Problems, Chapter 14 (with solutions)

NOTE: For problems requiring thermodynamic data, you should use the information in Appendix G of the OpenStax textbook (Standard thermodynamic properties for selected substances).

1) Which of the following is a state function (q, w, U, H)?

q and w are not state functions, U and H are state functions.

2) Using the data contained in OpenStax Appendix G find the value for $\Delta H°_{rxn}$ for the following process, carried out at T = 25.0 °C. Note that $\Delta H°_f$ = - 1274.5 kJ/mol for glucose, $C_6H_{12}O_6$(s). This process corresponds to the oxidation of glucose, and $\Delta H°_{rxn}$ represents the heat generated when glucose is metabolized in the human body.

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(\ell)$$
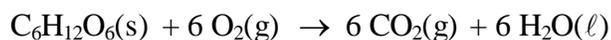
$$\Delta H°_{rxn} = [\ 6\ \Delta H°_f(CO_2(g)) + 6\ \Delta H°_f(H_2O(\ell))\ ] - [\ \Delta H°_f(C_6H_{12}O_6(s)) + 6\ \Delta H°_f(O_2(g))\ ]$$

$$= [\ 6\ (-393.51) + 6\ (-285.83)\ ] - [\ (-1274.5) + 6\ (0.0)\ ] = -2801.5\ kJ/mol$$

This reaction releases quite a bit of heat (it is an exothermic reaction), which can be used to provide energy for a variety of metabolic processes.

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

a) HCl(g) $^1/_2\ H_2(g) + {}^1/_2\ Cl_2(g) \rightarrow HCl(g)$

b) $C_6H_6(\ell)$ $6\ C(s) + 3\ H_2(g) \rightarrow C_6H_6(\ell)$

c) $Fe(NO_3)_3$(s) $Fe(s) + {}^3/_2\ N_2(g) + {}^9/_2\ O_2(g) \rightarrow Fe(NO_3)_3(s)$

4) CFC-113a is a chlorofluorocarbon whose use is now tightly regulated by international treaty. The formula for CFC-113a is ($CCl_3CF_3(\ell)$). Give the correctly balanced formation reaction for $CCl_3CF_3(\ell)$. Be sure to indicate the correct phase (s, ℓ, g) for all reactants and products.

The formation reaction produces exactly 1 mole of a single product from elements in their most stable form. Therefore, the formation reaction for CFC-113a is

$$2\ C(s) + {}^3/_2\ Cl_2(g) + {}^3/_2\ F_2(g) \rightarrow CCl_3CF_3(\ell)$$
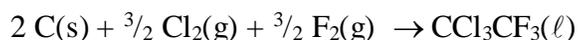
5) How does the entropy of a system change for each of the following processes?

    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 sublimes

        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)

6) For a chemical reaction to be spontaneous for standard conditions, which of the following, if any, must be true: $\Delta S°_{univ} > 0$, $\Delta S°_{syst} > 0$, $\Delta S°_{surr} > 0$.

The Second Law of Thermodynamics states that for any process to occur $\Delta S°_{univ} \geq 0$. If the process is spontaneous, then $\Delta S°_{univ} > 0$. Since $\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr}$, that means that for a spontaneous process $\Delta S°_{syst} + \Delta S°_{surr} > 0$. But a process can be spontaneous if $\Delta S°_{syst}$ is negative or if $\Delta S°_{surr}$ is negative, as long as the sum of the two is positive. Therefore, there is no requirement that either $\Delta S°_{syst}$ or $\Delta S°_{surr}$ be positive, only that the sum of the two be positive. So the only thing that must be true is $\Delta S°_{univ} > 0$. .

7) For each of the following processes, indicate whether the process is or is not spontaneous. If there is not sufficient information to tell whether the process is or is not spontaneous, say "cannot tell".

ΔS_{syst}	ΔS_{surr}	Process is spontaneous? (yes / no / cannot tell)
positive	positive	_____yes_____
negative	positive	_____cannot tell_____
negative	negative	_____no_____
positive	zero	_____yes_____

Recall $\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$. For the first and fourth process, ΔS_{univ} has to be positive, and so those processes must be spontaneous. For the third process ΔS_{univ} has to be negative, and so that process is not spontaneous. For the second process ΔS_{univ} could be positive, negative or zero, and so no prediction can be made.

