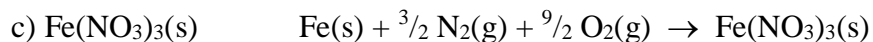
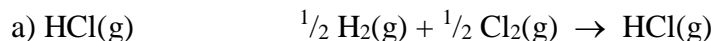


Problems, Chapter 14 (with solutions)

1) Give the correctly balanced formation reactions for each of the following pure chemical substances.



2) (14.8) How does the entropy of a system change for each of the following processes?

a) A solid melts

Entropy increases (liquids are more disordered than solids)

b) A liquid freezes

Entropy decreases (solids are more ordered than liquids)

c) A liquid boils

Entropy increases (gases are more disordered than liquids)

d) A vapor is converted into a solid

Entropy decreases (solids are more ordered than gases)

e) A vapor condenses into a liquid

Entropy decreases (liquids are more ordered than gases)

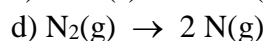
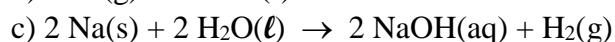
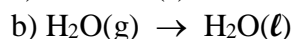
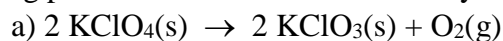
f) A solid sublimates

Entropy increases (gases are more disordered than solids)

g) A molecular solid dissolves in water

Entropy increases (a solute is more disordered than a solid)

3) (14.10) Predict whether the entropy change is positive or negative for each of the following processes. Give the reasons for your predictions.



We can make predictions based on the value of Δn_g , the change in the number of moles in the gas phase per mole of reaction.

a) $\Delta n_g = +1$, so the entropy change should be positive

b) $\Delta n_g = -1$, so the entropy change should be negative

c) $\Delta n_g = +1$, so the entropy change should be positive (since one of the products is a solute, that should also help make the entropy change positive)

d) $\Delta n_g = +1$, so the entropy change should be positive

4) 0.100 moles of an ideal gas expands from an initial volume $V_i = 1.000$ L to a final volume $V_f = 4.000$ L and at a constant temperature $T = 300$. K. Would you expect ΔS for the process to be positive, zero, or negative? Justify your answer.

Since temperature is held constant it does not play a role in determining the sign of ΔS . The volume of the system increases, and since a gas uniformly occupies the entire volume of the container it is in, each gas molecule has an increase in the uncertainty in its location. Because of this, randomness increases when a gas expands under conditions of constant temperature, and so $\Delta S > 0$.

5) For each pair of substances, choose the one you expect to have the higher standard molar entropy (S°) at 25. °C. Explain the reason for your choice.

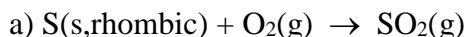
- a) $\text{NaNO}_3(\text{s})$ or $\text{NaNO}_3(\text{aq})$
- b) $\text{CH}_4(\text{g})$ or $\text{CH}_3\text{CH}_3(\text{g})$
- c) $\text{Br}_2(\ell)$ or $\text{Br}_2(\text{g})$
- d) $\text{Br}_2(\text{g})$ or $\text{F}_2(\text{g})$
- e) $\text{PCl}_3(\text{g})$ or $\text{PCl}_5(\text{g})$
- f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(\text{g})$ or $\text{SO}_2(\text{g})$

- a) $\text{NaNO}_3(\text{aq})$ - solutes are more disorganized than solids
- b) $\text{CH}_3\text{CH}_3(\text{g})$ - for a series of related molecules in the same phase, the larger molecule should have the larger value for entropy
- c) $\text{Br}_2(\text{g})$ - gases have a higher entropy than liquids
- d) $\text{Br}_2(\text{g})$ - for related molecules in the same phase, the larger molecule should have the larger value for entropy (note however this is a close case)
- e) $\text{PCl}_5(\text{g})$ - for related molecules in the same phase, the larger molecule should have the larger value for entropy
- f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(\text{g})$ - while the two molecules are not related, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ is much larger than SO_2 , and so expected to have a larger value for entropy

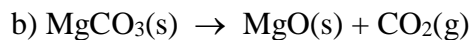
6) State the third law of thermodynamics and explain its significance.

