CHAPTER 19

SPONTANEOUS CHANGE: ENTROPY AND GIBBS ENERGY

PRACTICE EXAMPLES

1A **(E)** In general, $\Delta S > 0$ if $\Delta n_{\text{gas}} > 0$. This is because gases are very dispersed compared to liquids or solids; (gases possess large entropies). Recall that Δn_{gas} is the difference between the sum of the stoichiometric coefficients of the gaseous products and a similar sum for the reactants.

(a) $\Delta n_{\text{gas}} = 2 + 0 - (2 + 1) = -1$. One mole of gas is consumed here. We predict $\Delta S < 0$.

(b) $\Delta n_{\text{gas}} = 1 + 0 - 0 = +1$. Since one mole of gas is produced, we predict $\Delta S > 0$.

1B **(E) (a)** The outcome is uncertain in the reaction between ZnS(s) and $Ag_2O(s)$. We have used Δn_{gas} to estimate the sign of entropy change. There is no gas involved in this reaction and thus our prediction is uncertain.

(b) In the chlor-alkali process the entropy increases because two moles of gas have formed where none were originally present ($\Delta n_{gas} = (1 + 1 + 0) - (0 + 0) = 2$

2A **(E)** For a vaporization, $\Delta G^\circ_{\text{vap}} = 0 = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}}$. Thus, $\Delta S^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} / T_{\text{vap}}$.

We substitute the given values. $\Delta S^\circ_{\text{vap}} = \dfrac{\Delta H^\circ_{\text{vap}}}{T_{\text{vap}}} = \dfrac{20.2 \text{ kJ mol}^{-1}}{(-29.79 + 273.15)\text{ K}} = 83.0 \text{ J mol}^{-1} \text{ K}^{-1}$

2B **(E)** For a phase change, $\Delta G^\circ_{\text{tr}} = 0 = \Delta H^\circ_{\text{tr}} - T\Delta S^\circ_{\text{tr}}$. Thus, $\Delta H^\circ_{\text{tr}} = T\Delta S^\circ_{\text{tr}}$. We substitute in the given values. $\Delta H^\circ_{\text{tr}} = T\Delta S^\circ_{\text{tr}} = (95.5 + 273.2)\text{ K} \times 1.09 \text{ J mol}^{-1} \text{ K}^{-1} = 402 \text{ J/mol}$

3A **(M)** The entropy change for the reaction is expressed in terms of the standard entropies of the reagents.

$$\Delta S^\circ = 2S^\circ[NH_3(g)] - S^\circ[N_2(g)] - 3S^\circ[H_2(g)]$$
$$= 2\times192.5 \text{ J mol}^{-1}\text{K}^{-1} - 191.6 \text{ J mol}^{-1} \text{ K}^{-1} - 3\times130.7 \text{ J mol}^{-1} \text{ K}^{-1} = -198.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

Thus to form *one* mole of $NH_3(g)$, the standard entropy change is $-99.4 \text{ J mol}^{-1} \text{ K}^{-1}$

3B **(M)** The entropy change for the reaction is expressed in terms of the standard entropies of the reagents.

$$\Delta S^{o} = S^{o}[NO(g)] + S^{o}[NO_2(g)] - S^{o}[N_2O_3(g)]$$

$$138.5 \text{ J mol}^{-1} \text{ K}^{-1} = 210.8 \text{ J mol}^{-1} \text{ K}^{-1} + 240.1 \text{ J mol}^{-1} \text{ K}^{-1} - S^{\circ}[N_2O_3(g)]$$

$$= 450.9 \text{ J mol}^{-1} \text{ K}^{-1} - S^{\circ}[N_2O_3(g)]$$

$$S^{\circ}[N_2O_3(g)] = 450.9 \text{ J mol}^{-1} \text{ K}^{-1} - 138.5 \text{ J mol}^{-1} \text{ K}^{-1} = 312.4 \text{ J mol}^{-1} \text{ K}$$

4A **(E) (a)** Because $\Delta n_{gas} = 2 - (1+3) = -2$ for the synthesis of ammonia, we would predict $\Delta S < 0$ for the reaction. We already know that $\Delta H < 0$. Thus, the reaction falls into case 2, namely, a reaction that is spontaneous at low temperatures and non-spontaneous at high temperatures.

(b) For the formation of ethylene $\Delta n_{gas} = 1 - (2+0) = -1$ and thus $\Delta S < 0$. We are given that $\Delta H > 0$ and, thus, this reaction corresponds to case 4, namely, a reaction that is non-spontaneous at all temperatures.

4B **(E) (a)** Because $\Delta n_{gas} = +1$ for the decomposition of calcium carbonate, we would predict $\Delta S > 0$ for the reaction, favoring the reaction at high temperatures. High temperatures also favor this endothermic $(\Delta H^{o} > 0)$ reaction.

(b) The "roasting" of ZnS(s) has $\Delta n_{gas} = 2 - 3 = -1$ and, thus, $\Delta S < 0$. We are given that $\Delta H < 0$; thus, this reaction corresponds to case 2, namely, a reaction that is spontaneous at low temperatures, and non-spontaneous at high ones.

5A **(E)** The expression $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ is used with $T = 298.15$ K.

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -1648 \text{ kJ} - 298.15 \text{ K} \times (-549.3 \text{ J K}^{-1}) \times (1 \text{ kJ} / 1000 \text{ J})$$

$$= -1648 \text{ kJ} + 163.8 \text{ kJ} = -1484 \text{ kJ}$$

5B **(M)** We just need to substitute values from Appendix D into the supplied expression.

$$\Delta G^{\circ} = 2\Delta G_f^{\circ}[NO_2(g)] - 2\Delta G_f^{\circ}[NO(g)] - \Delta G_f^{\circ}[O_2(g)]$$

$$= 2 \times 51.31 \text{ kJ mol}^{-1} - 2 \times 86.55 \text{ kJ mol}^{-1} - 0.00 \text{ kJ mol}^{-1} = -70.48 \text{ kJ mol}^{-1}$$

6A **(M)** Pressures of gases and molarities of solutes in aqueous solution appear in thermodynamic equilibrium constant expressions. Pure solids and liquids (including solvents) do not appear.

(a) $K = \dfrac{P_{SiCl_4}}{P_{Cl_2}^2} = K_p$ **(b)** $K = \dfrac{[HOCl][H^+][Cl^-]}{P_{Cl_2}}$

$K = K_p$ for (a) because all terms in the K expression are gas pressures.

6B **(M)** We need the balanced chemical equation in order to write the equilibrium constant expression. We start by translating names into formulas.

$$\text{PbS(s)} + \text{HNO}_3\text{(aq)} \rightarrow \text{Pb(NO}_3\text{)}_2\text{(aq)} + \text{S(s)} + \text{NO(g)}$$

The equation then is balanced with the ion-electron method.

$$\text{oxidation}: \{\text{PbS(s)} \rightarrow \text{Pb}^{2+}\text{(aq)} + \text{S(s)} + 2e^- \qquad \} \times 3$$

$$\text{reduction}: \{\text{NO}_3^-\text{(aq)} + 4\text{H}^+\text{(aq)} + 3e^- \rightarrow \text{NO(g)} + 2\text{H}_2\text{O(l)} \quad \} \times 2$$

$$\text{net ionic}: 3\,\text{PbS(s)} + 2\text{NO}_3^-\text{(aq)} + 8\text{H}^+\text{(aq)} \rightarrow 3\text{Pb}^{2+}\text{(aq)} + 3\text{S(s)} + 2\text{NO(g)} + 4\text{H}_2\text{O(l)}$$

In writing the thermodynamic equilibrium constant, recall that neither pure solids (PbS(s) and S(s)) nor pure liquids $(H_2O(l))$ appear in the thermodynamic equilibrium constant expression. Note also that we have written $H^+(aq)$ here for brevity even though we understand that $H_3O^+(aq)$ is the acidic species in aqueous solution.

$$K = \frac{[Pb^{2+}]^3 p_{NO}^2}{[NO_3^-]^2[H^+]^8}$$

7A **(M)** Since the reaction is taking place at 298.15 K, we can use standard free energies of formation to calculate the standard free energy change for the reaction:

$$\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)}$$

$$\Delta G^\circ = 2\Delta G_f^\circ[\text{NO}_2\text{(g)}] - \Delta G_f^\circ[\text{N}_2\text{O}_4\text{(g)}] = 2\times 51.31\text{ kJ/mol} - 97.89\text{ kJ/mol} = +4.73\text{ kJ}$$

$\Delta G^o{}_{rxn}$ = +4.73 kJ . Thus, the forward reaction is non-spontaneous as written at 298.15 K.

7B **(M)** In order to answer this question we must calculate the reaction quotient and compare it to the K_p value for the reaction:

$$\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)} \qquad Q_p = \frac{(0.5)^2}{0.5} = 0.5$$

0.5 bar 0.5 bar

$\Delta G^o{}_{rxn}$ = +4.73 kJ = $-RT\ln K_p$; 4.73 kJ/mol = $-(8.3145 \times 10^{-3}$ kJ/K·mol)(298.15 K)$\ln K_p$

Therefore, K_p = 0.148. Since Q_p is greater than K_p, we can conclude that the reverse reaction will proceed spontaneously, i.e. NO_2 will spontaneously convert into N_2O_4.

8A **(D)** We first determine the value of ΔG° and then set $\Delta G^\circ = -RT\ln K$ to determine K.

$$\Delta G = \Delta G_f^\circ[\text{Ag}^+\text{(aq)}] + \Delta G_f^\circ[\text{I}^-\text{(aq)}] - \Delta G_f^\circ[\text{AgI(s)}]$$

$$= [(77.11 - 51.57) - (-66.19)]\text{ kJ/mol} = +91.73$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = -\frac{-91.73 \text{ kJ / mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -37.00$$

$K = e^{-37.00} = 8.5 \times 10^{-17}$

This is precisely equal to the value for the K_{sp} of AgI listed in Appendix D.

8B **(D)** We begin by translating names into formulas.

$MnO_2(s) + HCl(aq) \rightarrow Mn^{2+}(aq) + Cl_2(aq)$ Then we produce a balanced net ionic equation with the ion-electron method.

$$\text{oxidation}: 2\,Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

$$\text{reduction}: MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$$

$$\text{net ionic}: MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$

Next we determine the value of ΔG° for the reaction and then the value of *K*.

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\left[Mn^{2+}(aq)\right] + \Delta G_f^\circ\left[Cl_2(g)\right] + 2\Delta G_f^\circ\left[H_2O(l)\right] \\ &\quad - \Delta G_f^\circ\left[MnO_2(s)\right] - 4\Delta G_f^\circ\left[H^+(aq)\right] - 2\Delta G_f^\circ\left[Cl^-(aq)\right] \\ &= -228.1 \text{ kJ} + 0.0 \text{ kJ} + 2\times(-237.1 \text{ kJ}) \\ &\quad -(-465.1 \text{ kJ}) - 4\times 0.0 \text{ kJ} - 2\times(-131.2 \text{ kJ}) = +25.2 \text{ kJ}\end{aligned}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(+25.2\times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15\ K} = -10.1\underline{7} \qquad K = e^{-10.2} = 4\times 10^{-5}$$

Because the value of K is so much smaller than unity, we do not expect an appreciable forward reaction.

9A **(M)** We set equal the two expressions for ΔG° and solve for the absolute temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \qquad \Delta H^\circ = T\Delta S^\circ - RT\ln K = T\left(\Delta S^\circ - R\ln K\right)$$

$$T = \frac{\Delta H^\text{o}}{\Delta S^\text{o} - R\ln K} = \frac{-114.1\times 10^3 \text{ J/mol}}{\left[-146.4 - 8.3145\ \ln(150)\right]\text{J mol}^{-1} \text{ K}^{-1}} = 607 \text{ K}$$

9B **(D)** We expect the value of the equilibrium constant to increase as the temperature decreases since this is an exothermic reaction and exothermic reactions will have a larger equilibrium constant (shift right to form more products), as the temperature decreases. Thus, we expect K to be larger than 1000, which is its value at 4.3×10^2 K.

(a) The value of the equilibrium constant at 25° C is obtained directly from the value of ΔG^o, since that value is also for 25°C. Note:

$$\Delta G^\text{o} = \Delta H^\text{o} - T\Delta S^\text{o} = -77.1 \text{ kJ/mol} - 298.15 \text{ K}\left(-0.1213 \text{ kJ/mol}\cdot\text{K}\right) = -40.9 \text{ kJ/mol}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-40.9\times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\times 298.15 \text{ K}} = 16.5 \qquad K = e^{+16.5} = 1.5\times 10^7$$

(b) First, we solve for ΔG^{o} at $75^{\circ}\text{C} = 348\ \text{K}$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -77.1\ \frac{\text{kJ}}{\text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} - \left(348.15\ \text{K} \times \left(-121.3\frac{\text{J}}{\text{mol K}}\right)\right)$$

$$= -34.87 \times 10^{3}\ \text{J/mol}$$

Then we use this value to obtain the value of the equilibrium constant, as in part (a).

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-(-34.87 \times 10^{3}\ \text{J mol}^{-1})}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 348.15\ \text{K}} = 12.05 \qquad K = e^{+12.05} = 1.7 \times 10^{5}$$

As expected, K for this exothermic reaction decreases with increasing temperature.

10A **(M)** We use the value of $K_{\text{p}} = 9.1 \times 10^{2}$ at 800 K and $\Delta H^{o} = -1.8 \times 10^{5}\ \text{J / mol}$, for the appropriate terms, in the van't Hoff equation.

$$\ln \frac{5.8 \times 10^{-2}}{9.1 \times 10^{2}} = \frac{-1.8 \times 10^{5}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{800\ \text{K}} - \frac{1}{T\ \text{K}}\right) = -9.66; \quad \frac{1}{T} = \frac{1}{800} - \frac{9.66 \times 8.3145}{1.8 \times 10^{5}}$$

$$1/T = 1.25 \times 10^{-3} - 4.5 \times 10^{-4} = 8.0 \times 10^{-4} \qquad T = 1240\ \text{K} \approx 970^{\circ}\text{C}$$

This temperature is an estimate because it is an extrapolated point beyond the range of the data supplied.

10B **(M)** The temperature we are considering is $235^{\circ}\text{C} = 508\ \text{K}$. We substitute the value of $K_{\text{p}} = 9.1 \times 10^{2}$ at 800 K and $\Delta H^{o} = -1.8 \times 10^{5}$ J/mol, for the appropriate terms, in the van't Hoff equation.

$$\ln \frac{K_{\text{p}}}{9.1 \times 10^{2}} = \frac{-1.8 \times 10^{5}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{800\ \text{K}} - \frac{1}{508\ \text{K}}\right) = +15_{.6}; \quad \frac{K_{\text{p}}}{9.1 \times 10^{2}} = e^{+15.6} = 6 \times 10^{6}$$

$$K_{\text{p}} = 6 \times 10^{6} \times 9.1 \times 10^{2} = 5 \times 10^{9}$$

INTEGRATIVE EXAMPLE

11A **(D)** The value of ΔG^{o} can be calculated by finding the value of the equilibrium constant K_p at 25 ^{o}C. The equilibrium constant for the reaction is simply given by $K_p = p\{N_2O_5(g)\}$. The vapor pressure of $N_2O_5(g)$ can be determined from the Clausius-Clapeyron eqution, which is a specialized version of the van’t Hoff equation.