8) Predict whether the entropy change is positive or negative for each of the following processes. Give the reasons for your predictions.
a) $2 \text{ KClO}_4(s) \rightarrow 2 \text{ KClO}_3(s) + O_2(g)$
b) $H_2O(g) \rightarrow H_2O(\ell)$
c) $2 \text{ Na}(s) + 2 H_2O(\ell) \rightarrow 2 \text{ NaOH}(aq) + H_2(g)$
d) $N_2(g) \rightarrow 2 N(g)$

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 <u>positive</u>
b) $\Delta n_g = -1$, so the entropy change should be <u>negative</u>
c) $\Delta n_g = +1$, so the entropy change should be <u>positive</u> (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 <u>positive</u>

9) 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 $\Delta S > 0$.

10) 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) $\text{NaNO}_3(s)$ or $\text{NaNO}_3(aq)$
b) $CH_4(g)$ or $CH_3CH_3(g)$
c) $Br_2(\ell)$ or $Br_2(g)$
d) $Br_2(g)$ or $F_2(g)$
e) $PCl_3(g)$ or $PCl_5(g)$
f) $CH_3CH_2CH_2CH_3(g)$ or $SO_2(g)$

a) $\text{NaNO}_3(aq)$ - solutes are more disorganized than solids
b) $CH_3CH_3(g)$ - for a series of related molecules in the same phase, the larger molecule should have the larger value for entropy
c) $Br_2(g)$ - gases have a higher entropy than liquids
d) $Br_2(g)$ - 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) $PCl_5(g)$ - for related molecules in the same phase, the larger molecule should have the larger value for entropy
f) $CH_3CH_2CH_2CH_3(g)$ - while the two molecules are not related, $CH_3CH_2CH_2CH_3$ is much larger than SO_2, and so expected to have a larger value for entropy

11) 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.
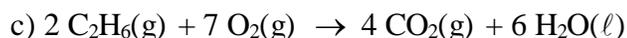
12) Using the data contained in OpenStax Appendix G, calculate the standard entropy change for the following reactions at $T = 25.\ °C$.

    a) $S(g) + O_2(g) \rightarrow SO_2(g)$
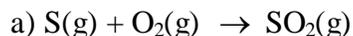
      $\Delta S°_{rxn} = [S°(SO_2(g))] - [S°(S(g)) + S°(O_2(g))]$

              $= [248.2] - [167.82 + 205.2] = -124.8\ \text{J/mol·K}$

    b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
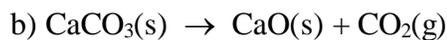
      $\Delta S°_{rxn} = [S°(CaO(s)) + S°(CO_2(g))] - [S°(CaCO_3(s))]$

              $= [38.1 + 213.8] - [110.0] = +141.9\ \text{J/mol·K}$

    c) $2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(\ell)$

      $\Delta S°_{rxn} = [4\ S°(CO_2(g)) + 6\ S°(H_2O(\ell))] - [2\ S°(C_2H_6(g)) + 7\ S°(O_2(g))]$

              $= [4\ (213.8) + 6\ (70.0)] - [2\ (229.2) + 7\ (205.2)] = -619.6\ \text{J/mol·K}$

13) Using the data contained in OpenStax Appendix G, calculate $\Delta G°_{rxn}$ for each of the following reactions at $25.\ °C$.

    a) $N_2(g) + O_2(g) \rightarrow 2\ NO(g)$
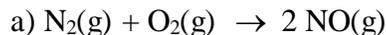
      $\Delta G°_{rxn} = [2\ \Delta G°_f(NO(g))] - [\Delta G°_f(N_2(g)) + \Delta G°_f(O_2(g))]$

           $= [2\ (87.6)] - [0 + 0] = 175.2\ \text{kJ/mol}$

    b) $H_2O(\ell) \rightarrow H_2O(g)$
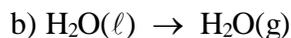
      $\Delta G°_{rxn} = [\Delta G°_f(H_2O(g))] - [\Delta G°_f(H_2O(\ell))]$

           $= [-228.59] - [-237.1] = 8.5\ \text{kJ/mol}$

c) $2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(\ell)$

$\Delta G°_{rxn} = [4\ \Delta G°_f(CO_2(g)) + 2\ \Delta G°_f(H_2O(\ell))] - [2\ \Delta G°_f(C_2H_2(g)) + 5\ \Delta G°_f(O_2(g))]$

$= [4\ (-394.36) + 2\ (-237.1)] - [2\ (209.2) + 5(0)] = -2470.0\ kJ/mol$

14) 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 make predictions based on the fact that $\Delta G = \Delta H - T\ \Delta S$, that $\Delta G < 0$ for a spontaneous reaction, and that both ΔH and ΔS are approximately independent of temperature.

