TEXTBOOK HOMEWORK

Note: In various textbook questions, the author assumes that you will look up the data (e.g. ΔH_f^o, ΔG_f^o, and S^o) in Appendix B in working the problem. You will, of course, be given the necessary data on your tests. However, you are responsible to know that $\Delta H_f^o = 0$ and $\Delta G_f^o = 0$ for elements in their standard states.

20.14 (a) $\Delta S^o > 0$ because a gas molecule is produced from condensed phase reactants

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(b) $\Delta S^o < 0$ because there are fewer moles of gas on the product side of the reaction

(c) $\Delta S^o > 0$ because a gas phase product from condensed phase reactants

20.16 (a) $\Delta S^o > 0$ because the decrease in pressure increases the volume of the gas, which which increases its disorder.

(b) $\Delta S^o < 0$ because aqueous (dissolved) product molecules have less disorder than the reactant molecules in the gas phase.

(c) $\Delta S^o > 0$ because gas phase product molecules have more disorder than the aqueous (dissolved) reactant molecules.

20.21 (a) Ribose < Glucose < Sucrose because disorder increases with great molecule complexity.

(b) $CaCO_3 < CaO + CO_2 < Ca + C + (3/2) O_2$ because disorder increases with higher number of gas phase molecules.

(c) $SF_4(g) < SF_6(g) < S_2F_{10}(g)$ because, within a given phase, disorder increases with greater molecular complexity.

20.28 Molar entropies taken from Appendix B.
(a) Predict $\Delta S^o < 0$ because less moles of product gas molecules.

$$\Delta S^o = \left[1S^o(N_2O) + 1S^o(NO_2)\right] - \left[3S^o(NO)\right]$$
$$= \left[1(219.7) + 1(239.9)\right] - \left[3(210.65)\right] = -172.35 \approx -172.4\,J/K$$

(b) Difficult Prediction. However, can guess $\lambda S^o > 0$ because $H_2O(g)$ product is more complex than $H_2(g)$. This difficult guess would not be given on a test.
$$\Delta S^o = \left[2S^o(Fe) + 3S^o(H_2O)\right] - \left[3S^o(H_2) + 1S^o(Fe_2O_3)\right]$$
$$= \left[2(27.3) + 3(188.72)\right] - \left[3(130.6) + 1(87.4)\right] = +141.56 \approx +141.6\,J/K$$

(c) Predict $\lambda S^o < 0$ because have gas on left, but not on right.
$$\Delta S^o = \left[1S^o(P_4O_{10})\right] - \left[1S^o(P_4) + 5S^o(O_2)\right]$$
$$= \left[1(229.)\right] - \left[1(41.1) + 5(205.0)\right] = -837.1 \approx -837\,J/K$$

20.40 Gibbs Free Energies of Formation taken from Appendix B. However, you should know that λG_f^o of an element in its standard state is zero (0).

(a)
$$\Delta G^o = \left[2\Delta G_f^o(MgO)\right] - \left[2\Delta G_f^o(Mg) + 1\Delta G_f^o(O_2)\right]$$
$$= \left[2(-569.0)\right] - \left[2(0) + 1(0)\right] = -1138.0\,kJ$$

(b)
$$\Delta G^o = \left[2\Delta G_f^o(CO_2) + 4\Delta G_f^o(H_2O)\right] - \left[2\Delta G_f^o(CH_3OH) + 3\Delta G_f^o(O_2)\right]$$
$$= \left[2(-394.4) + 4(-228.6)\right] - \left[2(-161.9) + 3(0)\right] = -1379.4\,kJ$$

(c)
$$\Delta G^o = \left[1\Delta G_f^o(BaCO_3)\right] - \left[1\Delta G_f^o(BaO) + 1\Delta G_f^o(CO_2)\right]$$
$$= \left[1(-1139.)\right] - \left[1(-520.4) + 1(-394.4)\right] = -224.2\,kJ$$

20.46 Values of λH_f^o and S^o taken from Appendix B

(a)
$$\Delta H^o = \left[1\Delta H_f^o(CO) + 2\Delta H_f^o(H_2)\right] - \left[1\Delta H_f^o(CH_3OH)\right]$$
$$= \left[1(-110.5) + 2(0)\right] - \left[1(-201.2)\right] = +90.7\,kJ$$

$$\Delta S^o = \left[1S^o(CO) + S^o(H_2)\right] - \left[1S^o(CH_3OH)\right]$$
$$= \left[1(197.5) + 2(130.6)\right] - \left[1(238)\right] = 220.7\,J/K$$
$$= 0.2207\,kJ/K$$

(b) Note: To maintain consistent units, I have converted ΔS^o to kJ/K

One may instead convert ΔG^o to J.

