to the standard entropy change: $\Delta H^\circ = 2\Delta H^\circ_f(\mathrm{Hg}(l)) + \Delta H^\circ_f(O_2(g)) - 2\Delta H^\circ_f(\mathrm{HgO}(s, \mathrm{red}))$

$= [2(0) + 0 - 2(-90.83)]\mathrm{kJ/mol} = 181.66\ \mathrm{kJ/mol}$

$$\Delta S^\circ = 2S^\circ(\mathrm{Hg}(l)) + S^\circ(O_2(g)) - 2S^\circ(\mathrm{HgO}(s,\ \mathrm{red}))$$

$= [2(75.9) + 205.0 - 2(70.29)]\mathrm{J/K{\bullet}mol} = 216.42\ \mathrm{J/K{\bullet}mol}$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{181.66 \times 10^3\ \mathrm{J/mol}}{216.42\ \mathrm{J/K \cdot mol}} = 839\ \mathrm{K} = 566\ ^\circ C$$

Above 566 °C the process is spontaneous.

74-9. Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

(a) Ammonia: $2\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\mathrm{H_2}(g)$

(b) Diborane: $B_2H_6(g) \longrightarrow 2\mathrm{B}(g) + 3\mathrm{H_2}(g)$

(c) Hydrazine: $N_2H_4(g) \longrightarrow \mathrm{N_2}(g) + 2\mathrm{H_2}(g)$

(d) Hydrogen peroxide: $H_2O_2(l) \longrightarrow \mathrm{H_2}O(g) + \frac{1}{2}O_2(g)$

Solution

In each case, determine ΔG°. Suitable fuels will have $\Delta G < 0$ (so that the combustion reaction is favourable) and $\Delta H < 0$ (so that the combustion is exothermic).

$$\Delta G^\circ = \Delta G^\circ_{\mathrm{f}_{\mathrm{N_2}(g)}} + 3\Delta G^\circ_{\mathrm{f}_{\mathrm{H_2}(g)}} - 2\Delta G^\circ_{\mathrm{f}_{\mathrm{NH_3}(g)}} = 0 + 3(0) - 2(-16.5) = 33\ \mathrm{kJ}$$

(a)
$$\Delta H^\circ = \Delta H^\circ_{\mathrm{f}_{\mathrm{N_2}(g)}} + 3\Delta H^\circ_{\mathrm{f}_{\mathrm{H_2}(g)}} - 2\Delta H^\circ_{\mathrm{f}_{\mathrm{NH_3}(g)}} = 0 + 3(0) - 2(-46.11) = 92.22\ \mathrm{kJ}$$

$$\Delta G^\circ = 2\Delta G^\circ_{\mathrm{f}_{\mathrm{B}(g)}} + 3\Delta G^\circ_{\mathrm{f}_{\mathrm{H_2}(g)}} - \Delta G^\circ_{\mathrm{f}_{\mathrm{B_2H_6}(g)}} = 2(518.8) + 3(0) - 86.6 = 951\ \mathrm{kJ}$$

(b)
$$\Delta H^\circ = 2\Delta H^\circ_{\mathrm{f}_{\mathrm{B}(g)}} + 3\Delta H^\circ_{\mathrm{f}_{\mathrm{H_2}(g)}} - \Delta H^\circ_{\mathrm{f}_{\mathrm{B_2H_6}(g)}} = 2(562.7) + 3(0) - 36 = 1089\ \mathrm{kJ}$$

$$\Delta G^\circ = \Delta G^\circ_{\mathrm{f}_{\mathrm{N}_2(g)}} + 2\Delta G^\circ_{\mathrm{f}_{\mathrm{H}_2(g)}} - \Delta G^\circ_{\mathrm{f}_{\mathrm{N}_2\mathrm{H}_4(g)}} = 0 + 2(0) - 159.3 = -159.3\ \mathrm{kJ}$$

(c) $$\Delta H^\circ = \Delta H^\circ_{\mathrm{f}_{\mathrm{N}_2(g)}} + 2\Delta H^\circ_{\mathrm{f}_{\mathrm{H}_2(g)}} - \Delta H^\circ_{\mathrm{f}_{\mathrm{N}_2\mathrm{H}_4(g)}} = 0 + 2(0) - 95.4 = -95.4\ \mathrm{kJ}$$

$$\Delta G^\circ = \Delta G^\circ_{\mathrm{f}_{\mathrm{H}_2\mathrm{O}(g)}} + \frac{1}{2}\Delta G^\circ_{\mathrm{f}_{\mathrm{O}_2(g)}} - \Delta G^\circ_{\mathrm{f}_{\mathrm{H}_2\mathrm{O}_2(l)}} = 0 + \frac{1}{2}(0) - 120.4 = -120.4\ \mathrm{kJ}$$

(d) $$\Delta H^\circ = \Delta H^\circ_{\mathrm{f}_{\mathrm{H}_2\mathrm{O}(g)}} + \frac{1}{2}\Delta H^\circ_{\mathrm{f}_{\mathrm{O}_2(g)}} - \Delta H^\circ_{\mathrm{f}_{\mathrm{H}_2\mathrm{O}_2(l)}} = 0 + \frac{1}{2}(0) - 187.8 = -187.8\ \mathrm{kJ}$$

Both reactions (c) and (d) are suitable under the given conditions.

74-10. Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Solution

The reaction of interest is: $C(s, \text{diamond}) \longrightarrow \mathrm{C}(s, \text{graphite})$

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

$$\Delta H^\circ = [1\ \mathrm{mol}(0\ \mathrm{kJ/mol})] - [1\ \mathrm{mol}(1.89\ \mathrm{kJ/mol})] = -1.89\ \mathrm{kJ}$$

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

$$\Delta S^\circ = \left[1\ \mathrm{mol}\left(5.74\frac{J}{\mathrm{mol}K}\right)\right] - \left[1\ \mathrm{mol}\left(2.38\frac{J}{\mathrm{mol}K}\right)\right] = 3.36\frac{J}{\mathrm{mol}K}$$

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

$$\Delta G^\circ = \left[1\ \mathrm{mol}\left(0\frac{J}{\mathrm{mol}\cdot K}\right)\right] - \left[1\ \mathrm{mol}\left(2.90\frac{J}{\mathrm{mol}\cdot K}\right)\right] = -2.90\frac{J}{\mathrm{mol}\cdot K}$$

The conversion is spontaneous, $\Delta G^o < 0$, and is both enthalpy driven (exothermic, $\Delta H^o < 0$) and entropy driven, $\Delta S^o > 0$. However, the conversion is so slow that diamonds are effectively very stable.