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

15) Consider the following chemical reaction, carried out at $T = 298.\ K$

$N_2O_4(g) \rightarrow 2\ NO_2(g)$
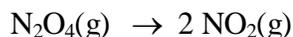
Thermochemical data for the reactant and product are given below (given at $T = 298.\ K$).

substance	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (kJ/mol)	$S°$ (J/mol·K)
$NO_2(g)$	33.85	51.8	240.46
$N_2O_4(g)$	9.66	98.29	304.3

a) Find $\Delta H°_{rxn}$, $\Delta G°_{rxn}$, and $\Delta S°_{rxn}$ for the above reaction.

$\Delta H°_{rxn} = 2\ \Delta H°_f(NO_2(g)) - \Delta H°_f(N_2O_4(g))$

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

$\Delta G°_{rxn} = 2\ \Delta G°_f(NO_2(g)) - \Delta G°_f(N_2O_4(g))$

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

$\Delta S°_{rxn} = 2\ S°(NO_2(g)) - S°(N_2O_4(g))$

$= 2\ (240.46) - 304.3 = 176.6\ J/mol·K$

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

$$\Delta G°_{rxn} = \Delta H°_{rxn} - T \Delta S°_{rxn} = 58.0 \text{ kJ/mol} - (298. \text{ K}) (176.6 \times 10^{-3} \text{ kJ/mol·K})$$

$$= 5.4 \text{ kJ/mol}$$

This is the same value (to within roundoff error) we obtained when we calculated $\Delta G°_{rxn}$ directly in part a.

c) Find $\Delta S°_{syst}$, $\Delta S°_{surr}$, and $\Delta S°_{univ}$ for the above reaction.

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

$$\Delta S°_{syst} = \Delta S°_{rxn} = 176.6 \text{ J/mol·K}$$

$$\Delta S°_{surr} = - \Delta H°_{rxn}/T = - (58.0 \times 10^3 \text{ J/mol})/(298. \text{ K}) = - 194.6 \text{ J/mol·K}$$

$$\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr} = (176.6 \text{ J/mol·K}) + (- 194.6 \text{ J/mol·K})$$

$$= - 18.0 \text{ J/mol·K}$$

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. K. What are they? Is the above reaction spontaneous at T = 298. K and constant pressure? Explain.

The reaction will be spontaneous for standard conditions if $\Delta S°_{univ} > 0$ or if $\Delta G°_{rxn} < 0$. Using the information found above we have $\Delta S°_{univ} = - 18.0 \text{ J/mol·K}$ and $\Delta G°_{rxn} = 5.3 \text{ kJ/mol}$. Both of these indicate that the reaction is not spontaneous at T = 298. K and standard conditions.

e) Is there a temperature where $NO_2(g)$ and $N_2O_4(g)$ exist at equilibrium for standard conditions ($p(NO_2) = p(N_2O_4) = 1.00$ atm)? If so, at what temperature does this occur?

Since $\Delta H°_{rxn} > 0$ and $\Delta S°_{rxn} > 0$, we expect the reaction will be spontaneous for standard conditions at high temperatures but not at low temperatures (see problem 14). The temperature at which $NO_2(g)$ and $N_2O_4(g)$ exist at equilibrium for standard condition is approximately

$$T_{eq} \cong \Delta H°_{rxn}/\Delta S°_{rxn} = (58.0 \times 10^3 \text{ J/mol})/(176.6 \text{ J/mol·K}) = 328. \text{ K} = 55. °C$$

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

16) Thermodynamic data for several pure chemical substances are given below (at T =298.0 K).