Stepwise approach:

We first determine the value of ΔH_{sub}.

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \ln \frac{760\ \text{mmHg}}{100\ \text{mmHg}} = \frac{\Delta H_{sub}}{8.314\text{Jmol}^{-1}\text{K}^{-1}}\left(\frac{1}{7.5 + 273.15} - \frac{1}{32.4 + 273.15}\right)$$

$$\Delta H_{sub} = \frac{2.028}{3.49 \times 10^{-5}} = 5.81 \times 10^{4}\ \text{J/mol}$$

Using the same formula, we can now calculate the vapor pressure of N_2O_5 at 25 ^{o}C.

$$\ln\frac{p_3}{100\text{ mmHg}} = \frac{5.81\times10^4\text{ J/mol}}{8.314\text{Jmol}^{-1}\text{K}^{-1}}\left(\frac{1}{280.7}-\frac{1}{298.2}\right) = 1.46 \Rightarrow \frac{p_3}{100\text{ mmHg}} = e^{1.46} = 4.31$$

$$p_3 = 4.31\times100\text{mmHg}\times\frac{1\text{ atm}}{760\text{ mmHg}} = 0.567\text{atm} = K_p$$

$$\Delta G^o = -RT\ln K_p = -(8.314\times10^{-3}\text{kJmol}^{-1}\text{K}^{-1}\times298.15\text{K})\ln(0.567) = 1.42\text{kJ/mol}$$

Conversion pathway approach:

$$\ln\frac{p_2}{p_1} = \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow \Delta H_{sub} = \frac{R\ln\frac{p_2}{p_1}}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\Delta H_{sub} = \frac{8.314\text{Jmol}^{-1}\text{K}^{-1}\times\ln\frac{760\text{mmHg}}{100\text{mmHg}}}{\left(\frac{1}{7.5+273.15}-\frac{1}{32.4+273.15}\right)} = \frac{2.028}{3.49\times10^{-5}}\text{Jmol}^{-1} = 5.81\times10^4\text{ Jmol}^{-1}$$

$$\ln\frac{p_3}{p_1} = \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow p_3 = p_1 e^{\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$p_3 = 100mmHg\times e^{\frac{5.81\times10^4\text{ Jmol}^{-1}}{8.314\text{JK}^{-1}\text{mol}^{-1}}\left(\frac{1}{280.7}-\frac{1}{298.2}\right)\text{K}^{-1}} = 431\text{mmHg}\times\frac{1\text{atm}}{760\text{mmHg}} = 0.567\text{atm} = K_p$$

$$\Delta G^o = -RT\ln K_p = -(8.314\times10^{-3}\text{kJmol}^{-1}\text{K}^{-1}\times298.15\text{K})\ln(0.567) = 1.42\text{kJ/mol}$$

11B **(D)** The standard entropy change for the reaction (ΔS^o) can be calculated from the known values of ΔH^o and ΔG^o.

Stepwise approach:

$$\Delta G^o = \Delta H^o - T\Delta S^o \Rightarrow \Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-454.8\text{kJmol}^{-1} - (-323.1\text{kJmol}^{-1})}{298.15\text{K}} = -441.7\text{JK}^{-1}\text{mol}^{-1}$$

Plausible chemical reaction for the production of ethylene glycol can also be written as:

$$2C(s)+3H_2(g)+O_2(g) \longrightarrow CH_2OHCH_2OH(l)$$

Since $\Delta S^o = \sum\{S^o_{products}\} - \sum\{S^o_{reac\tan ts}\}$ it follows that:

$$\Delta S^o_{rxn} = S^o(CH_2OHCH_2OH(l)) - [2\times S^o(C(s)) + 3\times S^o(H_2(g)) + S^o(O_2(g))]$$

$$-441.7\text{JK}^{-1}\text{mol}^{-1} = S^o(CH_2OHCH_2OH(l)) - [2\times5.74\text{JK}^{-1}\text{mol}^{-1} + 3\times130.7\text{JK}^{-1}\text{mol}^{-1} + 205.1\text{JK}^{-1}\text{mol}^{-1}]$$

$$S^o(CH_2OHCH_2OH(l)) = -441.7\text{JK}^{-1}\text{mol}^{-1} + 608.68\text{JK}^{-1}\text{mol}^{-1} = 167\text{JK}^{-1}\text{mol}^{-1}$$

Conversion pathway approach:

$$\Delta G^o = \Delta H^o - T\Delta S^o \Rightarrow \Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-454.8\text{kJmol}^{-1} - (-323.1\text{kJmol}^{-1})}{298.15\text{K}} = -441.7\text{JK}^{-1}\text{mol}^{-1}$$

$$-441.7\text{JK}^{-1}\text{mol}^{-1} = S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)}) - [2 \times 5.74\text{JK}^{-1}\text{mol}^{-1} + 3 \times 130.7\text{JK}^{-1}\text{mol}^{-1} + 205.1\text{JK}^{-1}\text{mol}^{-1}]$$

$$S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)}) = -441.7\text{JK}^{-1}\text{mol}^{-1} + 608.68\text{JK}^{-1}\text{mol}^{-1} = 167\text{JK}^{-1}\text{mol}^{-1}$$

EXERCISES

Spontaneous Change and Entropy

1. **(E) (a)** The freezing of ethanol involves a *decrease* in the entropy of the system. There is a reduction in mobility and in the number of forms in which their energy can be stored when they leave the solution and arrange themselves into a crystalline state.

(b) The sublimation of dry ice involves converting a solid that has little mobility into a highly dispersed vapor which has a number of ways in which energy can be stored (rotational, translational). Thus, the entropy of the system *increases* substantially.

(c) The burning of rocket fuel involves converting a liquid fuel into the highly dispersed mixture of the gaseous combustion products. The entropy of the system *increases* substantially.

2. **(E)** Although there is a substantial change in entropy involved in **(a)** changing H_2O(1iq., 1 atm) to H_2O(g, 1 atm), it is not as large as **(c)** converting the liquid to a gas at 10 mmHg. The gas is more dispersed, (less ordered), at lower pressures. In **(b),** if we start with a solid and convert it to a gas at the lower pressure, the entropy change should be even larger, since a solid is more ordered (concentrated) than a liquid. Thus, in order of increasing ΔS, the processes are: **(a)** $<$ **(c)** $<$ **(b)**.

3. **(E)** The first law of thermodynamics states that energy is neither created nor destroyed (thus, “The energy of the universe is constant”). A consequence of the second law of thermodynamics is that entropy of the universe increases for all spontaneous, that is, naturally occurring, processes (and therefore, “the entropy of the universe increases toward a maximum”).

4. **(E)** When pollutants are produced they are usually dispersed throughout the environment. These pollutants thus start in a relatively compact form and end up dispersed throughout a large volume mixed with many other substances. The pollutants are highly dispersed, thus, they have a high entropy. Returning them to their original compact form requires reducing this entropy, which is a highly non-spontaneous process. If we have had enough foresight to retain these pollutants in a reasonably compact form, such as disposing of them in a *secure* landfill, rather than dispersing them in the atmosphere or in rivers and seas, the task of permanently removing them from the environment, and perhaps even converting them to useful forms, would be considerably easier.

5. **(E) (a)** Increase in entropy because a gas has been created from a liquid, a condensed phase.

(b) Decrease in entropy as a condensed phase, a solid, is created from a solid and a gas.

(c) For this reaction we cannot be certain of the entropy change. Even though the number of moles of gas produced is the same as the number that reacted, we cannot conclude that the entropy change is zero because not all gases have the same molar entropy.

(d) $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$ Decrease in entropy since five moles of gas with high entropy become only four moles of gas, with about the same quantity of entropy per mole.

6. **(E) (a)** At 75° C, 1 mol H_2O (g, 1 atm) has a greater entropy than 1 mol H_2O (1iq., 1 atm) since a gas is much more dispersed than a liquid.

(b) $50.0 \text{ g Fe} \times \dfrac{1 \text{ mol Fe}}{55.8 \text{ g Fe}} = 0.896$ mol Fe has a higher entropy than 0.80 mol Fe, both (s) at 1 atm and 5° C, because entropy is an extensive property that depends on the amount of substance present.

(c) 1 mol Br_2 (1iq., 1 atm, 8° C) has a higher entropy than 1 mol Br_2 (s, 1atm, -8° C) because solids are more ordered (concentrated) substances than are liquids, and furthermore, the liquid is at a higher temperature.

(d) 0.312 mol SO_2 (g, 0.110 atm, 32.5° C) has a higher entropy than 0.284 mol O_2 (g, 15.0 atm, 22.3° C) for at least three reasons. First, entropy is an extensive property that depends on the amount of substance present (more moles of SO_2 than O_2). Second, entropy increases with temperature (temperature of SO_2 is greater than that for O_2. Third, entropy is greater at lower pressures (the O_2 has a much higher pressure). Furthermore, entropy generally is higher per mole for more complicated molecules.

7. **(E) (a)** Negative; A liquid (moderate entropy) combines with a solid to form another solid.

(b) Positive; One mole of high entropy gas forms where no gas was present before.

(c) Positive; One mole of high entropy gas forms where no gas was present before.

(d) Uncertain; The number of moles of gaseous products is the same as the number of moles of gaseous reactants.

(e) Negative; Two moles of gas (and a solid) combine to form just one mole of gas.

8. **(M)** The entropy of formation of a compound would be the difference between the absolute entropy of one mole of the compound and the sum of the absolute entropies of the appropriate amounts of the elements constituting the compound, with each species in its most stable form.

Stepwise approach:
It seems as though $CS_2(1)$ would have the highest molar entropy of formation of the compounds listed, since it is the only substance whose formation does not involve the consumption of high entropy gaseous reactants. This prediction can be checked by determining ΔS_f^o values from the data in Appendix D:

(a) $C(\text{graphite}) + 2H_2(g) \rightleftharpoons CH_4(g)$

$$\Delta S_f^o[CH_4(g)] = S^o[CH_4(g)] - S^o[C(\text{graphite})] - 2S^o[H_2(g)]$$
$$= 186.3\ \text{J mol}^{-1}\text{K}^{-1} - 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 2 \times 130.7\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= -80.8\ \text{J mol}^{-1}\text{K}^{-1}$$

(b) $2C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons CH_3CH_2OH(l)$

$$\Delta S_f^o[CH_3CH_2OH(l)] = S^o[CH_3CH_2OH(l)] - 2S^o[C(\text{graphite})] - 3S^o[H_2(g)] - \frac{1}{2}S^o[O_2(g)]$$
$$= 160.7\ \text{J mol}^{-1}\text{K}^{-1} - 2\times 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 3\times 130.7\ \text{J mol}^{-1}\text{K}^{-1} - \tfrac{1}{2}\times 205.1\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= -345.4\ \text{J mol}^{-1}\text{K}^{-1}$$

(c) $C(\text{graphite}) + 2S(\text{rhombic}) \rightleftharpoons CS_2(l)$

$$\Delta S_f^\circ[CS_2(l)] = S^o[CS_2(l)] - S^o[C(\text{graphite})] - 2S^o[S(\text{rhombic})]$$
$$= 151.3\ \text{J mol}^{-1}\ \text{K}^{-1} - 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 2\times 31.80\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= 82.0\ \text{J mol}^{-1}\text{K}^{-1}$$

Conversion pathway approach:
CS_2 would have the highest molar entropy of formation of the compounds listed, because it is the only substance whose formation does not involve the consumption of high entropy gaseous reactants.

(a) $C(\text{graphite}) + 2H_2(g) \rightleftharpoons CH_4(g)$

$$\Delta S_f^o[CH_4(g)] = 186.3\ \text{J mol}^{-1}\text{K}^{-1} - 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 2 \times 130.7\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= -80.8\ \text{J mol}^{-1}\text{K}^{-1}$$

(b) $2C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons CH_3CH_2OH(l)$

$$\Delta S_f^o[CH_3CH_2OH(l)] = (160.7 - 2\times 5.74 - 3\times 130.7 - \tfrac{1}{2}\times 205.1)\text{J mol}^{-1}\text{K}^{-1}$$
$$= -345.4\ \text{J mol}^{-1}\text{K}^{-1}$$

(c) $C(\text{graphite}) + 2S(\text{rhombic}) \rightleftharpoons CS_2(l)$

$$\Delta S_f^\circ[CS_2(l)] = 151.3\ \text{J mol}^{-1}\ \text{K}^{-1} - 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 2\times 31.80\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= 82.0\ \text{J mol}^{-1}\text{K}^{-1}$$

Phase Transitions

9. **(M) (a)** $\Delta H^\circ_{\text{vap}} = \Delta H^\circ_{\text{f}}[\text{H}_2\text{O(g)}] - \Delta H^\circ_{\text{f}}[\text{H}_2\text{O(l)}] = -241.8 \text{ kJ/mol} - (-285.8 \text{ kJ/mol})$
$= +44.0 \text{ kJ/mol}$

$$\Delta S^\circ_{\text{vap}} = S^\circ\left[\text{H}_2\text{O}(\text{g})\right] - S^\circ\left[\text{H}_2\text{O}(\text{l})\right] = 188.8 \text{ J mol}^{-1}\text{ K}^{-1} - 69.91 \text{ J mol}^{-1}\text{K}^{-1}$$
$$= 118.9 \text{ J mol}^{-1}\text{K}^{-1}$$

There is an alternate, but incorrect, method of obtaining $\Delta S^\circ_{\text{vap}}$.

$$\Delta S^\circ_{\text{vap}} = \frac{\Delta H^\circ_{\text{vap}}}{T} = \frac{44.0\times10^3 \text{ J/mol}}{298.15\text{K}} = 148 \text{ J mol}^{-1}\text{ K}^{-1}$$

This method is invalid because the temperature in the denominator of the equation must be the temperature at which the liquid-vapor transition is at equilibrium. Liquid water and water vapor at 1 atm pressure (standard state, indicated by $^\circ$) are in equilibrium only at $100^\circ\text{ C} = 373\text{ K}$.

(b) The reason why $\Delta H^\circ_{\text{vap}}$ is different at 25° C from its value at 100° C has to do with the heat required to bring the reactants and products down to 298 K from 373 K. The specific heat of liquid water is higher than the heat capacity of steam. Thus, more heat is given off by lowering the temperature of the liquid water from 100° C to 25° C than is given off by lowering the temperature of the same amount of steam. Another way to think of this is that hydrogen bonding is more disrupted in water at 100°C than at 25°C (because the molecules are in rapid—thermal—motion), and hence, there is not as much energy needed to convert liquid to vapor (thus $\Delta H^\circ_{\text{vap}}$ has a smaller value at 100° C. The reason why $\Delta S^\circ_{\text{vap}}$ has a larger value at 25° C than at 100° C has to do with dispersion. A vapor at 1 atm pressure (the case at both temperatures) has about the same entropy. On the other hand, liquid water is more disordered (better able to disperse energy) at higher temperatures since more of the hydrogen bonds are disrupted by thermal motion. (The hydrogen bonds are totally disrupted in the two vapors).