The third law of thermodynamics states that the absolute entropy of a perfect crystal of a pure substance at absolute zero is exactly equal to 0 J/K. The significance of this is that it makes it possible to assign values for absolute entropy for pure substances at temperatures above absolute zero using experimental data.

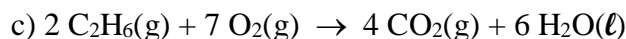
7) (14.14) Using the data in Appendix 2, calculate the standard entropy change for the following reactions at $T = 25$. °C.



$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [S^\circ(\text{SO}_2(\text{g}))] - [S^\circ(\text{S}(\text{s},\text{rhombic})) + S^\circ(\text{O}_2(\text{g}))] \\ &= [248.5] - [31.88 + 205.0] = + 11.6 \text{ J/mol}\cdot\text{K}\end{aligned}$$

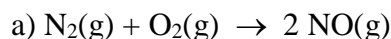


$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [S^\circ(\text{MgO}(\text{s})) + S^\circ(\text{CO}_2(\text{g}))] - [S^\circ(\text{MgCO}_3(\text{s}))] \\ &= [26.78 + 213.6] - [65.69] = + 174.7 \text{ J/mol}\cdot\text{K}\end{aligned}$$

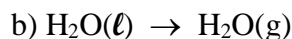


$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [4 S^\circ(\text{CO}_2(\text{g})) + 6 S^\circ(\text{H}_2\text{O}(\ell))] - [2 S^\circ(\text{C}_2\text{H}_6(\text{g})) + 7 S^\circ(\text{O}_2(\text{g}))] \\ &= [4(213.6) + 6(69.9)] - [2(229.5) + 7(205.0)] = - 620.2 \text{ J/mol}\cdot\text{K}\end{aligned}$$

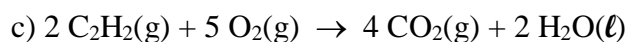
8) (14.30) Using the data in Appendix 2, calculate $\Delta G^\circ_{\text{rxn}}$ for each of the following reactions at 25. °C.



$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [2 \Delta G^\circ_{\text{f}}(\text{NO}(\text{g}))] - [\Delta G^\circ_{\text{f}}(\text{N}_2(\text{g})) + \Delta G^\circ_{\text{f}}(\text{O}_2(\text{g}))] \\ &= [2(86.7)] - [0 + 0] = 173.4 \text{ kJ/mol}\end{aligned}$$

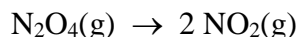


$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [\Delta G^\circ_{\text{f}}(\text{H}_2\text{O}(\text{g}))] - [\Delta G^\circ_{\text{f}}(\text{H}_2\text{O}(\ell))] \\ &= [- 228.6] - [- 237.2] = 8.6 \text{ kJ/mol}\end{aligned}$$



$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [4\Delta G^\circ_{\text{f}}(\text{CO}_2(\text{g})) + 2\Delta G^\circ_{\text{f}}(\text{H}_2\text{O}(\ell))] - [2\Delta G^\circ_{\text{f}}(\text{C}_2\text{H}_2(\text{g})) + 5\Delta G^\circ_{\text{f}}(\text{O}_2(\text{g}))] \\ &= [4(- 394.4) + 2(- 237.2)] - [2(209.2) + 5(0)] = - 2470.4 \text{ kJ/mol}\end{aligned}$$

9) Consider the following chemical reaction, carried out at $T = 298. \text{ K}$



Thermochemical data for the reactant and product are given below (given at $T = 298. \text{ K}$).