(1) T = 28 °C = 301 K
$$\Delta G^o = \Delta H^o - T\Delta S^o = +90.7\,kJ - (301\,K)(0.2207\,kJ\,/\,K) = +24.3\,kJ$$

(2) T = 128 °C = 401 K
$$\Delta G^o = \Delta H^o - T\Delta S^o = +90.7\,kJ - (401\,K)(0.2207\,kJ\,/\,K) = +2.2\,kJ$$

(3) T = 228 °C = 501 K
$$\Delta G^o = \Delta H^o - T\Delta S^o = +90.7\,kJ - (501\,K)(0.2207\,kJ\,/\,K) = -19.9\,kJ$$

(c) For the reactants and products in their standard states, the reaction is non-spontaneous at 28 °C, near equilibrium at 128 °C and spontaneous at 228 °C. This illustrates that the effect of positive ΔS^o in driving a reaction towards spontaneity becomes more important at higher temperatures.

20.48 Let's first calculate ΔH^o and ΔS^o for the reaction $Br_2(l)\ \rightleftharpoons\ Br_2(g)$ from data in Appendix B.

$$\Delta H^o = \Delta H_f^o[Br_2(g)] - \Delta H_f^o[Br_2(l)]$$
$$= 30.91\,kJ - 0\,kJ = 30.91\,kJ$$

Note that $\Delta H_f^o[Br_2(l)] = 0$ because that is the most stable form of bromine at 1 atm and 25 °C.

$$\Delta S^o = S^o[Br_2(g)] - S^o[Br_2(l)]$$
$$= 245.38\,J\,/\,K - 152.23\,J\,/\,K = 93.15\,J\,/\,K$$
$$= 0.09315\,kJ\,/\,K$$

Note that (1) unlike the enthalpy of formation, the absolute molar entropy of $Br_2(l) \neq 0$ and (2) we have converted ΔS^o to kJ/K to have consistent units. We could have just as easily converted ΔH^o to J.

We determine the normal boiling point by recognizing that liquid and gas are in

equilibrium at the substance's normal boiling point. Therefore, $\Delta G^o = 0$ at this temperature.

$$\Delta G^o = \Delta H^o - T\Delta S^o = 0$$

$$T = \frac{\Delta H^o}{\Delta S^o} = \frac{30.91\,kJ}{0.09315\,kJ\,/\,K} = 332\,K - 273 = 59\,^oC$$

20.51 Values of ΔH_f^o and S^o taken from Appendix B

$$\Delta H^o = \left[2\,\Delta H_f^o(C_2H_5OH) + 2\,\Delta H_f^o(CO)\right] - \left[1\Delta H_f^o(C_6H_{12}O_6)\right]$$
$$= \left[2(-277.63) + 2(-393.5)\right] - \left[1(-1273.3)\right] = -68.96\,kJ \approx -69.0\,kJ$$

$$\Delta S^o = \left[2\,S^o(C_2H_5OH) + 2\,S^o(CO)\right] - \left[1S^o(C_6H_{12}O_6)\right]$$
$$= \left[2(161) + 2(213.7)\right] - \left[1(212.1)\right] = +537.3\,J\,/\,K \quad \backslash$$
$$= 0.5373\,kJ\,/\,K$$

$$\Delta G^o = \Delta H^o - T\Delta S^o = -69.0\,kJ - (298\,K)(0.5373\,kJ\,/\,K) = -229.1\,kJ$$

No, Temperature will have no effect on reaction spontaneity. That's because a reaction with $\Delta H^o < 0$ and $\Delta S^o > 0$ will yield $\Delta G^o < 0$ at all temperatures.

20.56 T = 298 K

(a)
$$\Delta G^o = \left[1\Delta G_f^o(NO_2)\right] - \left[1\Delta G_f^o(NO) + (1/2)\Delta G_f^o(O_2)\right]$$
$$= \left[1(51)\right] - \left[1(86.6) + (1/2)(0)\right] = -35.6\,kJ = -3.56x10^4\,J$$

$$\ln(K) = -\frac{\Delta G^o}{RT} = -\frac{-(3.56x10^4\,J\,/\,mol}{(8.31\,J\,/\,mol - K)(298\,K)} = +14.38$$