10. **(M)** In this problem we are given standard enthalpies of the formation (ΔH^o_f) of liquid and gas pentane at 298.15 K and asked to estimate the normal boiling point of pentane, ΔG^o_{vap} and furthermore comment on the significance of the sign of ΔG^o_{vap}. The general strategy in solving this problem is to first determine ΔH^o_{vap} from the known enthalpies of formation. Trouton's rule can then be used to determine the normal boiling point of pentane. Lastly, $\Delta G^o_{vap,298K}$ can be calculated using $\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}}$.

Stepwise approach:

Calculate ΔH^o_{vap} from the known values of ΔH^o_f (part a):

$$C_5H_{12}(l) \rightleftharpoons C_5H_{12}(g)$$

$$\Delta H^o_f \quad -173.5 \text{ kJmol}^{-1} \qquad -146.9 \text{ kJmol}^{-1}$$

$$\Delta H^o_{vap} = -146.9 - (-173.5)\text{kJmol}^{-1} = 26.6\text{kJmol}^{-1}$$

Determine normal boiling point using Trouton's rule (part a):

$$\Delta S^o_{vap} = \frac{\Delta H^o_{vap}}{T_{nbp}} = 87\text{Jmol}^{-1}\text{K}^{-1}$$

$$T_{nbp} = \frac{\Delta H^o_{vap}}{\Delta S^o_{vap}} = \frac{26.6kJmol^{-1}}{\frac{87kJK^{-1}mol^{-1}}{1000}} = 306K$$

$$T_{nbp} = 32.9^oC$$

Use $\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}}$ to calculate $\Delta G^\circ_{\text{vap,298K}}$ (part b):

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

$$\Delta G^\circ_{\text{vap,298K}} = 26.6\text{kJmol}^{-1} - 298.15K \times \frac{87\text{kJmol}^{-1}\text{K}^{-1}}{1000}$$

$$\Delta G^\circ_{\text{vap,298K}} = 0.66\text{kJmol}^{-1}$$

Comment on the value of $\Delta G^\circ_{\text{vap,298K}}$ (part c):

The positive value of $\Delta G^\circ_{\text{vap}}$ indicates that normal boiling (having a vapor pressure of 1.00 atm) for pentane should be non-spontaneous (will not occur) at 298. The vapor pressure of pentane at 298 K should be less than 1.00 atm.

Conversion pathway approach:

$$C_5H_{12}(l) \rightleftharpoons C_5H_{12}(g)$$

$$\Delta H^o_f \quad -173.5 \text{ kJmol}^{-1} \qquad -146.9 \text{ kJmol}^{-1}$$

$$\Delta H^o_{vap} = -146.9 - (-173.5)\text{kJmol}^{-1} = 26.6\text{kJmol}^{-1}$$

$$\Delta S^o_{vap} = \frac{\Delta H^o_{vap}}{T_{nbp}} = 87\text{Jmol}^{-1}\text{K}^{-1} \Rightarrow T_{nbp} = \frac{\Delta H^o_{vap}}{\Delta S^o_{vap}} = \frac{26.6\text{kJmol}^{-1}}{\frac{87\text{kJK}^{-1}\text{mol}^{-1}}{1000}} = 306K$$

$$\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\,\Delta S^\circ_{\text{vap}} = 26.6\text{kJmol}^{-1} - 298.15K \times \frac{87\text{kJmol}^{-1}\text{K}^{-1}}{1000} = 0.66\text{kJmol}^{-1}$$

11. **(M)** Trouton's rule is obeyed most closely by liquids that do not have a high degree of order within the liquid. In both HF and CH_3OH, hydrogen bonds create considerable order within the liquid. In $C_6H_5CH_3$, the only attractive forces are non-directional London forces, which have no preferred orientation as hydrogen bonds do. Thus, of the three choices, liquid $C_6H_5CH_3$ would most closely follow Trouton's rule.

12. **(E)** $\Delta H^{\circ}_{\text{vap}} = \Delta H^{\circ}_{\text{f}}[\text{Br}_2(\text{g})] - \Delta H^{\circ}_{\text{f}}[\text{Br}_2(\text{l})] \approx 30.91 \text{ kJ/mol} - 0.00 \text{ kJ/mol} = 30.91 \text{ kJ/mol}$

$$\Delta S^{\circ}_{\text{vap}} = \frac{\Delta H^{\circ}_{\text{vap}}}{T_{\text{vap}}} \approx 87 \text{ J mol}^{-1}\text{ K}^{-1} \text{ or } \quad T_{\text{vap}} = \frac{\Delta H^{\circ}_{\text{vap}}}{\Delta S^{\circ}_{\text{vap}}} \approx \frac{30.91\times10^{3}\text{ J/mol}}{87\text{ J mol}^{-1}\text{K}^{-1}} = 3.5\times10^{2}\text{ K}$$

The accepted value of the boiling point of bromine is $58.8^{\circ}\text{C} = 332 \text{ K} = 3.32\times10^{2} \text{ K}$. Thus, our estimate is in reasonable agreement with the measured value.

13. **(M)** The liquid water-gaseous water equilibrium $H_2O\text{ (l, 0.50 atm)} \rightleftharpoons H_2O\text{ (g, 0.50 atm)}$ can only be established at one temperature, namely the boiling point for water under 0.50 atm external pressure. We can estimate the boiling point for water under 0.50 atm external pressure by using the Clausius-Clapeyron equation:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H^{o}_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

We know that at 373 K, the pressure of water vapor is 1.00 atm. Let's make P_1 = 1.00 atm, P_2 = 0.50 atm and T_1 = 373 K. Thus, the boiling point under 0.50 atm pressure is T_2. To find T_2 we simply insert the appropriate information into the Clausius-Clapeyron equation and solve for T_2:

$$\ln\frac{0.50\text{ atm}}{1.00\text{ atm}} = \frac{40.7\text{ kJ mol}^{-1}}{8.3145\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{373\text{ K}} - \frac{1}{T_2}\right)$$

$$-1.4\underline{16}\times10^{-4}\text{ K} = \left(\frac{1}{373\text{ K}} - \frac{1}{T_2}\right)$$

Solving for T_2 we find a temperature of 354 K or 81°C. Consequently, to achieve an equilibrium between gaseous and liquid water under 0.50 atm pressure, the temperature must be set at 354 K.

14. **(M)** Figure 12-19 (phase diagram for carbon dioxide) shows that at –60°C and under 1 atm of external pressure, carbon dioxide exists as a gas. In other words, neither solid nor liquid CO_2 can exist at this temperature and pressure. Clearly, of the three phases, gaseous CO_2 must be the most stable and, hence, have the lowest free energy when T = –60 °C and P_{ext} = 1.00 atm.

Gibbs Energy and Spontaneous Change

15. **(E)** Answer (b) is correct. Br—Br bonds are broken in this reaction, meaning that it is endothermic, with $\Delta H > 0$. Since the number of moles of gas increases during the reaction, $\Delta S > 0$. And, because $\Delta G = \Delta H - T\,\Delta S$, this reaction is non-spontaneous ($\Delta G > 0$) at low temperatures where the ΔH term predominates and spontaneous ($\Delta G < 0$) at high temperatures where the $T\,\Delta S$ term predominates.

16. **(E)** Answer (d) is correct. A reaction that proceeds only through electrolysis is a reaction that is non-spontaneous. Such a reaction has $\Delta G > 0$.

<u>17.</u> **(E) (a)** $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} < 0$ (since $\Delta n_{gas} < 0$) for this reaction. Thus, this reaction is case 2 of Table 19-1. It is spontaneous at low temperatures and non-spontaneous at high temperatures.

(b) We are unable to predict the sign of ΔS° for this reaction, since $\Delta n_{gas} = 0$. Thus, no strong prediction as to the temperature behavior of this reaction can be made. Since $\Delta H^{o} > 0$, we can, however, conclude that the reaction will be non-spontaneous at low temperatures.

(c) $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$ (since $\Delta n_{gas} > 0$) for this reaction. This is case 3 of Table 19-1. It is non-spontaneous at low temperatures, but spontaneous at high temperatures.

18. **(E) (a)** $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} < 0$ (since $\Delta n_{gas} < 0$) for this reaction. This is case 4 of Table 19-1. It is non-spontaneous at all temperatures.

(b) $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} > 0$ (since $\Delta n_{gas} > 0$) for this reaction. This is case 1 of Table 19-1. It is spontaneous at all temperatures.

(c) $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} < 0$ (since $\Delta n_{gas} < 0$) for this reaction. This is case 2 of Table 19-1. It is spontaneous at low temperatures and non-spontaneous at high temperatures.

<u>19.</u> **(E)** First of all, the process is clearly spontaneous, and therefore $\Delta G < 0$. In addition, the gases are more dispersed when they are at a lower pressure and therefore $\Delta S > 0$. We also conclude that $\Delta H = 0$ because the gases are ideal and thus there are no forces of attraction or repulsion between them.

20. **(E)** Because an ideal solution forms spontaneously, $\Delta G < 0$. Also, the molecules of solvent and solute that are mixed together in the solution are in a more dispersed state than the separated solvent and solute. Therefore, $\Delta S > 0$. However, in an ideal solution, the attractive forces between solvent and solute molecules equal those forces between solvent molecules and those between solute molecules. Thus, $\Delta H = 0$. There is no net energy of interaction.

<u>21.</u> **(M) (a)** An exothermic reaction (one that gives off heat) may not occur spontaneously if, at the same time, the system becomes more ordered (concentrated) that is, $\Delta S^{\circ} < 0$. This is particularly true at a high temperature, where the $T\Delta S$ term dominates the ΔG expression. An example of such a process is freezing water (clearly exothermic because the reverse process, melting ice, is endothermic), which is not spontaneous at temperatures above $0\ ^{\circ}C$.

(b) A reaction in which $\Delta S > 0$ need not be spontaneous if that process also is endothermic. This is particularly true at low temperatures, where the ΔH term dominates the ΔG expression. An example is the vaporization of water (clearly an endothermic process, one that requires heat, and one that produces a gas, so $\Delta S > 0$), which is not spontaneous at low temperatures, that is, below $100\ ^\circ\text{C}$ (assuming P_{ext} = 1.00 atm).

22. **(M)** In this problem we are asked to explain whether the reaction AB(g)→A(g)+B(g) is always going to be spontaneous at high rather than low temperatures. In order to answer this question, we need to determine the signs of ΔH, ΔS and consequently ΔG. Recall that $\Delta G = \Delta H - T\Delta S$.

Stepwise approach:

Determine the sign of ΔS:

We are generating two moles of gas from one mole. The randomness of the system increases and ΔS must be greater than zero.

Determine the sign of ΔH:

In this reaction, we are breaking A-B bond. Bond breaking requires energy, so the reaction must be endothermic. Therefore, ΔH is also greater than zero.

Use $\Delta G = \Delta H - T\Delta S$ to determine the sign of ΔG:

$\Delta G = \Delta H - T\Delta S$. Since ΔH is positive and ΔS is positive there will be a temperature at which $T\Delta S$ will become greater than ΔH. The reaction will be favored at high temperatures and disfavored at low temperatures.

Conversion pathway approach:

ΔS for the reaction is greater than zero because we are generating two moles of gas from one mole. ΔH for the reaction is also greater than zero because we are breaking A-B (bond breaking requires energy). Because $\Delta G = \Delta H - T\Delta S$, there will be a temperature at which $T\Delta S$ will become greater than ΔH. The reaction will be favored at high temperatures and disfavored at low temperatures.

Standard Gibbs Energy Change

23. (M) $\Delta H^\circ = \Delta H_f^\circ\left[\text{NH}_4\text{Cl}(\text{s})\right] - \Delta H_f^\circ\left[\text{NH}_3(\text{g})\right] - \Delta \text{H}_f^\circ\left[\text{HCl}(\text{g})\right]$

$$= -314.4\ \text{kJ/mol} - (-46.11\ \text{kJ/mol} - 92.31\ \text{kJ/mol}) = -176.0\ \text{kJ/mol}$$

$$\Delta G^\circ = \Delta G_f^\circ\left[\text{NH}_4\text{Cl}(\text{s})\right] - \Delta G_f^\circ\left[\text{NH}_3(\text{g})\right] - \Delta G_f^\circ\left[\text{HCl}(\text{g})\right]$$

$$= -202.9\ \text{kJ/mol} - (-16.48\ \text{kJ/mol} - 95.30\ \text{kJ/mol}) = -91.1\ \text{kJ/mol}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-176.0\ \text{kJ/mol} + 91.1\ \text{kJ/mol}}{298\ \text{K}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = -285\ \text{J mol}^{-1}$$

24. **(M)** **(a)** $\Delta G^\circ = \Delta G_f^\circ\left[\text{C}_2\text{H}_6(\text{g})\right] - \Delta G_f^\circ\left[\text{C}_2\text{H}_2(\text{g})\right] - 2\Delta G_f^\circ\left[\text{H}_2(\text{g})\right]$

$$= -32.82\ \text{kJ/mol} - 209.2\ \text{kJ/mol} - 2(0.00\ \text{kJ/mol}) = -242.0\ \text{kJ/mol}$$

(b) $\Delta G^\circ = 2\Delta G_f^\circ\left[\text{SO}_2(\text{g})\right] + \Delta G_f^\circ\left[\text{O}_2(\text{g})\right] - 2\Delta G_f^\circ\left[\text{SO}_3(\text{g})\right]$

$$= 2(-300.2\ \text{kJ/mol}) + 0.00\ \text{kJ/mol} - 2(-371.1\ \text{kJ/mol}) = +141.8\ \text{kJ/mol}$$

(c) $\Delta G^o = 3\Delta G_f^\circ[Fe(s)] + 4\Delta G_f^\circ[H_2O(g)] - \Delta G_f^\circ[Fe_3O_4(s)] - 4\Delta G_f^\circ[H_2(g)]$

$= 3(0.00\text{ kJ/mol}) + 4(-228.6\text{ kJ/mol}) - (-1015\text{ kJ/mol}) - 4(0.00\text{ kJ/mol}) = 101\text{ kJ/mol}$

(d) $\Delta G^o = 2\Delta G_f^\circ[Al^{3+}(aq)] + 3\Delta G_f^\circ[H_2(g)] - 2\Delta G_f^\circ[Al(s)] - 6\Delta G_f^\circ[H^+(aq)]$

$= 2(-485\text{ kJ/mol}) + 3(0.00\text{ kJ/mol}) - 2(0.00\text{kJ/mol}) - 6(0.00\text{ kJ/mol}) = -970.\text{ kJ/mol}$

25. **(M) (a)** $\Delta S^o = 2S^o[POCl_3(l)] - 2S^o[PCl_3(g)] - S^o[O_2(g)]$

$= 2(222.4\text{ J/K}) - 2(311.7\text{ J/K}) - 205.1\text{ J/K} = -383.7\text{ J/K}$

$\Delta G^o = \Delta H^o - T\Delta S^o = -620.2\times10^3\text{ J} - (298\text{ K})(-383.7\text{ J/K}) = -506\times10^3\text{ J} = -506\text{ kJ}$

(b) The reaction proceeds spontaneously in the forward direction when reactants and products are in their standard states, because the value of ΔG^o is less than zero.