substance	$\Delta H^\circ_{\text{f}}$ (kJ/mol)	$\Delta G^\circ_{\text{f}}$ (kJ/mol)	S° (J/mol·K)
$\text{NO}_2(\text{g})$	33.85	51.8	240.46
$\text{N}_2\text{O}_4(\text{g})$	9.66	98.29	304.3

a) Find $\Delta H^\circ_{\text{rxn}}$, $\Delta G^\circ_{\text{rxn}}$, and $\Delta S^\circ_{\text{rxn}}$ for the above reaction.

$$\Delta H^\circ_{\text{rxn}} = 2 \Delta H^\circ_f(\text{NO}_2(\text{g})) - \Delta H^\circ_f(\text{N}_2\text{O}_4(\text{g}))$$

$$= 2 (33.85) - 9.66 = 58.0 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{rxn}} = 2 \Delta G^\circ_f(\text{NO}_2(\text{g})) - \Delta G^\circ_f(\text{N}_2\text{O}_4(\text{g}))$$

$$= 2 (51.8) - 98.29 = 5.3 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = 2 S^\circ(\text{NO}_2(\text{g})) - S^\circ(\text{N}_2\text{O}_4(\text{g}))$$

$$= 2 (240.46) - 304.3 = 176.9 \text{ J/mol}\cdot\text{K}$$

b) Based on the definition of free energy, we expect $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$. Using your answer in part a, check to see if this is true for the above reaction.

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} = 58.0 \text{ kJ/mol} - (298. \text{ K}) (176.9 \times 10^{-3} \text{ kJ/mol}\cdot\text{K})$$

$$= 5.3 \text{ kJ/mol}$$

This is the same value we obtained when we calculated $\Delta G^\circ_{\text{rxn}}$ directly in part a.

c) Find $\Delta S^\circ_{\text{syst}}$, $\Delta S^\circ_{\text{surr}}$, and $\Delta S^\circ_{\text{univ}}$ for the above reaction.

This is a chemical reaction carried out at standard conditions, and so

$$\Delta S^\circ_{\text{syst}} = \Delta S^\circ_{\text{rxn}} = 176.9 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ_{\text{surr}} = - \Delta H^\circ_{\text{rxn}}/T = - (58.0 \times 10^3 \text{ J/mol})/(298.2 \text{ K}) = - 194.5 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{syst}} + \Delta S^\circ_{\text{surr}} = (176.9 \text{ J/mol}\cdot\text{K}) + (- 194.5 \text{ J/mol}\cdot\text{K})$$

$$= - 17.6 \text{ J/mol}\cdot\text{K}$$

d) Using the information above there are two ways in which we can decide whether the above reaction is spontaneous at constant pressure and a constant temperature $T = 298. \text{ K}$. What are they? Is the above reaction spontaneous at $T = 298. \text{ K}$ and constant pressure? Explain.

The reaction will be spontaneous for standard conditions if $\Delta S^\circ_{\text{univ}} > 0$ or if $\Delta G^\circ_{\text{rxn}} < 0$. Using the information found above we have $\Delta S^\circ_{\text{univ}} = - 17.6 \text{ J/mol}\cdot\text{K}$ and $\Delta G^\circ_{\text{rxn}} = 5.3 \text{ kJ/mol}$. Both of these indicate that the reaction is not spontaneous at $T = 298. \text{ K}$ and standard conditions.

e) Is there a temperature where $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ exist at equilibrium for standard conditions ($p(\text{NO}_2) = p(\text{N}_2\text{O}_4) = 1.00 \text{ atm}$)? If so, at what temperature does this occur?

