Problems, Chapter 14 (without solutions)

1) (14.8) How does the entropy of a system change for each of the following processes? a) A solid melts; b) A liquid freezes; c) A liquid boils; d) A vapor is converted into a solid; e) A vapor condenses into a liquid; f) A solid sublimes; g) A molecular solid dissolves in water

2) (14.10) Predict whether the entropy change is positive or negative for each of the following processes. Give the reasons for your predictions.

a) $2\ KClO_4(s) \rightarrow 2\ KClO_3(s) + O_2(g)$

b) $H_2O(g) \rightarrow H_2O(\ell)$

c) $2\ Na(s) + 2\ H_2O(\ell) \rightarrow 2\ NaOH(aq) + H_2(g)$

d) $N_2(g) \rightarrow 2\ N(g)$

3) 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.

4) 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) $NaNO_3(s)$ or $NaNO_3(aq)$; 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 $SO_2(g)$

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

6) (14.14) Using the data in Appendix 2, calculate the standard entropy change for the following reactions at T = 25. °C.

a) $S(s,rhombic) + O_2(g) \rightarrow SO_2(g)$

b) $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

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

7) (14.30) Calculate $\Delta G°_{rxn}$ for each of the following reactions at 25. °C.

a) $N_2(g) + O_2(g) \rightarrow 2\ NO(g)$

b) $H_2O(\ell) \rightarrow H_2O(g)$

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

8) 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.

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.

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

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.

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?

9) 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).

10) 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?

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

11) 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

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

12) 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 for this problem are found in Appendix 2.

a) $2\ CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

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

13) Using the data in Appendix 2, predict the normal boiling point temperature for $Br_2(\ell)$.

14) 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 $\Delta H°_{vap}$, $\Delta G°_{vap}$, and $\Delta S°_{vap}$ for this process and the conditions that are given in the problem.

15 (14.41) 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; b) ammonia melts at - 77.7 °C; c) ammonia melts at - 100.0 °C.