26. **(M) (a)** $\Delta S^o = S^o[Br_2(l)] + 2S^o[HNO_2(aq)] - 2S^o[H^+(aq)] - 2S^o[Br^-(aq)] - 2S^o[NO_2(g)]$

$= 152.2\text{ J/K} + 2(135.6\text{ J/K}) - 2(0\text{ J/K}) - 2(82.4\text{ J/K}) - 2(240.1\text{ J/K}) = -221.6\text{ J/K}$

$\Delta G^o = \Delta H^o - T\Delta S^o = -61.6\times10^3\text{ J} - (298\text{ K})(-221.6\text{ J/K}) = +4.4\times10^3\text{ J} = +4.4\text{ kJ}$

(b) The reaction does not proceed spontaneously in the forward direction when reactants and products are in their standard states, because the value of ΔG^o is greater than zero.

27. **(M)** We combine the reactions in the same way as for any Hess's law calculations.

(a)

$N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g)$	$\Delta G^o = -\frac{1}{2}(+208.4\text{ kJ}) = -104.2\text{ kJ}$
$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$	$\Delta G^o = +102.6\text{ kJ}$
Net: $N_2O(g) + \frac{3}{2}O_2(g) \rightarrow 2NO_2(g)$	$\Delta G^o = -104.2 + 102.6 = -1.6\text{ kJ}$

This reaction reaches an equilibrium condition, with significant amounts of all species being present. This conclusion is based on the relatively small absolute value of ΔG^o.

(b)

$2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g)$	$\Delta G^o = 2(-33.0\text{ kJ}) = -66.0\text{ kJ}$
$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$	$\Delta G^o = -1010.5\text{ kJ}$
$4NO(g) \rightarrow 2N_2(g) + 2O_2(g)$	$\Delta G^o = -2(+173.1\text{ kJ}) = -346.2\text{ kJ}$
Net: $6H_2(g) + 3O_2(g) \rightarrow 6H_2O(l)$	$\Delta G^o = -66.0\text{ kJ} - 1010.5\text{ kJ} - 346.2\text{ kJ} = -1422.7\text{ kJ}$

This reaction is three times the desired reaction, which therefore has $\Delta G^o = -1422.7\text{ kJ} \div 3 = -474.3\text{ kJ}$.

The large negative ΔG^o value indicates that this reaction will go to completion at $25^\circ C$.

(c)
$$4NH_3(g)+5O_2(g)\rightarrow 4NO(g)+6H_2O(l) \qquad \Delta G^o = -1010.5 \text{ kJ}$$
$$4NO(g)\rightarrow 2N_2(g)+2O_2(g) \qquad \Delta G^o = -2(+173.1 \text{ kJ}) = -346.2 \text{ kJ}$$
$$2N_2(g)+O_2(g)\rightarrow 2N_2O(g) \qquad \Delta G^o = +208.4 \text{ kJ}$$
$$4NH_3(g)+4O_2(g)\rightarrow 2N_2O(g)+6H_2O(l) \qquad \Delta G^o = -1010.5\,\text{kJ} - 346.2\,\text{kJ} + 208.4\,\text{kJ} = -1148.3\,\text{kJ}$$

This reaction is twice the desired reaction, which, therefore, has ΔG^o = -574.2 kJ. The very large negative value of the ΔG^o for this reaction indicates that it will go to completion.

28. **(M)** We combine the reactions in the same way as for any Hess's law calculations.

(a)
$$COS(g)+2CO_2(g)\rightarrow SO_2(g)+3CO(g) \qquad \Delta G^o = -(-246.4 \text{ kJ}) = +246.6 \text{ kJ}$$
$$2CO(g)+2H_2O(g)\rightarrow 2CO_2(g)+2H_2(g) \qquad \Delta G^o = 2(-28.6 \text{ kJ}) = -57.2 \text{ kJ}$$
$$COS(g)+2H_2O(g)\rightarrow SO_2(g)+CO(g)+2H_2(g) \qquad \Delta G^o = +246.6 - 57.2 = +189.4 \text{ kJ}$$

This reaction is spontaneous in the reverse direction, because of the large positive value of ΔG^o

(b)
$$COS(g)+2CO_2(g)\rightarrow SO_2(g)+3CO(g) \qquad \Delta G^o = -(-246.4 \text{ kJ}) = +246.6 \text{ kJ}$$
$$3CO(g)+3H_2O(g)\rightarrow 3CO_2(g)+3H_2(g) \qquad \Delta G^o = 3(-28.6 \text{ kJ}) = -85.8 \text{ kJ}$$
$$COS(g)+3H_2O(g)\rightarrow CO_2(g)+SO_2(g)+3H_2(g) \qquad \Delta G^o = +246.6 - 85.8 = +160.8 \text{ kJ}$$

This reaction is spontaneous in the reverse direction, because of the large positive value of ΔG^o.

(c)
$$COS(g)+H_2(g)\rightarrow CO(g)+H_2S(g) \qquad \Delta G^o = -(+1.4) \text{ kJ}$$
$$CO(g)+H_2O(g)\rightarrow CO_2(g)+H_2(g) \qquad \Delta G^o = -28.6 \text{ kJ} = -28.6 \text{ kJ}$$
$$COS(g)+H_2O(g)\rightarrow CO_2(g)+H_2S(g) \qquad \Delta G^o = -1.4 \text{ kJ} - 28.6 \text{ kJ} = -30.0 \text{ kJ}$$

The negative value of the ΔG^o for this reaction indicates that it is spontaneous in the forward direction.

<u>**29.**</u> **(D)** The combustion reaction is : $C_6H_6(l)+\frac{15}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(g \text{ or } l)$

(a)
$$\begin{aligned}\Delta G^o &= 6\Delta G_f^\circ[CO_2(g)] + 3\Delta G_f^\circ[H_2O(l)] - \Delta G_f^\circ[C_6H_6(l)] - \tfrac{15}{2}\Delta G_f^\circ[O_2(g)] \\ &= 6(-394.4 \text{ kJ}) + 3(-237.1 \text{ kJ}) - (+124.5 \text{ kJ}) - \tfrac{15}{2}(0.00 \text{ kJ}) = -3202 \text{ kJ}\end{aligned}$$

(b)
$$\begin{aligned}\Delta G^o &= 6\Delta G_f^\circ[CO_2(g)] + 3\Delta G_f^\circ[H_2O(g)] - \Delta G_f^\circ[C_6H_6(l)] - \tfrac{15}{2}\Delta G_f^\circ[O_2(g)] \\ &= 6(-394.4 \text{ kJ}) + 3(-228.6 \text{ kJ}) - (+124.5 \text{ kJ}) - \tfrac{15}{2}(0.00 \text{ kJ}) = -3177 \text{ kJ}\end{aligned}$$

We could determine the difference between the two values of ΔG° by noting the difference between the two products: $3H_2O(l) \rightarrow 3H_2O(g)$ and determining the value of ΔG° for this difference:

$$\Delta G^{\circ} = 3\Delta G_f^{\circ}\left[H_2O(g)\right] - 3\Delta G_f^{\circ}\left[H_2O(l)\right] = 3\left[-228.6 - (-237.1)\right] \text{ kJ} = 25.5 \text{ kJ}$$

30. **(M)** We wish to find the value of the ΔH° for the given reaction: $F_2(g) \rightarrow 2\,F(g)$

$$\Delta S^{\circ} = 2S^{\circ}\left[F(g)\right] - S^{\circ}\left[F_2(g)\right] = 2\left(158.8 \text{ J K}^{-1}\right) - \left(202.8 \text{ J K}^{-1}\right) = +114.8 \text{ J K}^{-1}$$

$$\Delta H^{\circ} = \Delta G^{\circ} + T\Delta S^{\circ} = 123.9 \times 10^3 \text{ J} + \left(298 \text{ K} \times 114.8 \text{ J/K}\right) = 158.1 \text{ kJ/mole of bonds}$$

The value in Table 10.3 is 159 kJ/mol, which is in quite good agreement with the value found here.

31. **(M)** **(a)** $\Delta S^{\circ}_{rxn} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$

$= [1 \text{ mol} \times 301.2 \text{ J K}^{-1}\text{mol}^{-1} + 2 \text{ mol} \times 188.8 \text{ J K}^{-1}\text{mol}^{-1}] - [2 \text{ mol} \times 247.4 \text{ J K}^{-1}\text{mol}^{-1} + 1 \text{ mol} \times 238.5 \text{ J K}^{-1}\text{mol}^{-1}] = -54.5 \text{ J K}^{-1}$

$\Delta S^{\circ}_{rxn} = = -0.0545 \text{ kJ K}^{-1}$

(b) $\Delta H^{\circ}_{rxn} = \Sigma(\text{bonds broken in reactants (kJ/mol)}) - \Sigma(\text{bonds broken in products(kJ/ mol)})$

$= [4 \text{ mol} \times (389 \text{ kJ mol}^{-1})_{\text{N-H}} + 4 \text{ mol} \times (222 \text{ kJ mol}^{-1})_{\text{O-F}}] - [4 \text{ mol} \times (301 \text{ kJ mol}^{-1})_{\text{N-F}} + 4 \text{ mol} \times (464 \text{ kJ mol}^{-1})_{\text{O-H}}]$

$\Delta H^{\circ}_{rxn} = -616 \text{ kJ}$

(c) $\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn} = -616 \text{ kJ} - 298 \text{ K}(-0.0545 \text{ kJ K}^{-1}) = -600 \text{ kJ}$

Since the ΔG°_{rxn} is negative, the reaction is spontaneous, and hence feasible (at 25 °C). Because both the entropy and enthalpy changes are *negative*, this reaction will be more highly favored at low temperatures (i.e., the reaction is enthalpy driven)

32. **(D)** In this problem we are asked to find ΔG° at 298 K for the decomposition of ammonium nitrate to yield dinitrogen oxide gas and liquid water. Furthermore, we are asked to determine whether the decomposition will be favored at temperatures above or below 298 K. In order to answer these questions, we first need the balanced chemical equation for the process. From the data in Appendix D, we can determine $\Delta H^{\circ}_{\text{rxn}}$ and $\Delta S^{\circ}_{\text{rxn}}$. Both quantities will be required to determine $\Delta G^{\circ}_{\text{rxn}}$ ($\Delta G^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}}$). Finally the magnitude of $\Delta G^{\circ}_{\text{rxn}}$ as a function of temperature can be judged depending on the values of $\Delta H^{\circ}_{\text{rxn}}$ and $\Delta S^{\circ}_{\text{rxn}}$.

Stepwise approach:

First we need the balanced chemical equation for the process:

$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$

Now we can determine $\Delta H^{\circ}_{\text{rxn}}$ by utilizing ΔH_f° values provided in Appendix D:

	$NH_4NO_3(s)$	$\xrightarrow{\Delta}$	$N_2O(g)$	+	$2H_2O(l)$
ΔH_f°	-365.6 kJmol^{-1}		82.05 kJmol^{-1}		-285.6 kJmol^{-1}

$\Delta H^{\circ}_{\text{rxn}} = \Sigma\Delta H_f^{\circ}{}_{\text{products}} - \Sigma\Delta H_f^{\circ}{}_{\text{reactants}}$

$\Delta H^{\circ}_{\text{rxn}} = [2 \text{ mol}(-285.8 \text{ kJ mol}^{-1}) + 1 \text{ mol}(82.05 \text{ kJ mol}^{-1})] - [1 \text{ mol } (-365.6 \text{ kJ mol}^{-1})]$

$\Delta H°_{rxn} = -124.0$ kJ

Similarly, $\Delta S°_{rxn}$ can be calculated utilizing $S°$ values provided in Appendix D

$$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$$

S^o 15.1 Jmol^{-1}K^{-1} 219.9 Jmol^{-1}K^{-1} 69.91 Jmol^{-1}K^{-1}

$\Delta S°_{rxn} = \Sigma S°_{products} - \Sigma S°_{reactants}$

$\Delta S°_{rxn} = [2\text{ mol} \times 69.91\text{ J K}^{-1}\text{mol}^{-1} + 1\text{ mol} \times 219.9\text{ J K}^{-1}\text{mol}^{-1}] - [1\text{ mol} \times 151.1\text{ J K}^{-1}\text{mol}^{-1}]$

$\Delta S°_{rxn} = 208.6\text{ J K}^{-1} = 0.2086\text{ kJ K}^{-1}$

To find $\Delta G°_{rxn}$ we can either utilize $\Delta G°_f$ values provided in Appendix D or $\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$:

$\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn} = -124.0\text{ kJ} - 298.15\text{ K} \times 0.2086\text{ kJK}^{-1}$

$\Delta G°_{rxn} = -186.1$ kJ

Magnitude of $\Delta G°_{rxn}$ as a function of temperature can be judged depending on the values of $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$:

Since $\Delta H°_{rxn}$ is <u>negative</u> and $\Delta S°_{rxn}$ is <u>positive</u>, the decomposition of ammonium nitrate is spontaneous at all temperatures. However, as the temperature increases, the $T\Delta S$ term gets larger and as a result, the decomposition reaction shift towards producing more products. Consequently, we can say that the reaction is more highly favored <u>above</u> 298 K (it will also be faster at higher temperatures)

Conversion pathway approach:

From the balanced chemical equation for the process

$$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$$

we can determine $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ by utilizing ΔH_f^o and $S°$ values provided in Appendix D:

$\Delta H°_{rxn} = [2\text{ mol}(-285.8\text{ kJ mol}^{-1}) + 1\text{ mol}(82.05\text{ kJ mol}^{-1})] - [1\text{ mol}(-365.6\text{ kJ mol}^{-1})]$

$\Delta H°_{rxn} = -124.0$ kJ

$\Delta S°_{rxn} = [2\text{ mol} \times 69.91\text{ J K}^{-1}\text{mol}^{-1} + 1\text{ mol} \times 219.9\text{ J K}^{-1}\text{mol}^{-1}] - [1\text{ mol} \times 151.1\text{ J K}^{-1}\text{mol}^{-1}]$

$\Delta S°_{rxn} = 208.6\text{ J K}^{-1} = 0.2086\text{ kJ K}^{-1}$

$\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn} = -124.0\text{ kJ} - 298.15\text{ K} \times 0.2086\text{ kJK}^{-1}$

$\Delta G°_{rxn} = -186.1$ kJ

Since $\Delta H°_{rxn}$ is <u>negative</u> and $\Delta S°_{rxn}$ is <u>positive</u>, the decomposition of ammonium nitrate is spontaneous at all temperatures. However, as the temperature increases, the $T\Delta S$ term gets larger and as a result, the decomposition reaction shift towards producing more products. The reaction is highly favored above 298 K (it will also be faster).

The Thermodynamic Equilibrium Constant

<u>**33.**</u> **(E)** In all three cases, $K_{eq} = K_p$ because only gases, pure solids, and pure liquids are present in the chemical equations. There are no factors for solids and liquids in K_{eq} expressions, and gases appear as partial pressures in atmospheres. That makes K_{eq} the same as K_p for these three reactions.