Since $\Delta H^\circ_{\text{rxn}} > 0$ and $\Delta S^\circ_{\text{rxn}} > 0$, we expect the reaction will be spontaneous for standard conditions at high temperatures but not at low temperatures (see problem 9). The temperature at which $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ exist at equilibrium for standard condition is approximately

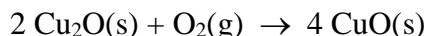
$$T_{\text{eq}} \cong \Delta H^\circ_{\text{rxn}} / \Delta S^\circ_{\text{rxn}} = (58.0 \times 10^3 \text{ J/mol}) / (176.7 \text{ J/mol}\cdot\text{K}) = 328. \text{ K} = 55. \text{ }^\circ\text{C}$$

The reason this temperature is approximate is that we have used the values for $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ at $T = 298. \text{ K}$. Both $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ slowly change when temperature changes, and this change has not been taken into account in finding T_{eq} .

10) Thermodynamic data for several pure chemical substances are given below (at $T = 298.0 \text{ K}$).

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol·K)
CuO(s)	- 157.3	- 129.7	42.63
Cu ₂ O(s)	- 168.6	- 146.0	93.14
O ₂ (g)	0.0	0.0	205.14

a) Using the above information, find the values for $\Delta H^\circ_{\text{rxn}}$, $\Delta G^\circ_{\text{rxn}}$, and $\Delta S^\circ_{\text{rxn}}$ for the following reaction, at $T = 298. \text{ K}$.



$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [4 \Delta H^\circ_f(\text{CuO}(\text{s}))] - [2 \Delta H^\circ_f(\text{Cu}_2\text{O}) + \Delta H^\circ_f(\text{O}_2(\text{g}))] \\ &= [4 (- 157.3)] - [2 (- 168.6) + 0.0] = - 292.0 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [4 \Delta G^\circ_f(\text{CuO}(\text{s}))] - [2 \Delta G^\circ_f(\text{Cu}_2\text{O}) + \Delta G^\circ_f(\text{O}_2(\text{g}))] \\ &= [4 (- 129.7)] - [2 (- 146.0) + 0.0] = - 226.8 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [4 S^\circ(\text{CuO}(\text{s}))] - [2 S^\circ(\text{Cu}_2\text{O}) + S^\circ(\text{O}_2(\text{g}))] \\ &= [4 (42.63)] - [2 (93.15) + 205.14] = - 220.92 \text{ J/mol}\cdot\text{K} \end{aligned}$$

b) Find $\Delta S^\circ_{\text{syst}}$, $\Delta S^\circ_{\text{surr}}$, and $\Delta S^\circ_{\text{univ}}$ for the above reaction at $T = 298.0 \text{ K}$.

$$\Delta S^\circ_{\text{syst}} = \Delta S^\circ_{\text{rxn}} = - 220.92 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ_{\text{surr}} = - \Delta H^\circ_{\text{rxn}} / T = - (- 292000. \text{ J/mol}) / (298.2 \text{ K}) = 979.21 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^{\circ}_{\text{univ}} = \Delta S^{\circ}_{\text{sys}} + \Delta S^{\circ}_{\text{surr}} = (-220.92) + (979.21) = +758.29 \text{ J/mol}\cdot\text{K}$$

c) Will the above reaction be spontaneous for standard conditions at $T = 298.0 \text{ K}$? Justify your answer?

We can look at either $\Delta G^{\circ}_{\text{rxn}}$ or $\Delta S^{\circ}_{\text{univ}}$ to answer this question (both should give us the same answer).

Since $\Delta G^{\circ}_{\text{rxn}} < 0$, the reaction is spontaneous for standard conditions and $T = 298.0 \text{ K}$.

Since $\Delta S^{\circ}_{\text{univ}} > 0$, the reaction is spontaneous for standard conditions and $T = 298.0 \text{ K}$.

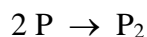
While looking at either $\Delta G^{\circ}_{\text{rxn}}$ or $\Delta S^{\circ}_{\text{univ}}$ allows us to determine whether or not the reaction is spontaneous, it is much easier to calculate the value for $\Delta G^{\circ}_{\text{rxn}}$, which is why we usually use this to make the determination.