Substance	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (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 $\Delta H°_{rxn}$, $\Delta G°_{rxn}$, and $\Delta S°_{rxn}$ for the following reaction, at T = 298. K.
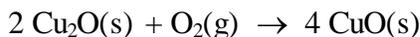
$$2 \ Cu_2O(s) + O_2(g) \rightarrow 4 \ CuO(s)$$

$\Delta H°_{rxn} = [\ 4 \ \Delta H°_f(CuO(s)) \ ] - [\ 2 \ \Delta H°_f(Cu_2O) + \Delta H°_f(O_2(g)) \ ]$

$= [\ 4 \ (- 157.3) \ ] - [\ 2 \ (- 168.6) + 0.0 \ ] = - 292.0$ kJ/mol

$\Delta G°_{rxn} = [\ 4 \ \Delta G°_f(CuO(s)) \ ] - [\ 2 \ \Delta G°_f(Cu_2O) + \Delta G°_f(O_2(g)) \ ]$

$= [\ 4 \ (- 129.7) \ ] - [\ 2 \ (- 146.0) + 0.0 \ ] = - 226.8$ kJ/mol

$\Delta S°_{rxn} = [\ 4 \ S°(CuO(s)) \ ] - [\ 2 \ S°(Cu_2O) + S°(O_2(g)) \ ]$

$= [\ 4 \ (42.63) \ ] - [\ 2 \ (93.15) + 205.14 \ ] = - 220.92$ J/mol·K

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

$\Delta S°_{syst} = \Delta S°_{rxn} = - 220.92$ J/mol·K

$\Delta S°_{surr} = - \Delta H°_{rxn}/T = - (- 292000. \ J/mol)/(298. \ K) = 979.9$ J/mol·K

$\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr} = (- 220.92) + (979.9) = + 759.0$ J/mol·K

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

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

Since $\Delta G°_{rxn} < 0$, the reaction is spontaneous for standard conditions and T = 298. K

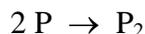Since $\Delta S°_{univ} > 0$, the reaction is spontaneous for standard conditions and T = 298 K.

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

17) Complete the table below. You may assume that both $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ have values that are independent of temperature.

$\Delta H°_{rxn}$	$\Delta S°_{rxn}$	When is the reaction spontaneous?
positive	**positive**	Reaction is spontaneous at high temperatures
negative	negative	**Reaction is spontaneous at low temperatures**
negative	**positive**	Reaction is always spontaneous

The answer to problem 14 will tell you how to fill in the table.

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

$$2 P \rightarrow P_2$$

At T = 25. °C, we have $\Delta H°_{rxn} = 17.0$ kJ/mol and $\Delta S°_{rxn} = 60.0$ J/mol·K.

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

$$\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn} = (17.0 \text{ kJ/mol}) - (298.2 \text{ K})(60.0 \times 10^{-3} \text{ kJ/mol·K})$$

$$= -0.9 \text{ kJ/mol}$$

Since $\Delta G°_{rxn} < 0$, 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 $\Delta H°_{rxn} > 0$ and $\Delta S°_{rxn} > 0$, we expect the reaction will be spontaneous for standard conditions at high temperatures but not at low temperatures (see problem 14). The temperature at which P and P_2 exist at equilibrium for standard condition is approximately

$$T_{eq} \cong \Delta H°_{rxn}/\Delta S°_{rxn} = (17.0 \times 10^3 \text{ J/mol})/(60.0 \text{ J/mol·K}) = 283.3 = 10.1 °C$$

Therefore, if T < 10.2 °C and standard conditions dimerization is not favored.

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

a) $\Delta H°_{rxn}$ = - 95. kJ/mol, $\Delta S°_{rxn}$ = - 157. J/mol·K, T = 298. K

$\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr} = \Delta S°_{rxn} - \Delta H°_{rxn}/T$

$= (- 157.$ J/mol·K$) - (- 95000.$ J/mol$)/(298.$ K$) = + 161.8$ J/mol·K

Reaction is spontaneous.

b) $\Delta H°_{rxn}$ = - 95. kJ/mol, $\Delta S°_{rxn}$ = - 157. J/mol·K, T = 855. K

$\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr} = \Delta S°_{rxn} - \Delta H°_{rxn}/T$

$= (- 157.$ J/mol·K$) - (- 95000.$ J/mol$)/(855.$ K$) = - 45.9$ J/mol·K

Reaction is not spontaneous.