We now recall that $K_p = K_c(RT)^{\Delta n}$. Hence, in these three cases we have:

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta n_{gas} = 2 - (2+1) = -1$; $K = K_p = K_c(RT)^{-1}$

(b) $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$; $\Delta n_{gas} = 1 - (\frac{1}{2} + \frac{1}{2}) = 0$; $K = K_p = K_c$

(c) $NH_4HCO_3(s) \rightleftharpoons NH_3(g) + CO_2(g) + H_2O(l)$;

$\Delta n_{gas} = 2 - (0) = +2$ $K = K_p = K_c(RT)^2$

34. (M) (a) $K = \dfrac{P\{H_2(g)\}^4}{P\{H_2O(g)\}^4}$

(b) Terms for both solids, Fe(s) and $Fe_3O_4(s)$, are properly excluded from the thermodynamic equilibrium constant expression. (Actually, each solid has an activity of 1.00.) Thus, the equilibrium partial pressures of both $H_2(g)$ and $H_2O(g)$ do not depend on the amounts of the two solids present, as long as some of each solid is present. One way to understand this is that any chemical reaction occurs on the surface of the solids, and thus is unaffected by the amount present.

(c) We can produce $H_2(g)$ from $H_2O(g)$ without regard to the proportions of Fe(s) and $Fe_3O_4(s)$ with the qualification, that there must always be some Fe(s) present for the production of $H_2(g)$ to continue.

35. (M) In this problem we are asked to determine the equilibrium constant and the change in Gibbs free energy for the reaction between carbon monoxide and hydrogen to yield methanol. The equilibrium concentrations of each reagent at 483K were provided. We proceed by first determining the equilibrium constant. Gibbs free energy can be calculated using $\Delta G^o = -RT\ln K$.

Stepwise approach:

First determine the equilibrium constant for the reaction at 483K:

$$CO(g)+2H_2(g) \rightleftharpoons CH_3OH(g)$$

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911 \times 0.0822^2} = 14.5$$

Now use $\Delta G^o = -RT\ln K$ to calculate the change in Gibbs free energy at 483 K:

$\Delta G^o = -RT\ln K$

$\Delta G^o = -8.314 \times 483 \times \ln(14.5)\text{Jmol}^{-1} = -1.1 \times 10^4\,\text{Jmol}^{-1}$

$\Delta G^o = -11\text{kJmol}^{-1}$

Conversion pathway approach:

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911 \times 0.0822^2} = 14.5$$

$\Delta G^o = -RT\ln K = -8.314 \times 483 \times \ln(14.5)\text{Jmol}^{-1} = -1.1 \times 10^4\,\text{Jmol}^{-1}$

$\Delta G^o = -11\text{kJmol}^{-1}$

36. **(M)** Gibbs free energy for the reaction ($\Delta G^o = \Delta H^o - T\Delta S^o$) can be calculated using ΔH_f^o and S^o values for CO(g), H_2(g) and CH_3OH(g) from Appendix D.

$$\Delta H^o = \Delta H_f^o(\mathrm{CH_3OH(g)}) - [\Delta H_f^o(\mathrm{CO(g)}) + 2\Delta H_f^o(\mathrm{H_2(g)})]$$

$$\Delta H^o = -200.7\mathrm{kJmol^{-1}} - (-110.5\mathrm{kJmol^{-1}} + 0\mathrm{kJmol^{-1}}) = -90.2\mathrm{kJmol^{-1}}$$

$$\Delta S^o = S^o(\mathrm{CH_3OH(g)}) - [S^o(\mathrm{CO(g)}) + 2S^o(\mathrm{H_2(g)})]$$

$$\Delta S^o = 239.8\mathrm{JK^{-1}mol^{-1}} - (197.7\mathrm{JK^{-1}mol^{-1}} + 2\times 130.7\mathrm{JK^{-1}mol^{-1}}) = -219.3\mathrm{JK^{-1}mol^{-1}}$$

$$\Delta G^o = -90.2\mathrm{kJmol^{-1}} - \frac{483K \times (-219.3)\mathrm{kJK^{-1}mol^{-1}}}{1000} = 15.7\mathrm{kJmol^{-1}}$$

Equilibrium constant for the reaction can be calculated using $\Delta G^o = -RT\ln K$

$$\ln K = \frac{-\Delta G^o}{RT} \Rightarrow \ln K = \frac{-15.7\times 1000\,Jmol^{-1}}{8.314\,JK^{-1}mol^{-1}\times 483K} = -3.9 \Rightarrow K = e^{-3.9} = 2.0\times 10^{-2}$$

The values are different because in this case, the calculated K is the thermodynamic equilibrium constant that represents the reactants and products in their standard states. In Exercise 35, the reactants and products were not in their standard states.

Relationships Involving ΔG, ΔG^o, Q and K

37. **(M)** $\Delta G^o = 2\Delta G_f^\circ[\mathrm{NO(g)}] - \Delta G_f^\circ[\mathrm{N_2O(g)}] - 0.5\,\Delta G_f^\circ[\mathrm{O_2(g)}]$

$$= 2(86.55\ \mathrm{kJ/mol}) - (104.2\ \mathrm{kJ/mol}) - 0.5(0.00\ \mathrm{kJ/mol}) = 68.9\ \mathrm{kJ/mol}$$

$$= -RT\ln K_p = -(8.3145\times 10^{-3}\ \mathrm{kJ\ mol^{-1}\ K^{-1}})(298\ \mathrm{K})\ln K_p$$

$$\ln K_p = -\frac{68.9\ \mathrm{kJ/mol}}{8.3145\times 10^{-3}\ \mathrm{kJ\ mol^{-1}\ K^{-1}}\times 298\ \mathrm{K}} = -27.8 \qquad K_p = e^{-27.8} = 8\times 10^{-13}$$

38. **(M) (a)** $\Delta G^o = 2\Delta G_f^\circ[\mathrm{N_2O_5(g)}] - 2\Delta G_f^\circ[\mathrm{N_2O_4(g)}] - \Delta G_f^\circ[\mathrm{O_2(g)}]$

$$= 2(115.1\ \mathrm{kJ/mol}) - 2(97.89\ \mathrm{kJ/mol}) - (0.00\ \mathrm{kJ/mol}) = 34.4\ \mathrm{kJ/mol}$$

(b) $\Delta G^o = -RT\ln K_p \qquad \ln K_p = -\dfrac{\Delta G^o}{RT} = -\dfrac{34.4\times 10^3\ \mathrm{J/mol}}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\times 298\,\mathrm{K}} = -13.9$

$$K_p = e^{-13.9} = 9\times 10^{-7}$$

39. **(M)** We first balance each chemical equation, then calculate the value of ΔG^o with data from Appendix D, and finally calculate the value of K_{eq} with the use of $\Delta G^o = -RT\ln K$.

(a) $4\mathrm{HCl(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\mathrm{H_2O(g)} + 2\mathrm{Cl_2(s)}$

$$\Delta G^o = 2\Delta G_f^\circ[\mathrm{H_2O(g)}] + 2\Delta G_f^\circ[\mathrm{Cl_2(g)}] - 4\Delta G_f^\circ[\mathrm{HCl(g)}] - \Delta G_f^\circ[\mathrm{O_2(g)}]$$

$$= 2\times\left(-228.6\frac{\mathrm{kJ}}{\mathrm{mol}}\right) + 2\times 0\frac{\mathrm{kJ}}{\mathrm{mol}} - 4\times\left(-95.30\frac{\mathrm{kJ}}{\mathrm{mol}}\right) - 0\frac{\mathrm{kJ}}{\mathrm{mol}} = -76.0\ \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{+76.0\times 10^3\,\mathrm{J/mol}}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\times 298\ \mathrm{K}} = +30.7 \qquad K = e^{+30.7} = 2\times 10^{13}$$

(b) $3Fe_2O_3(s) + H_2(g) \rightleftharpoons 2Fe_3O_4(s) + H_2O(g)$

$$\Delta G^o = 2\Delta G_f^\circ[Fe_3O_4(s)] + \Delta G_f^\circ[H_2O(g)] - 3\Delta G_f^\circ[Fe_2O_3(s)] - \Delta G_f^\circ[H_2(g)]$$
$$= 2\times(-1015 \text{ kJ/mol}) - 228.6 \text{ kJ/mol} - 3\times(-742.2 \text{ kJ/mol}) - 0.00 \text{ kJ/mol}$$
$$= -32 \text{ kJ/mol}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{32\times10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 13; \quad K = e^{+13} = 4\times10^5$$

(c) $2Ag^+(aq) + SO_4{}^{2-}(aq) \rightleftharpoons Ag_2SO_4(s)$

$$\Delta G^o = \Delta G_f^\circ[Ag_2SO_4(s)] - 2\Delta G_f^\circ[Ag^+(aq)] - \Delta G_f^\circ[SO_4^{2-}(aq)]$$
$$= -618.4 \text{ kJ/mol} - 2 \times 77.11 \text{ kJ/mol} - (-744.5 \text{ kJ/mol}) = -28.1 \text{ kJ/mol}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{28.1\times10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 11.3; \quad K = e^{+11.3} = 8\times10^4$$

40. **(E)** $\Delta S^o = S^o\{CO_2(g)\} + S^o\{H_2(g)\} - S^o\{CO(g)\} - S^o\{H_2O(g)\}$

$$= 213.7 \text{ J mol}^{-1} \text{ K}^{-1} + 130.7 \text{ J mol}^{-1} \text{ K}^{-1} - 197.7 \text{ J mol}^{-1} \text{ K}^{-1} - 188.8 \text{ J mol}^{-1}\text{K}^{-1}$$
$$= -42.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

41. **(M)** In this problem we need to determine in which direction the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is spontaneous when the partial pressure of SO_2, O_2, and SO_3 are 1.0×10^{-4}, 0.20 and 0.10 atm, respectively. We proceed by first determining the standard free energy change for the reaction (ΔG^o) using tabulated data in Appendix D. Change in Gibbs free energy for the reaction (ΔG) is then calculated by employing the equation $\Delta G = \Delta G^o + RT \ln Q_p$, where Q_p is the reaction quotient. Based on the sign of ΔG, we can determine in which direction is the reaction spontaneous.

Stepwise approach:

First determine ΔG^o for the reaction using data in Appendix D:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$\Delta G^o = 2\Delta G_f^o[SO_3(g)] - 2\Delta G_f^o[SO_2(g)] - \Delta G_f^o[O_2(g)]$$
$$\Delta G^o = 2 \times (-371.1 \text{ kJ/mol}) - 2 \times (-300.2 \text{ kJ/mol}) - 0.0 \text{ kJ/mol}$$
$$\Delta G^o = -141.8 \text{kJ}$$

Calculate ΔG by employing the equation $\Delta G = \Delta G^o + RT \ln Q_p$, where Q_p is the reaction quotient:

$$\Delta G = \Delta G^o + RT \ln Q_p$$

$$Q_p = \frac{P\{SO_3(g)\}^2}{P\{O_2(g)\}P\{SO_2(g)\}^2}$$

$$Q_p = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})(1.0\times10^{-4} \text{ atm})^2} = 5.0\times10^6$$

ΔG = –141.8 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(5.0 × 10^6)
ΔG = –141.8 kJ + 38.2 kJ = –104 kJ.
Examine the sign of ΔG to decide in which direction is the reaction spontaneous:
Since ΔG is negative, the reaction is spontaneous in the forward direction.
Conversion pathway approach:

$$\Delta G^o = 2\Delta G_f^o\left[SO_3(g)\right] - 2\Delta G_f^o\left[SO_2(g)\right] - \Delta G_f^o\left[O_2(g)\right]$$

$$\Delta G^o = 2\times(-371.1 \text{ kJ/mol}) - 2\times(-300.2 \text{ kJ/mol}) - 0.0 \text{ kJ/mol=-141.8kJ}$$

$$\Delta G = \Delta G^o + RT\ln Q_p$$

$$Q_p = \frac{P\{SO_3(g)\}^2}{P\{O_2(g)\}P\{SO_2(g)\}^2} = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})(1.0\times10^{-4} \text{ atm})^2} = 5.0\times10^6$$

ΔG = –141.8 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(5.0 × 10^6)=-104 kJ.
Since ΔG is negative, the reaction is spontaneous in the forward direction.

42. **(M)** We begin by calculating the standard free energy change for the reaction:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$\Delta G^\circ = 2\Delta G_f^\circ\left[HCl(g)\right] - \Delta G_f^\circ\left[Cl_2(g)\right] - \Delta G_f^\circ\left[H_2(g)\right]$$

$$= 2\times(-95.30 \text{ kJ/mol}) - 0.0 \text{ kJ/mol} - 0.0 \text{ kJ/mol} = -190.6 \text{ kJ}$$

Now we can calculate ΔG by employing the equation $\Delta G = \Delta G^o + RT\ln Q_p$, where

$$Q_p = \frac{P\{HCl(g)\}^2}{P\{H_2(g)\}P\{Cl_2(g)\}} \;;\; Q_p = \frac{(0.5 \text{ atm})^2}{(0.5 \text{ atm})(0.5 \text{ atm})} = 1$$

ΔG = –190.6 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(1)
ΔG = –190.6 kJ + 0 kJ = –190.6 kJ.

Since ΔG is negative, the reaction is spontaneous in the forward direction.

<u>43.</u> **(M)** In order to determine the direction in which the reaction is spontaneous, we need to calculate the non-standard free energy change for the reaction. To accomplish this, we will employ the equation $\Delta G = \Delta G^o + RT\ln Q_c$, where

$$Q_c = \frac{[H_3O^+(aq)]\,[CH_3CO_2^-(aq)]}{[CH_3CO_2H(aq)]} \;;\; Q_c = \frac{(1.0\times10^{-3} \text{ M})^2}{(0.10 \text{ M})} = 1.0\times10^{-5}$$

ΔG = 27.07 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(1.0 × 10^{-5})
ΔG = 27.07 kJ + (–28.53 kJ) = –1.46 kJ.

Since ΔG is negative, the reaction is spontaneous in the forward direction.

44. **(M)** As was the case for exercise 39, we need to calculate the non-standard free energy change for the reaction. Once again, we will employ the equation $\Delta G = \Delta G^{o} + RT\ln Q$, but this time

$$Q_c = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]}\ ;\ Q_c = \frac{(1.0\times10^{-3}\ M)^2}{(0.10\ M)} = 1.0\times10^{-5}$$

ΔG = 29.05 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(1.0 × 10^{-5})

ΔG = 29.05 kJ + (–28.53 kJ) = 0.52 kJ.

Since ΔG is positive, the reaction is spontaneous in the reverse direction.

<u>45.</u> **(E)** The relationship $\Delta S^{o} = (\Delta G^{o} - \Delta H^{o})/T$ (Equation (b)) is incorrect. Rearranging this equation to put ΔG^{o} on one side by itself gives $\Delta G^{o} = \Delta H^{o} + T\Delta S^{o}$. This equation is not valid. The $T\Delta S^{o}$ term should be subtracted from the ΔH^{o} term, not added to it.