11) Predict the spontaneity of a reaction (and the temperature dependence of the spontaneity) for each possible combination of signs for ΔH and ΔS (for the system).

We may use Table 14.4 of Burdge to answer this question

- a) ΔH negative, ΔS positive Always spontaneous
- b) ΔH positive, ΔS negative Never spontaneous
- c) ΔH negative, ΔS negative Spontaneous at low T but not at high T
- d) ΔH positive, ΔS positive Spontaneous at high T but not at low T

12) Consider the formation of a dimeric protein P_2 by the process



At $T = 25.0^{\circ}\text{C}$, we have $\Delta H^{\circ}_{\text{rxn}} = 17.0 \text{ kJ/mol}$ and $\Delta S^{\circ}_{\text{rxn}} = 60.0 \text{ J/mol}\cdot\text{K}$.

a) Is dimerization favored for standard conditions at this temperature?

$$\begin{aligned} \Delta G^{\circ}_{\text{rxn}} &= \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}} = (17.0 \text{ kJ/mol}) - (298.2 \text{ K})(60.0 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}) \\ &= -0.9 \text{ kJ/mol} \end{aligned}$$

Since $\Delta G^{\circ}_{\text{rxn}} < 0$, the reaction is spontaneous at this temperature and standard conditions.

b) Comment on the effect of lowering the temperature. At what temperature (if any) would dimerization not be favored for standard conditions?

Since $\Delta H^\circ_{\text{rxn}} > 0$ and $\Delta S^\circ_{\text{rxn}} > 0$, we expect the reaction will be spontaneous for standard conditions at high temperatures but not at low temperatures (see problem 9d). The temperature at which $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ exist at equilibrium for standard condition is approximately

$$T_{\text{eq}} \cong \Delta H^\circ_{\text{rxn}} / \Delta S^\circ_{\text{rxn}} = (17.0 \times 10^3 \text{ J/mol}) / (60.0 \text{ J/mol}\cdot\text{K}) = 283.3. = 10.2 \text{ }^\circ\text{C}$$

Therefore, if $T < 10.2 \text{ }^\circ\text{C}$ and standard conditions dimerization is not favored.

13) Given the values of $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and T below, determine ΔS_{univ} and predict whether or not each reaction will be spontaneous.

a) $\Delta H^\circ_{\text{rxn}} = -95. \text{ kJ/mol}$, $\Delta S^\circ_{\text{rxn}} = -157. \text{ J/mol}\cdot\text{K}$, $T = 298. \text{ K}$

$$\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}} = \Delta S^\circ_{\text{rxn}} - \Delta H^\circ_{\text{rxn}}/T$$

$$= (-157. \text{ J/mol}\cdot\text{K}) - (-95000. \text{ J/mol}) / (298. \text{ K}) = +161.8 \text{ J/mol}\cdot\text{K}$$

Reaction is spontaneous.

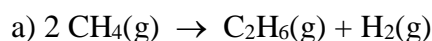
b) $\Delta H^\circ_{\text{rxn}} = -95. \text{ kJ/mol}$, $\Delta S^\circ_{\text{rxn}} = -157. \text{ J/mol}\cdot\text{K}$, $T = 855. \text{ K}$

$$\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}} = \Delta S^\circ_{\text{rxn}} - \Delta H^\circ_{\text{rxn}}/T$$

$$= (-157. \text{ J/mol}\cdot\text{K}) - (-95000. \text{ J/mol}) / (855. \text{ K}) = -45.9 \text{ J/mol}\cdot\text{K}$$

Reaction is not spontaneous.