20) For each reaction calculate $\Delta H°_{rxn}$, $\Delta S°_{rxn}$, and $\Delta G°_{rxn}$ at 25. °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. °C? Data are contained in OpenStax Appendix G.
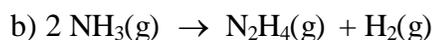
a) $2 CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

$\Delta H°_{rxn} = [\Delta H°_f(C_2H_6(g))] - [2 \Delta H°_f(CH_4(g))]$

$= [(- 84.0)] - [2 (- 74.6)] = 65.2$ kJ/mol

$\Delta S°_{rxn} = [S°(C_2H_6(g)) + S°(H_2(g))] - [2 S°(CH_4(g))]$

$= [(229.2) + (130.7)] - [2 (186.3)] = - 12.7$ J/mol·K

$\Delta G°_{rxn} = [\Delta G°_f(C_2H_6(g))] - [2 \Delta G°_f(CH_4(g))]$

$= [(- 32.0)] - [2 (- 50.5)] = 69.0$ kJ/mol

$\Delta G°_{rxn} > 0$, so reaction is not spontaneous. $\Delta H°_{rxn} > 0$ and $\Delta S°_{rxn} < 0$, so the reaction is not spontaneous at any temperature (see problem 14).

b) $2 NH_3(g) \rightarrow N_2H_4(g) + H_2(g)$

$\Delta H°_{rxn} = [\Delta H°_f(N_2H_4(g))] - [2 \Delta H°_f(NH_3(g))]$

$= [(95.4)] - [2 (- 45.9)] = 187.2$ kJ/mol

$\Delta S^\circ_{rxn} = [S^\circ(N_2H_4(g)) + S^\circ(H_2(g))] - [2\ S^\circ(NH_3(g))]$

$= [(238.5) + (130.7)] - [2\ (192.8)] = -16.4\ \text{J/mol·K}$

$\Delta G^\circ_{rxn} = [\Delta G^\circ_f(N_2H_4(g))] - [2\ \Delta G^\circ_f(NH_3(g))]$

$= [(159.4)] - [2\ (-16.5)] = 192.4\ \text{kJ/mol}$

$\Delta G^\circ_{rxn} > 0$, so reaction is not spontaneous. $\Delta H^\circ_{rxn} > 0$ and $\Delta S^\circ_{rxn} < 0$, so the reaction is not spontaneous at any temperature (see problem 14).

21) Using the data contained in OpenStax Appendix G, predict the normal boiling point temperature for $Br_2(\ell)$.

The boiling process may be written as

$Br_2(\ell) \leftrightharpoons Br_2(g)$
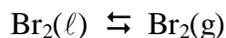
At the normal boiling point $\Delta G^\circ_{rxn} = 0$. The temperature at which this occurs is approximately

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

$\Delta H^\circ_{rxn} = [\Delta H^\circ_f(Br_2(g))] - [\Delta H^\circ_f Br_2(\ell))]$

$= [(30.91)] - [0] = 30.91\ \text{kJ/mol}$

$\Delta S^\circ_{rxn} = [S^\circ(Br_2(g))] - [S^\circ(Br_2(\ell))]$

$= [245.5] - [152.23] = 93.3\ \text{J/mol·K}$

$T^\circ_{vap} \cong (30910.\ \text{J/mol})/(93.3\ \text{J/mol·K}) = 331.\ \text{K} = 58.\ °C$

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

22) 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. °C and p = 1.000 atm. Based on this information find ΔH°_{vap}, ΔG°_{vap}, and ΔS°_{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 $\Delta G^\circ_{vap} = 0$.

The number of moles of n-hexane is

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

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

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

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

$$\Delta G^\circ_{vap} = 0 = \Delta H^\circ_{vap} - T \, \Delta S^\circ_{vap}$$

and so $\Delta H^\circ_{vap} = T \, \Delta S^\circ_{vap}$

Therefore $\quad \Delta S^\circ_{vap} = \dfrac{\Delta H^\circ_{vap}}{T} = \dfrac{28860 \text{ J/mol}}{342. \text{ K}} = 84.4 \text{ J/mol·K}$

23) The normal melting point for ammonia (NH_3) is - 77.7 °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 °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 °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 °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 14.