46. **(E)** The ΔG^{o} value is a powerful thermodynamic parameter because it can be used to determine the equilibrium constant for the reaction at each and every chemically reasonable temperature via the equation $\Delta G^{o} = -RT \ln K$.

<u>47.</u> **(M) (a)** To determine K_p we need the equilibrium partial pressures. In the ideal gas law, each partial pressure is defined by $P = nRT/V$. Because R, T, and V are the same for each gas, and because there are the same number of partial pressure factors in the numerator as in the denominator of the K_p expression, we can use the ratio of amounts to determine K_p.

$$K_p = \frac{P\{CO(g)\}\,P\{H_2O(g)\}}{P\{CO_2(g)\}\,P\{H_2(g)\}} = \frac{n\{CO(g)\}\,n\{H_2O(g)\}}{n\{CO_2(g)\}\,n\{H_2(g)\}} = \frac{0.224\ \text{mol CO}\times 0.224\ \text{mol H}_2\text{O}}{0.276\ \text{mol CO}_2\times 0.276\ \text{mol H}_2} = 0.659$$

(b) $\Delta G^{o}_{1000K} = -RT\ \ln\ K_p = -8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times 1000.\ \text{K}\times\ln(0.659)$

$= 3.467\times10^{3}$ J/mol = 3.467 kJ/mol

(c)

$$Q_p = \frac{0.0340\ \text{mol CO}\times 0.0650\,\text{mol H}_2\text{O}}{0.0750\ \text{mol CO}_2\times 0.095\ \text{mol H}_2} = 0.31 < 0.659 = K_p$$

Since Q_p is smaller than K_p, the reaction will proceed to the right, forming products, to attain equilibrium, i.e., $\Delta G = 0$.

48. **(M) (a)** We know that $K_p = K_c(RT)^{\Delta n}$. For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta n_{gas} = 2-(2+1) = -1$, and therefore a value of K_p can be obtained.

$$K_p = K_c(RT)^{-1} = \frac{2.8\times10^{2}}{\frac{0.08206\ \text{L atm}}{\text{mol K}}\times 1000\ \text{K}} = 3.41 = K$$

We recognize that $K = K_p$ since all of the substances involved in the reaction are gases. We can now evaluate ΔG^{o}.

$$\Delta G^{\circ} = -RT\ \ln\ K_{eq} = -\frac{8.3145\ \text{J}}{\text{mol}\ \ \text{K}} \times 1000\ \text{K} \times \ln(3.41) = -1.02 \times 10^{4}\ \text{J/mol} = -10.2\ \text{kJ/mol}$$

(b) We can evaluate Q_c for this situation and compare the value with that of $K_c = 2.8 \times 10^2$ to determine the direction of the reaction to reach equilibrium.

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\dfrac{0.72\ \text{mol SO}_3}{2.50\ \text{L}}\right)^2}{\left(\dfrac{0.40\ \text{mol SO}_2}{2.50\ \text{L}}\right)^2 \times \left(\dfrac{0.18\ \text{mol O}_2}{2.50\ \text{L}}\right)} = 45 < 2.8 \times 10^2 = K_c$$

Since Q_c is smaller than K_c the reaction will shift right, producing sulfur trioxide and consuming sulfur dioxide and molecular oxygen, until the two values are equal.

<u>49.</u> **(M) (a)** $K = K_c$

$$\Delta G^{\circ} = -RT\ \ln\ K_{eq} = -\left(8.3145 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(445 + 273\right)\text{K}\ \ln\ 50.2 = -23.4\ \text{kJ}$$

(b) $K = K_p = K_c\left(RT\right)^{\Delta n_g} = 1.7 \times 10^{-13}\left(0.0821 \times 298\right)^{1/2} = 8.4 \times 10^{-13}$

$$\Delta G^{\circ} = -RT\ \ln\ K_p = -\left(8.3145 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(298\ \text{K}\right)\ \ln\ \left(8.4 \times 10^{-13}\right)$$

$$\Delta G^{\circ} = +68.9\ \text{kJ/mol}$$

(c) $K = K_p = K_c\left(RT\right)^{\Delta n} = 4.61 \times 10^{-3}\left(0.08206 \times 298\right)^{+1} = 0.113$

$$\Delta G^{\circ} = -RT\ \ln\ K_p = -\left(8.3145 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(298\text{K}\right)\ln\left(0.113\right) = +5.40\ \text{kJ/mol}$$

(d) $K = K_c = 9.14 \times 10^{-6}$

$$\Delta G^{\circ} = -RT\ \ln\ K_c = -\left(8.3145 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(298\ \text{K}\right)\ln\left(9.14 \times 10^{-6}\right)$$

$$\Delta G^{\circ} = +28.7\ \text{kJ/mol}$$

50. **(M) (a)** The first equation involves the formation of one mole of $Mg^{2+}(aq)$ from $Mg(OH)_2(s)$ and $2H^{+}(aq)$, while the second equation involves the formation of only half-a-mole of $Mg^{2+}(aq)$. We would expect a free energy change of half the size if only half as much product is formed.

(b) The value of K for the first reaction is the square of the value of K for the second reaction. The equilibrium constant expressions are related in the same fashion.

$$K_1 = \frac{\left[Mg^{2+}\right]}{\left[H^{+}\right]^2} = \left(\frac{\left[Mg^{2+}\right]^{1/2}}{\left[H^{+}\right]}\right)^2 = \left(K_2\right)^2$$

(c) The equilibrium solubilities will be the same regardless which expression is used. The equilibrium conditions (solubilities in this instance) are the same no matter how we choose to express them in an equilibrium constant expression.

51. **(E)** $\Delta G^{o} = -RT \ln K_{p} = -\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\text{K}^{-1}\right)\left(298\,\text{K}\right)\ln\left(6.5\times10^{11}\right) = -67.4\ \text{kJ/mol}$

$$
\begin{array}{ll}
\text{CO(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{COCl}_2\text{(g)} & \Delta G^{o} = -67.4\,\text{kJ/mol} \\
\text{C(graphite)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)} & \Delta G_f^{\circ} = -137.2\ \text{kJ/mol} \\
\hline
\text{C(graphite)} + \tfrac{1}{2}\text{O}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{COCl}_2\text{(g)} & \Delta G_f^{\circ} = -204.6\ \text{kJ/mol}
\end{array}
$$

ΔG_f° of $COCl_2(g)$ given in Appendix D is -204.6 kJ/mol, thus the agreement is excellent.

52. **(M)** In each case, we first determine the value of ΔG^{o} for the solubility reaction. From that, we calculate the value of the equilibrium constant, K_{sp}, for the solubility reaction.

(a) $\text{AgBr(s)} \rightleftharpoons \text{Ag}^{+}\text{(aq)} + \text{Br}^{-}\text{(aq)}$

$$\Delta G^{o} = \Delta G_f^{\circ}\left[\text{Ag}^{+}\text{(aq)}\right] + \Delta G_f^{\circ}\left[\text{Br}^{-}\text{(aq)}\right] - \Delta G_f^{\circ}\left[\text{AgBr(s)}\right]$$
$$= 77.11\ \text{kJ/mol} - 104.0\ \text{kJ/mol} - \left(-96.90\ \text{kJ/mol}\right) = +70.0\ \text{kJ/mol}$$

$$\ln K = \frac{-\Delta G^{o}}{RT} = \frac{-70.0\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times298.15\ \text{K}} = -28.2; \qquad K_{sp} = e^{-28.2} = 6\times10^{-13}$$

(b) $\text{CaSO}_4\text{(s)} \rightleftharpoons \text{Ca}^{2+}\text{(aq)} + \text{SO}_4^{\ 2-}\text{(aq)}$

$$\Delta G^{o} = \Delta G_f^{\ o}\left[\text{Ca}^{2+}\text{(aq)}\right] + \Delta G_f^{\ o}\left[\text{SO}_4^{\ 2-}\text{(aq)}\right] - \Delta G_f^{\ o}\left[\text{CaSO}_4\text{(s)}\right]$$
$$= -553.6\ \text{kJ/mol} - 744.5\ \text{kJ/mol} - \left(-1332\ \text{kJ/mol}\right) = +34\ \text{kJ/mol}$$

$$\ln K = \frac{-\Delta G^{o}}{RT} = \frac{-34\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times298.15\ \text{K}} = -14; \qquad K_{sp} = e^{-14} = 8\times10^{-7}$$

(c) $\text{Fe(OH)}_3\text{(s)} \rightleftharpoons \text{Fe}^{3+}\text{(aq)} + 3\text{OH}^{-}\text{(aq)}$

$$\Delta G^{o} = \Delta G_f^{\circ}\left[\text{Fe}^{3+}\text{(aq)}\right] + 3\,\Delta G_f^{\circ}\left[\text{OH}^{-}\text{(aq)}\right] - \Delta G_f^{\circ}\left[\text{Fe(OH)}_3\text{(s)}\right]$$
$$= -4.7\ \text{kJ/mol} + 3\times\left(-157.2\ \text{kJ/mol}\right) - \left(-696.5\ \text{kJ/mol}\right) = +220.2\ \text{kJ/mol}$$

$$\ln K = \frac{-\Delta G^{o}}{RT} = \frac{-220.2\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times298.15\ \text{K}} = -88.83 \qquad K_{sp} = e^{-88.83} = 2.6\times10^{-39}$$

53. **(M)(a)** We can determine the equilibrium partial pressure from the value of the equilibrium constant.

$$\Delta G^{o} = -RT\ln K_{p} \qquad \ln K_{p} = -\frac{\Delta G^{o}}{RT} = -\frac{58.54\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times298.15\ \text{K}} = -23.63$$

$$K_{p} = P\{\text{O}_2\text{(g)}\}^{1/2} = e^{-23.63} = 5.5\times10^{-11} \qquad P\{\text{O}_2\text{(g)}\} = \left(5.5\times10^{-11}\right)^{2} = 3.0\times10^{-21}\ \text{atm}$$

(b) Lavoisier did two things to increase the quantity of oxygen that he obtained. First, he ran the reaction at a high temperature, which favors the products (i.e., the side with molecular oxygen.) Second, the molecular oxygen was removed immediately after it was formed, which causes the equilibrium to shift to the right continuously (the shift towards products as result of the removal of the O_2 is an example of Le Châtelier's principle).

54. **(D) (a)** We determine the values of ΔH^o and ΔS^o from the data in Appendix D, and then the value of ΔG^o at $25^\circ C = 298$ K.

$$\Delta H^o = \Delta H_f^\circ[CH_3OH(g)] + \Delta H_f^\circ[H_2O(g)] - \Delta H_f^\circ[CO_2(g)] - 3\,\Delta H_f^\circ[H_2(g)]$$

$$= -200.7 \text{ kJ/mol} + (-241.8 \text{ kJ/mol}) - (-393.5 \text{ kJ/mol}) - 3(0.00 \text{ kJ/mol}) = -49.0 \text{ kJ/mol}$$

$$\Delta S^o = S^o[CH_3OH(g)] + S^o[H_2O(g)] - S^o[CO_2(g)] - 3\,S^o[H_2(g)]$$

$$= (239.8 + 188.8 - 213.7 - 3\times 130.7)\text{ J mol}^{-1}\text{K}^{-1} = -177.2 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o = -49.0 \text{ kJ/mol} - 298 \text{ K}(-0.1772 \text{ kJ mol}^{-1}\text{K}^{-1}) = +3.81 \text{ kJ/mol}$$

Because the value of ΔG^o is positive, this reaction does not proceed in the forward direction at 25° C.

(b) Because the value of ΔH^o is negative and that of ΔS^o is negative, the reaction is *non-spontaneous* at high temperatures, if reactants and products are *in their standard states*. The reaction will proceed slightly in the forward direction, however, to produce an equilibrium mixture with small quantities of $CH_3OH(g)$ and $H_2O(g)$. Also, because the forward reaction is exothermic, this reaction is favored by lowering the temperature. That is, the value of K increases with decreasing temperature.

(c) $$\Delta G^o_{500K} = \Delta H^o - T\,\Delta S^o = -49.0 \text{ kJ/mol} - 500.\text{K}(-0.1772 \text{ kJ mol}^{-1}\text{K}^{-1}) = 39.6 \text{ kJ/mol}$$

$$= 39.6\times 10^3 \text{ J/mol} = -RT\ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-39.6\times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{K}^{-1}\times 500.\text{ K}} = -9.53; \quad K_p = e^{-9.53} = 7.3\times 10^{-5}$$

(d)

Reaction:	$CO_2(g) +$	$3H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$	$+H_2O(g)$
Initial:	1.00 atm	1.00 atm		0 atm	0 atm
Changes:	$-x$ atm	$-3x$ atm		$+x$ atm	$+x$ atm
Equil:	$(1.00 - x)$ atm	$(1.00 - 3x)$ atm		x atm	x atm

$$K_p = 7.3\times 10^{-5} = \frac{P\{CH_3OH\}P\{H_2O\}}{P\{CO_2\}P\{H_2\}^3} = \frac{x\cdot x}{(1.00-x)(1.00-3x)^3} \approx x^2$$

$x = \sqrt{7.3\times 10^{-5}} = 8.5\times 10^{-3}$ atm $= P\{CH_3OH\}$ Our assumption, that $3x \ll 1.00$ atm, is valid.