14) For each reaction calculate $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and $\Delta G^\circ_{\text{rxn}}$ at $25. \text{ }^\circ\text{C}$, and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from $25. \text{ }^\circ\text{C}$? Data for this problem are found in Appendix 2.



$$\Delta H^\circ_{\text{rxn}} = [\Delta H^\circ_{\text{f}}(\text{C}_2\text{H}_6(\text{g}))] - [2 \Delta H^\circ_{\text{f}}(\text{CH}_4(\text{g}))]$$

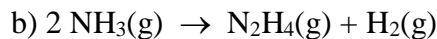
$$= [(-84.68)] - [2(-74.6)] = 64.5 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = [S^\circ(\text{C}_2\text{H}_6(\text{g})) + S^\circ(\text{H}_2(\text{g}))] - [2 S^\circ(\text{CH}_4(\text{g}))]$$

$$= [(229.2) + (130.7)] - [2(186.3)] = -12.7 \text{ J/mol}\cdot\text{K}$$

$$\begin{aligned}\Delta G^{\circ}_{\text{rxn}} &= [\Delta G^{\circ}_{\text{f}}(\text{C}_2\text{H}_6(\text{g}))] - [2 \Delta G^{\circ}_{\text{f}}(\text{CH}_4(\text{g}))] \\ &= [(-32.0)] - [2(-50.5)] = 69.0 \text{ kJ/mol}\end{aligned}$$

$\Delta G^{\circ}_{\text{rxn}} > 0$, so reaction is not spontaneous. $\Delta H^{\circ}_{\text{rxn}} > 0$ and $\Delta S^{\circ}_{\text{rxn}} < 0$, so the reaction is not spontaneous at any temperature (see problem 9b).



$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}} &= [\Delta H^{\circ}_{\text{f}}(\text{N}_2\text{H}_4(\text{g}))] - [2 \Delta H^{\circ}_{\text{f}}(\text{NH}_3(\text{g}))] \\ &= [(95.4)] - [2(-45.9)] = 187.2 \text{ kJ/mol}\end{aligned}$$

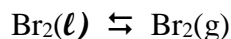
$$\begin{aligned}\Delta S^{\circ}_{\text{rxn}} &= [S^{\circ}(\text{N}_2\text{H}_4(\text{g})) + S^{\circ}(\text{H}_2(\text{g}))] - [2 S^{\circ}(\text{NH}_3(\text{g}))] \\ &= [(238.5) + (130.7)] - [2(192.8)] = -16.4 \text{ J/mol}\cdot\text{K}\end{aligned}$$

$$\begin{aligned}\Delta G^{\circ}_{\text{rxn}} &= [\Delta G^{\circ}_{\text{f}}(\text{N}_2\text{H}_4(\text{g}))] - [2 \Delta G^{\circ}_{\text{f}}(\text{NH}_3(\text{g}))] \\ &= [(159.4)] - [2(-16.4)] = 192.2 \text{ kJ/mol}\end{aligned}$$

$\Delta G^{\circ}_{\text{rxn}} > 0$, so reaction is not spontaneous. $\Delta H^{\circ}_{\text{rxn}} > 0$ and $\Delta S^{\circ}_{\text{rxn}} < 0$, so the reaction is not spontaneous at any temperature (see problem 9b).

15) Using the data in Appendix 2, predict the normal boiling point temperature for $\text{Br}_2(\ell)$.

The boiling process may be written as



At the normal boiling point $\Delta G^{\circ}_{\text{rxn}} = 0$. The temperature at which this occurs is approximately

$$T_{\text{eq}} = T_{\text{boil}} = T^{\circ}_{\text{vap}} \cong \Delta H^{\circ}_{\text{rxn}} / \Delta S^{\circ}_{\text{rxn}}$$

$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}} &= [\Delta H^{\circ}_{\text{f}}(\text{Br}_2(\text{g}))] - [\Delta H^{\circ}_{\text{f}}(\text{Br}_2(\ell))] \\ &= [(30.7)] - [0] = 30.7 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^{\circ}_{\text{rxn}} &= [S^{\circ}(\text{Br}_2(\text{g}))] - [S^{\circ}(\text{Br}_2(\ell))] \\ &= [245.13] - [152.3] = 92.8 \text{ J/mol}\cdot\text{K}\end{aligned}$$

$$T^{\circ}_{\text{vap}} \cong (30700. \text{ J/mol}) / (92.8 \text{ J/mol}\cdot\text{K}) = 331. \text{ K} = 58. \text{ }^{\circ}\text{C}$$

This is in excellent agreement with the experimental value $T^{\circ}_{\text{vap}} = 58.78\text{ }^{\circ}\text{C}$.