$$K = e^{+14.38} = 1.75x10^6$$

(b)
$$\Delta G^o = \left[1\Delta G_f^o(H_2) + 1\Delta G_f^o(Cl_2)\right] - \left[2\,\Delta G_f^o(HCl)\right]$$
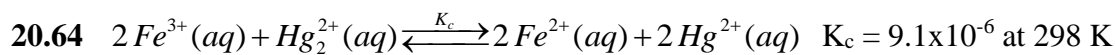$$= \left[1(0) + 1(0)\right] - \left[2(-95.3)\right] = +190.6\,kJ\,/\,mol = +1.906x10^5\,J\,/\,mol$$

$$\ln(K) = -\frac{\Delta G^o}{RT} = -\frac{+1.906x10^5 \, J/mol}{(8.31 \, J/mol-K)(298\,K)} = -76.97$$

$$K = e^{-76.97} = 3.7x10^{-34}$$

(c) $\Delta G^o = \left[2\Delta G_f^o(CO)\right] - \left[2\Delta G_f^o(C-graph) + 1\Delta G_f^o(O_2)\right]$

$= \left[2(-137.2)\right] - \left[2(0) + 1(0)\right] = -274.4 \, kJ/mol = -2.744x10^5 \, J/mol$

$$\ln(K) = -\frac{\Delta G^o}{RT} = -\frac{-2.744x10^5 \, J/mol}{(8.31 \, J/mol-K)(298\,K)} = +110.81$$

$$K = e^{+110.81} = 1.3x10^{48}$$

20.64 $2\,Fe^{3+}(aq) + Hg_2^{2+}(aq) \underset{}{\overset{K_c}{\rightleftharpoons}} 2\,Fe^{2+}(aq) + 2\,Hg^{2+}(aq)$ $K_c = 9.1 \times 10^{-6}$ at 298 K

(a) $\Delta G^o = -RT\ln(K_c) = -(8.31 \, J/mol-K)(298\,K)\ln\left(9.1x10^{-6}\right)$

$= 2.87x10^4 \, J/mol = 28.7 \, kJ/mol$

(b) If reactants and products are in the standard-state (c=1.00 M), then ΔG = ΔG°.

Because ΔG° > 0, the reaction with standard-state concentrations is NOT spontaneous as written. Instead, it is spontaneous in the opposite direct. The reaction will move to the left.
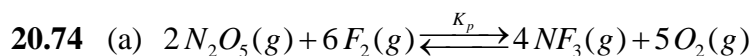
(c) $Q = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2^{2+}]} = \frac{(0.01)^2(0.025)^2}{(0.20)^2(0.01)} = 1.563x10^{-4}$

$\Delta G = \Delta G^o + RT\ln(Q) = 2.87x10^4 \, J/mol + (8.31 \, J/mol-K)(298\,K)\ln(1.563x10^{-4})$

$= 2.87x10^4 \, J/mol + (-2.17x10^4 \, J/mol) = 7.0x10^3 \, J/mol = 7.0 \, kJ/mol$

Note that because ΔG > 0, reactant will move to left at the initial concentrations given.

However, if the product concentrations are each increased by a factor of 10, for example, then one gets Q=1.563x10⁻⁷, and ΔG = +2.87x10⁴ +(-3.88x10⁴) = -1.0x10⁴ J/mol. Under these initial conditions, the reaction would move to the right.

20.74 (a) $2\,N_2O_5(g) + 6\,F_2(g) \underset{}{\overset{K_p}{\rightleftharpoons}} 4\,NF_3(g) + 5\,O_2(g)$

(b) Values of ΔG_f° are taken from Appendix B

$\Delta G^o = \left[4\Delta G_f^o(NF_3) + 5\Delta G_f^o(O_2)\right] - \left[2\Delta G_f^o(N_2O_5) + 6\Delta G_f^o(F_2)\right]$

$= \left[4(-83.3) + 5(0)\right] - \left[2(118) + 6(0)\right] = -569.2 \, kJ = -5.692x10^5 \, J/mol$

(c) $Q = \dfrac{P_{NF_3}^4 P_{O_2}^5}{P_{N_2O_5}^2 P_{F_2}^6} = \dfrac{(0.25)^4 (0.50)^5}{(0.20)^2 (0.20)^6} = 47.68$

$\Delta G = \Delta G^o + RT \ln(Q) = -5.692x10^5 \, J / mol + (8.31 \, J / mol - K)(298 \, K) \ln(47.68)$

$= -5.692x10^5 \, J / mol + (+5.97x10^3 \, J / mol) = -5.60x10^5 \, J / mol = -560. \, kJ / mol$