ΔG^o and K as Function of Temperature

55 **(M)(a)** $$\Delta S^o = S^o[Na_2CO_3(s)] + S^o[H_2O(l)] + S^o[CO_2(g)] - 2S^o[NaHCO_3(s)]$$

$$= 135.0\ \frac{\text{J}}{\text{K mol}} + 69.91\frac{\text{J}}{\text{K mol}} + 213.7\ \frac{\text{J}}{\text{K mol}} - 2\left(101.7\ \frac{\text{J}}{\text{K mol}}\right) = +215.2\ \frac{\text{J}}{\text{K mol}}$$

(b) $\Delta H^{\circ} = \Delta H_f^{\circ}\left[Na_2CO_3(s)\right] + \Delta H_f^{\circ}\left[H_2O(l)\right] + \Delta H_f^{\circ}\left[CO_2(g)\right] - 2\Delta H_f^{\circ}\left[NaHCO_3(s)\right]$

$$= -1131\frac{kJ}{mol} - 285.8\frac{kJ}{mol} - 393.5\frac{kJ}{mol} - 2\left(-950.8\frac{kJ}{mol}\right) = +91\frac{kJ}{mol}$$

(c) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 91 \text{ kJ/mol} - (298 \text{ K})(215.2\times10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})$

$$= 91 \text{ kJ/mol} - 64.13 \text{ kJ/mol} = 27 \text{ kJ/mol}$$

(d) $\Delta G^{\circ} = -RT\ln K \qquad \ln K = -\frac{\Delta G^{\circ}}{RT} = -\frac{27\times10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{K}^{-1}\times 298 \text{ K}} = -10.\underline{9}$

$K = e^{-10.9} = 2\times10^{-5}$

56. **(M) (a)** $\Delta S^{\circ} = S^{\circ}\left[CH_3CH_2OH(g)\right] + S^{\circ}\left[H_2O(g)\right] - S^{\circ}\left[CO(g)\right] - 2S^{\circ}\left[H_2(g)\right] - S^{\circ}\left[CH_3OH(g)\right]$

$$\Delta S^{\circ} = 282.7\frac{J}{K\text{ mol}} + 188.8\frac{J}{K\text{ mol}} - 197.7\frac{J}{K\text{ mol}} - 2\left(130.7\frac{J}{K\text{ mol}}\right) - 239.8\frac{J}{K\text{ mol}}$$

$$\Delta S^{\circ} = -227.4\frac{J}{K\text{ mol}}$$

$$\Delta H^{\circ} = \Delta H_f^{\circ}\left[CH_3CH_2OH(g)\right] + \Delta H_f^{\circ}\left[H_2O(g)\right] - \Delta H_f^{\circ}\left[CO(g)\right] - 2\Delta H_f^{\circ}\left[H_2(g)\right] - \Delta H_f^{\circ}\left[CH_3OH(g)\right]$$

$$\Delta H^{\circ} = -235.1\frac{kJ}{mol} - 241.8\frac{kJ}{mol} - \left(-110.5\frac{kJ}{mol}\right) - 2\left(0.00\frac{kJ}{mol}\right) - \left(-200.7\frac{kJ}{mol}\right)$$

$$\Delta H^{\circ} = -165.7\frac{kJ}{mol}$$

$$\Delta G^{\circ} = -165.7\frac{kJ}{mol} - (298 \text{ K})\left(-227.4\times10^{-3}\frac{kJ}{K\text{ mol}}\right) = -165.4\frac{kJ}{mol} + 67.8\frac{kJ}{mol} = -97.9\frac{kJ}{mol}$$

(b) $\Delta H^{\circ} < 0$ for this reaction. Thus it is favored at low temperatures. Also, because $\Delta n_{gas} = +2 - 4 = -2$, which is less than zero, the reaction is favored at high pressures.

(c) First we assume that neither ΔS° nor ΔH° varies significantly with temperature. Then we compute a value for ΔG° at 750 K. From this value of ΔG°, we compute a value for K_p.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -165.7 \text{ kJ/mol} - (750.\text{K})(-227.4\times10^{-3} \text{ kJ mol}^{-1}\text{ K}^{-1})$$

$$= -165.7 \text{ kJ/mol} + 170.6 \text{ kJ/mol} = +4.9 \text{ kJ/mol} = -RT\ln K_p$$

$$\ln K_p = -\frac{\Delta G^{\circ}}{RT} = -\frac{4._9\times10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1}\times 750.\text{K}} = -0.79 \qquad K_p = e^{-0.79} = 0.5$$

57. **(E)** In this problem we are asked to determine the temperature for the reaction between iron(III) oxide and carbon monoxide to yield iron and carbon dioxide given ΔG^{o}, ΔH^{o}, and ΔS^{o}. We proceed by rearranging $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ in order to express the temperature as a function of ΔG^{o}, ΔH^{o}, and ΔS^{o}.

Stepwise approach:
Rearrange $\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$ in order to express T as a function of ΔG^{o}, ΔH^{o}, and ΔS^{o}:

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

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

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

Calculate *T*:

$$T=\frac{-24.8\times10^{3}\ \text{J}-\left(-45.5\times10^{3}\ \text{J}\right)}{15.2\ \text{J/K}}=1.36\times10^{3}\ \text{K}$$

Conversion pathway approach:

$$\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}\Rightarrow T=\frac{\Delta H^{\circ}-\Delta G^{\circ}}{\Delta S^{\circ}}=\frac{-24.8\times10^{3}\ \text{J}-\left(-45.5\times10^{3}\ \text{J}\right)}{15.2\ \text{J/K}}=1.36\times10^{3}\ \text{K}$$

58. **(E)** We use the van't Hoff equation with $\Delta H^{\circ}=-1.8\times10^{5}$ J/mol, $T_1=800.$ K, $T_2=100.^{\circ}\text{C}=373\text{K}$, and $K_1=9.1\times10^{2}$.

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{-1.8\times10^{5}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{800\ \text{K}}-\frac{1}{373\text{K}}\right)=31$$

$$\frac{K_2}{K_1}=\text{e}^{31}=2.\underline{9}\times10^{13}=\frac{K_2}{9.1\times10^{2}}\qquad K_2=\left(2.\underline{9}\times10^{13}\right)\left(9.1\times10^{2}\right)=3\times10^{16}$$

<u>**59.**</u> **(M)** We first determine the value of ΔG° at 400°C, from the values of ΔH° and ΔS°, which are calculated from information listed in Appendix D.

$$\Delta H^{\circ}=2\Delta H_{\text{f}}^{\circ}\left[\text{NH}_3(\text{g})\right]-\Delta H_{\text{f}}^{\circ}\left[\text{N}_2(\text{g})\right]-3\Delta H_{\text{f}}^{\circ}\left[\text{H}_2(\text{g})\right]$$
$$=2(-46.11\,\text{kJ/mol})-(0.00\,\text{kJ/mol})-3(0.00\ \text{kJ/mol})=-92.22\,\text{kJ/mol N}_2$$

$$\Delta S^{\circ}=2S^{\circ}\left[\text{NH}_3(\text{g})\right]-S^{\circ}\left[\text{N}_2(\text{g})\right]-3S^{\circ}\left[\text{H}_2(\text{g})\right]$$
$$=2\left(192.5\ \text{J mol}^{-1}\ \text{K}^{-1}\right)-\left(191.6\ \text{J mol}^{-1}\ \text{K}^{-1}\right)-3\left(130.7\ \text{J mol}^{-1}\ \text{K}^{-1}\right)=-198.7\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$$\Delta G^{\circ}=\Delta H^{\circ}-T\ \Delta S^{\circ}=-92.22\ \text{kJ/mol}-673\ \text{K}\times\left(-0.1987\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)$$
$$=+41.51\,\text{kJ/mol}=-RT\ \ln K_{\text{p}}$$

$$\ln K_{\text{p}}=\frac{-\Delta G^{\circ}}{RT}=\frac{-41.51\times10^{3}\,\text{J/mol}}{8.3145\,\text{J mol}^{-1}\text{K}^{-1}\times673\text{K}}=-7.42;\quad K_{\text{p}}=\text{e}^{-7.42}=6.0\times10^{-4}$$

60. **(M) (a)** $\Delta H^\circ = \Delta H_f^\circ[CO_2(g)] + \Delta H_f^\circ[H_2(g)] - \Delta H_f^\circ[CO(g)] - \Delta H_f^\circ[H_2O(g)]$

$= -393.5 \text{ kJ/mol} - 0.00 \text{ kJ/mol} - (-110.5 \text{ kJ/mol}) - (-241.8 \text{ kJ/mol}) = -41.2 \text{ kJ/mol}$

$$\Delta S^\circ = S^\circ[CO_2(g)] + S^\circ[H_2(g)] - S^\circ[CO(g)] - S^\circ[H_2O(g)]$$
$$= 213.7 \text{ J mol}^{-1}\text{ K}^{-1} + 130.7 \text{ J mol}^{-1}\text{ K}^{-1} - 197.7 \text{ J mol}^{-1}\text{ K}^{-1} - 188.8 \text{ J mol}^{-1}\text{ K}^{-1}$$
$$= -42.1 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o = -41.2\text{kJ/mol} - 298.15\text{K} \times (-42.1 \times 10^{-3})\text{kJ/molK}$$
$$\Delta G^o = -41.2\text{kJ/mol} + 12.6\text{kJ/mol} = -28.6\text{kJ/mol}$$

(b) $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = -41.2 \text{ kJ/mol} - (875 \text{ K})(-42.1 \times 10^{-3} \text{ kJ mol}^{-1}\text{ K}^{-1})$

$= -41.2 \text{ kJ/mol} + 36.8 \text{ kJ/mol} = -4.4 \text{ kJ/mol} = -RT \ln K_p$

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{-4.4 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 875\text{K}} = +0.60 \qquad K_p = e^{+0.60} = 1.8$$

61. **(M)** We assume that both ΔH° and ΔS° are constant with temperature.

$$\Delta H^\circ = 2\Delta H_f^\circ[SO_3(g)] - 2\Delta H_f^\circ[SO_2(g)] - \Delta H_f^\circ[O_2(g)]$$
$$= 2(-395.7 \text{ kJ/mol}) - 2(-296.8 \text{ kJ/mol}) - (0.00 \text{ kJ/mol}) = -197.8 \text{ kJ/mol}$$
$$\Delta S^\circ = 2S^\circ[SO_3(g)] - 2S^\circ[SO_2(g)] - S^\circ[O_2(g)]$$
$$= 2(256.8 \text{ J mol}^{-1}\text{ K}^{-1}) - 2(248.2 \text{ J mol}^{-1}\text{ K}^{-1}) - (205.1 \text{ J mol}^{-1}\text{ K}^{-1})$$
$$= -187.9 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \qquad \Delta H^\circ = T\Delta S^\circ - RT\ln K \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K}$$

$$T = \frac{-197.8 \times 10^3 \text{ J/mol}}{-187.9 \text{ J mol}^{-1}\text{ K}^{-1} - 8.3145 \text{ J mol}^{-1}\text{ K}^{-1} \ln(1.0 \times 10^6)} \approx 650 \text{ K}$$

This value compares very favorably with the value of $T = 6.37 \times 10^2$ that was obtained in Example 19-10.

62. **(E)** We use the van't Hoff equation to determine the value of ΔH° ($448^\circ\text{ C} = 721\text{ K}$ and $350^\circ\text{ C} = 623\text{ K}$).

$$\ln\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \ln\frac{50.0}{66.9} = -0.291 = \frac{\Delta H^\circ}{R}\left(\frac{1}{623} - \frac{1}{721}\right) = \frac{\Delta H^\circ}{R}(2.2 \times 10^{-4})$$

$$\frac{\Delta H^\circ}{R} = \frac{-0.291}{2.2 \times 10^{-4}\text{ K}^{-1}} = -1.3 \times 10^3 \text{ K};$$

$$\Delta H^\circ = -1.3 \times 10^3\text{K} \times 8.3145 \text{ J K}^{-1}\text{ mol}^{-1} = -11 \times 10^3\text{J mol}^{-1} = -11 \text{ kJ mol}^{-1}$$

63. **(M) (a)** $\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{57.2\times10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{298\text{ K}}-\frac{1}{273\text{ K}}\right) = -2.11$

$\frac{K_2}{K_1} = e^{-2.11} = 0.121 \qquad K_2 = 0.121\times0.113 = 0.014 \text{ at } 273\text{ K}$

(b) $\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{57.2\times10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{T_1}-\frac{1}{298\text{ K}}\right) = \ln\frac{0.113}{1.00} = -2.180$

$\left(\frac{1}{T_1}-\frac{1}{298\text{K}}\right) = \frac{-2.180\times8.3145}{57.2\times10^3}\text{K}^{-1} = -3.17\times10^{-4}\text{K}^{-1}$

$\frac{1}{T_1} = \frac{1}{298} - 3.17\times10^{-4} = 3.36\times10^{-3} - 3.17\times10^{-4} = 3.04\times10^{-3}\text{ K}^{-1}; \quad T_1 = 329\text{ K}$

64. **(D)** First we calculate ΔG^o at 298 K to obtain a value for K_{eq} at that temperature.

$\Delta G^o = 2\Delta G_f^\circ\left[NO_2(g)\right] - 2\Delta G_f^\circ\left[NO(g)\right] - \Delta G_f^\circ\left[O_2(g)\right]$

$= 2(51.31\text{ kJ/mol}) - 2(86.55\text{ kJ/mol}) - 0.00\text{ kJ/mol} = -70.48\text{ kJ/mol}$

$\ln K = \frac{-\Delta G^\circ}{RT} = -\frac{-70.48\times10^3\text{ J/mol K}}{\frac{8.3145\text{ J}}{\text{mol K}}\times298.15\text{ K}} = 28.43 \qquad K = e^{28.43} = 2.2\times10^{12}$

Now we calculate ΔH^o for the reaction, which then will be inserted into the van't Hoff equation.

$\Delta H^o = 2\Delta H_f^\circ\left[NO_2(g)\right] - 2\Delta H_f^\circ\left[NO(g)\right] - \Delta H_f^\circ\left[O_2(g)\right]$

$= 2(33.18\text{ kJ/mol}) - 2(90.25\text{ kJ/mol}) - 0.00\text{ kJ/mol} = -114.14\text{ kJ/mol}$

$\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{-114.14\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{298\text{ K}}-\frac{1}{373\text{ K}}\right) = -9.26$

$\frac{K_2}{K_1} = e^{-9.26} = 9.5\times10^{-5}; \quad K_2 = 9.5\times10^{-5}\times2.2\times10^{12} = 2.1\times10^8$

Another way to find K at 100 ºC is to compute $\Delta H^o\,(-114.14\text{ kJ/mol})$ from ΔH_f^o values and $\Delta S^o\left(-146.5\text{ J mol}^{-1}\text{ K}^{-1}\right)$ from S^o values. Then determine ΔG^o(–59.5 kJ/mol), and find K_p with the expression $\Delta G^o = -RT\ln K_p$. Not surprisingly, we obtain the same result, $K_p = 2.2\times10^8$.

65. **(M)** First, the van't Hoff equation is used to obtain a value of ΔH^o. $200^\circ\text{C} = 473\text{K}$ and $260^\circ\text{C} = 533\text{K}$.

$\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \ln\frac{2.15\times10^{11}}{4.56\times10^8} = 6.156 = \frac{\Delta H^o}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{533\text{K}}-\frac{1}{473\text{ K}}\right)$

$6.156 = -2.9\times10^{-5}\Delta H^o \qquad \Delta H^o = \frac{6.156}{-2.9\times10^{-5}} = -2.1\times10^5\text{J / mol} = -2.1\times10^2\text{kJ / mol}$

Another route to ΔH^{o} is the combination of standard enthalpies of formation.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

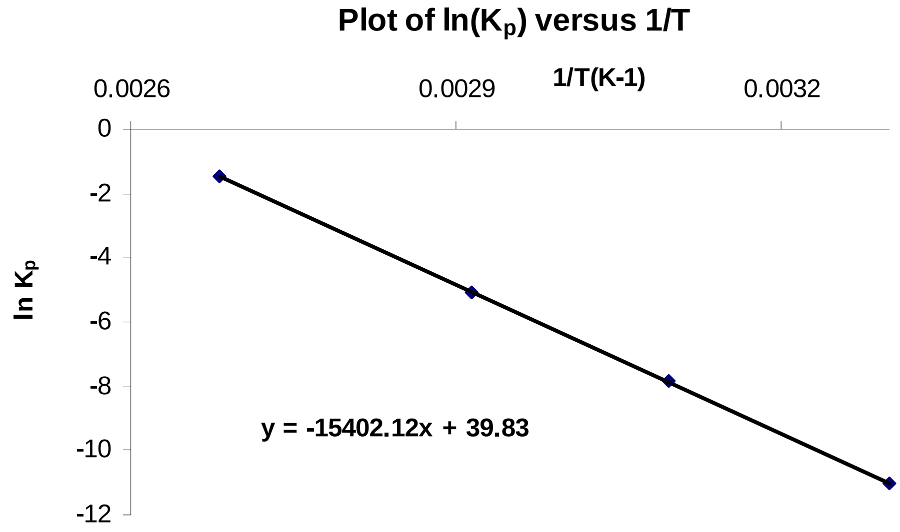
$$\Delta H^{o} = \Delta H_f^{\circ}[CH_4(g)] + \Delta H_f^{\circ}[H_2O(g)] - \Delta H_f^{\circ}[CO(g)] - 3\Delta H_f^{\circ}[H_2(g)]$$

$$= -74.81\text{ kJ/mol} - 241.8\text{ kJ/mol} - (-110.5) - 3\times 0.00\text{ kJ/mol} = -206.1\text{ kJ/mol}$$

Within the precision of the data supplied, the results are in good agreement.