16) It takes the addition of 3348. J of heat to convert 10.00 g of n-hexane (C_6H_{14} , MW = 86.18 g/mol) from a liquid to a vapor at the normal boiling point, $T = 69. ^{\circ}\text{C}$ and $p = 1.000\text{ atm}$. Based on this information find $\Delta H^{\circ}_{\text{vap}}$, $\Delta G^{\circ}_{\text{vap}}$, and $\Delta S^{\circ}_{\text{vap}}$ for this process and the conditions that are given in the problem.

At the normal boiling point the liquid and vapor phases of a substance exist at equilibrium, and so $\Delta G^{\circ}_{\text{vap}} = 0$.

The number of moles of n-hexane is

$$n = \frac{m}{\text{MW}} = \frac{10.00\text{ g}}{(86.18\text{ g/mol})} = 0.1160\text{ moles}$$

The amount of heat needed to convert 1.000 moles of liquid n-hexane into vapor at the normal boiling point is

$$q(\text{per mole}) = \frac{q}{n} = \frac{3348.\text{ J}}{0.1160\text{ mol}} = 28860.\text{ J/mol} = 28.86\text{ kJ/mol}$$

For a process carried out at constant temperature and pressure $q = \Delta H$. Therefore

$$\Delta H^{\circ}_{\text{vap}} = q(\text{per mole}) = 28.86\text{ kJ/mol}$$

Finally, for a process carried out at constant pressure and temperature

$$\Delta G^{\circ}_{\text{vap}} = 0 = \Delta H^{\circ}_{\text{vap}} - T \Delta S^{\circ}_{\text{vap}}$$

and so $\Delta H^{\circ}_{\text{vap}} = T \Delta S^{\circ}_{\text{vap}}$

$$\text{Therefore } \Delta S^{\circ}_{\text{vap}} = \frac{\Delta H^{\circ}_{\text{vap}}}{T} = \frac{28860\text{ J/mol}}{342.\text{ K}} = 84.4\text{ J/mol}\cdot\text{K}$$

17) (14.41) The normal melting point for ammonia (NH_3) is $-77.7\text{ }^{\circ}\text{C}$. Predict the signs of ΔH , ΔS , and ΔG of the system for the following processes at 1.00 atm:

a) ammonia melts at $-60.0\text{ }^{\circ}\text{C}$. Heat must be added to melt a solid, and so $\Delta H > 0$. Disorder is higher for a liquid than for a solid, and so $\Delta S > 0$. Melting (at 1.00 atm) is spontaneous at temperatures above the normal melting point, and so $\Delta G < 0$.

b) ammonia melts at $-77.7\text{ }^{\circ}\text{C}$. Heat must be added to melt a solid, and so $\Delta H > 0$. Disorder is higher for a liquid than for a solid, and so $\Delta S > 0$. At the normal melting point the solid and liquid are in equilibrium, and so $\Delta G = 0$.

c) ammonia melts at $-100.0\text{ }^{\circ}\text{C}$. Heat must be added to melt a solid, and so $\Delta H > 0$. Disorder is higher for a liquid than for a solid, and so $\Delta S > 0$. Melting (at 1.00 atm) is not spontaneous at temperatures below the normal melting point, and so $\Delta G > 0$.

Note that for melting at any temperature $\Delta H > 0$ and $\Delta S > 0$. It is only the value of ΔG that will have a different sign at different temperatures. Note also your answer is consistent with the answer to problem 11d.