66. **(D) (a)**

$t, ^{\circ}C$	T, K	$1/T, K^{-1}$	K_p	$\ln K_p$
30.	303	3.30×10^{-3}	1.66×10^{-5}	-11.006
50.	323	3.10×10^{-3}	3.90×10^{-4}	-7.849
70.	343	2.92×10^{-3}	6.27×10^{-3}	-5.072
100.	373	2.68×10^{-3}	2.31×10^{-1}	-1.465



$$\Delta H^{o} = -(8.3145\text{ J mol}^{-1}\text{K}^{-1})(-1.54\times 10^{4}\text{ K}) = 128\times 10^{3}\text{ J/mol} = 128\text{ kJ/mol}$$

(b) When the total pressure is 2.00 atm, and both gases have been produced from $NaHCO_3(s)$,

$$P\{H_2O(g)\} = P\{CO_2(g)\} = 1.00\text{ atm}$$

$$K_p = P\{H_2O(g)\}P\{CO_2(g)\} = (1.00)(1.00) = 1.00$$

Thus, $\ln K_p = \ln(1.00) = 0.000$. The corresponds to $1/T = 2.59\times 10^{-3}\text{ K}^{-1}$;
$T = 386\text{ K}$.
We can compute the same temperature from the van't Hoff equation.

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{128\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{T_1}-\frac{1}{303\ \text{K}}\right)=\ln\frac{1.66\times10^{-5}}{1.00}=-11.006$$

$$\left(\frac{1}{T_1}-\frac{1}{303\ \text{K}}\right)=\frac{-11.006\times8.3145}{128\times10^{3}}\ \text{K}^{-1}=-7.15\times10^{-4}\ \text{K}^{-1}$$

$$\frac{1}{T_1}=\frac{1}{303}-7.15\times10^{-4}=3.30\times10^{-3}-7.15\times10^{-4}=2.59\times10^{-3}\ \text{K}^{-1};\quad T_1=386\ \text{K}$$

This temperature agrees well with the result obtained from the graph.

Coupled Reactions

67. **(E) (a)** We compute ΔG° for the given reaction in the following manner

$$\begin{aligned}\Delta H^{\circ} &= \Delta H_f^{\circ}\left[\text{TiCl}_4(\text{l})\right]+\Delta H_f^{\circ}\left[\text{O}_2(\text{g})\right]-\Delta H_f^{\circ}\left[\text{TiO}_2(\text{s})\right]-2\Delta H_f^{\circ}\left[\text{Cl}_2(\text{g})\right]\\ &= -804.2\ \text{kJ/mol}+0.00\ \text{kJ/mol}-(-944.7\ \text{kJ/mol})-2(0.00\ \text{kJ/mol})\\ &= +140.5\ \text{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^{\circ} &= S^{\circ}\left[\text{TiCl}_4(\text{l})\right]+S^{\circ}\left[\text{O}_2(\text{g})\right]-S^{\circ}\left[\text{TiO}_2(\text{s})\right]-2S^{\circ}\left[\text{Cl}_2(\text{g})\right]\\ &= 252.3\ \text{J mol}^{-1}\ \text{K}^{-1}+205.1\ \text{J mol}^{-1}\ \text{K}^{-1}-\left(50.33\ \text{J mol}^{-1}\ \text{K}^{-1}\right)-2\left(223.1\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\\ &= -39.1\ \text{J mol}^{-1}\ \text{K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^{\circ} &= \Delta H^{\circ}-T\,\Delta S^{\circ}=+140.5\ \text{kJ/mol}-(298\ \text{K})\left(-39.1\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\\ &= +140.5\ \text{kJ/mol}+11.6\ \text{kJ/mol}=+152.1\ \text{kJ/mol}\end{aligned}$$

Thus the reaction is non-spontaneous at 25° C. (we also could have used values of ΔG_f° to calculate ΔG°).

(b) For the cited reaction, $\Delta G^{\circ}=2\Delta G_f^{\circ}\left[\text{CO}_2(\text{g})\right]-2\Delta G_f^{\circ}\left[\text{CO}(\text{g})\right]-\Delta G_f^{\circ}\left[\text{O}_2(\text{g})\right]$

$$\Delta G^{\circ}=2(-394.4\ \text{kJ/mol})-2(-137.2\ \text{kJ/mol})-0.00\ \text{kJ/mol}=-514.4\ \text{kJ/mol}$$

Then we couple the two reactions.

$$\text{TiO}_2(\text{s})+2\text{Cl}_2(\text{g})\longrightarrow\text{TiCl}_4(\text{l})+\text{O}_2(\text{g})\qquad \Delta G^{\circ}=+152.1\ \text{kJ/mol}$$

$$2\text{CO}(\text{g})+\text{O}_2(\text{g})\longrightarrow2\text{CO}_2(\text{g})\qquad \Delta G^{\circ}=-514.4\ \text{kJ/mol}$$

$$\text{TiO}_2(\text{s})+2\text{Cl}_2(\text{g})+2\text{CO}(\text{g})\longrightarrow\text{TiCl}_4(\text{l})+2\text{CO}_2(\text{g});\ \Delta G^{\circ}=-362.3\ \text{kJ/mol}$$

The coupled reaction has $\Delta G^{\circ}<0$, and, therefore, is spontaneous.

68. **(E)** If $\Delta G^{o} < 0$ for the sum of coupled reactions, the reduction of the oxide with carbon is spontaneous.

(a)
$$\mathrm{NiO(s) \rightarrow Ni(s) + \tfrac{1}{2}O_2(g)} \qquad \Delta G^{o} = +115\ \mathrm{kJ}$$
$$\mathrm{C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)} \qquad \Delta G^{o} = -250\ \mathrm{kJ}$$
$$\mathrm{Net: NiO}(s) + \mathrm{C(s) \rightarrow Ni(s) + CO(g)} \qquad \Delta G^{o} = +115\ \mathrm{kJ} - 250\ \mathrm{kJ} = -135\ \mathrm{kJ}$$
Therefore the coupled reaction is spontaneous

(b)
$$\mathrm{MnO(s) \rightarrow Mn(s) + \tfrac{1}{2}O_2(g)} \qquad \Delta G^{o} = +280\ \mathrm{kJ}$$
$$\mathrm{C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)} \qquad \Delta G^{o} = -250\ \mathrm{kJ}$$
$$\mathrm{Net: MnO(s) + C(s) \longrightarrow Mn(s) + CO(g)} \qquad \Delta G^{o} = +280\ \mathrm{kJ} - 250\ \mathrm{kJ} = +30\ \mathrm{kJ}$$
Therefore the coupled reaction is non-spontaneous

(c)
$$\mathrm{TiO_2(s) \longrightarrow Ti(s) + O_2(g)} \qquad \Delta G^{o} = +630\ \mathrm{kJ}$$
$$\mathrm{2C(s) + O_2(g) \longrightarrow 2CO(g)} \qquad \Delta G^{o} = 2(-250\ \mathrm{kJ}) = -500\ \mathrm{kJ}$$
$$\mathrm{Net: TiO_2(s) + 2C(s) \longrightarrow Ti(s) + 2CO(g)} \qquad \Delta G^{o} = +630\ \mathrm{kJ} - 500\ \mathrm{kJ} = +130\ \mathrm{kJ}$$
Therefore the coupled reaction is non-spontaneous

69. **(E)** In this problem we need to determine if the phosphorylation of arginine with ATP is a spontaneous reaction. We proceed by coupling the two given reactions in order to calculate ΔG_t^o for the overall reaction. The sign of ΔG_t^o can then be used to determine whether the reaction is spontaneous or not.

Stepwise approach:

First determine ΔG_t^o for the coupled reaction:

$$\mathrm{ATP{+}H_2O \longrightarrow ADP{+}P} \qquad \Delta G_t^o = -31.5\mathrm{kJmol^{-1}}$$
$$\mathrm{arginine{+}P \longrightarrow phosphorarginine{+}H_2O} \qquad \Delta G_t^o = -33.2\mathrm{kJmol^{-1}}$$

$$\mathrm{ATP{+}arginine \longrightarrow phosphorarginine{+}ADP}$$
$$\Delta G^o = (-31.5 + 33.2)\mathrm{kJmol^{-1}} = 1.7\mathrm{kJmol^{-1}}$$

Examine the sign of ΔG_t^o:

$\Delta G_t^o > 0$. Therefore, the reaction is not spontaneous.

Conversion pathway approach:

ΔG_t^o for the coupled reaction is:

$$\mathrm{ATP{+}arginine \longrightarrow phosphorarginine{+}ADP}$$
$$\Delta G^o = (-31.5 + 33.2)\mathrm{kJmol^{-1}} = 1.7\mathrm{kJmol^{-1}}$$

Since $\Delta G_t^o > 0$, the reaction is not spontaneous.

70. **(E)** By coupling the two reactions, we obtain:

$$\text{Glu}^- + \text{NH}_4^+ \longrightarrow \text{Gln} + \text{H}_2\text{O} \qquad \Delta G_t^o = 14.8\,\text{kJmol}^{-1}$$

$$\text{ATP} + \text{H}_2\text{O} \longrightarrow \text{ADP} + \text{P} \qquad \Delta G_t^o = -31.5\,\text{kJmol}^{-1}$$

$$\text{Glu}^- + \text{NH}_4^+ + \text{ATP} \longrightarrow \text{Gln} + \text{ADP} + \text{P} \qquad \Delta G^o = (14.8 - 31.5)\,\text{kJmol}^{-1} = -16.7\,\text{kJmol}^{-1}$$

Therefore, the reaction is spontaneous.

INTEGRATIVE AND ADVANCED EXERCISES

71. (M) (a) The normal boiling point of mercury is that temperature at which the mercury vapor pressure is 1.00 atm, or where the equilibrium constant for the vaporization equilibrium reaction has a numerical value of 1.00. This is also the temperature where $\Delta G° = 0$, since $\Delta G° = -RT \ln K_{\text{eq}}$ and $\ln(1.00) = 0$.

$$\text{Hg(l)} \rightleftharpoons \text{Hg(g)}$$

$$\Delta H° = \Delta H°_f\,[\text{Hg(g)}] - \Delta H°_f\,[\text{Hg(l)}] = 61.32\,\text{kJ/mol} - 0.00\,\text{kJ/mol} = 61.32\,\text{kJ/mol}$$

$$\Delta S° = S°[\text{Hg(g)}] - S°[\text{Hg(l)}] = 175.0\,\text{J mol}^{-1}\,\text{K}^{-1} - 76.02\,\text{J mol}^{-1}\,\text{K}^{-1} = 99.0\,\text{J mol}^{-1}\,\text{K}^{-1}$$

$$0 = \Delta H° - T\,\Delta S° = 61.32 \times 10^3\ \text{J/mol} - T \times 99.0\,\text{J mol}^{-1}\,\text{K}^{-1}$$

$$T = \frac{61.32 \times 10^3\ \text{J/mol}}{99.0\,\text{J mol}^{-1}\,\text{K}^{-1}} = 619\,\text{K}$$

(b) The vapor pressure in atmospheres is the value of the equilibrium constant, which is related to the value of the free energy change for formation of Hg vapor.

$$\Delta G°_f\ [\text{Hg(g)}] = 31.82\,\text{kJ/mol} = -RT \ln K_{\text{eq}}$$

$$\ln K = \frac{-31.82 \times 10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}} = -12.84 \qquad K = e^{-12.84} = 2.65 \times 10^{-6}\ \text{atm}$$

Therefore, the vapor pressure of Hg at 25ºC is 2.65×10^{-6} atm.

72. (M) (a) **TRUE;** It is the change in free energy for a process in which reactants and products are all in their standard states (regardless of whatever states might be mentioned in the statement of the problem). When liquid and gaseous water are each at 1 atm at 100 °C (the normal boiling point), they are in equilibrium, so that $\Delta G = \Delta G° = 0$ is only true when the difference of the standard free energies of products and reactants is zero. A reaction with ΔG° = 0 would be at equilibrium when products and reactants were all present under standard state conditions and the pressure of $H_2O(g)$ = 2.0 atm is not the standard pressure for $H_2O(g)$.

(b) **FALSE;** $\Delta G \neq 0$. The system is not at equilibrium.

(c) FALSE; $\Delta G°$ can have only one value at any given temperature, and that is the value corresponding to all reactants and products in their standard states, so at the normal boiling point $\Delta G° = 0$ [as was also the case in answering part (a)]. Water will not vaporize spontaneously under standard conditions to produce water vapor with a pressure of 2 atmospheres.

(d) TRUE; $\Delta G > 0$. The process of transforming water to vapor at 2.0 atm pressure at 100°C is not a spontaneous process; the condensation (reverse) process is spontaneous. (i.e. for the system to reach equilibrium, some $H_2O(l)$ must form)

73. (D) $\Delta G° = +\frac{1}{2}\Delta G°_f\,[Br_2(g)] + \frac{1}{2}\Delta G°_f\,[Cl_2(g)] - \Delta G°_f\,[BrCl(g)]$

$= +\frac{1}{2}(3.11\,\text{kJ/mol}) + \frac{1}{2}(0.00\,\text{kJ/mol}) - (-0.98\,\text{kJ/mol}) = +2.54\,\text{kJ/mol} = -RT\ln K_p$

$$\ln K_p = -\frac{\Delta G°}{RT} = -\frac{2.54\times10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}\times 298.15\,\text{K}} = -1.02 \qquad K_p = e^{-1.02} = 0.361$$

For ease of solving the problem, we double the reaction, which squares the value of the equilibrium constant. $K_{eq} = (0.357)^2 = 0.130$

Reaction:	$2\,BrCl(g) \rightleftharpoons$	$Br_2(g)$ +	$Cl_2(g)$
Initial:	$1.00\,\text{mol}$	$0\,\text{mol}$	$0\,\text{mol}$
Changes:	$-2x\,\text{mol}$	$+x\,\text{mol}$	$+x\,\text{mol}$
Equil:	$(1.00-2x)\text{mol}$	$x\,\text{mol}$	$x\,\text{mol}$

$$K_p = \frac{P\{Br_2(g)\}P\{Cl_2(g)\}}{P\{BrCl(g)\}^2} = \frac{[n\{Br_2(g)\}RT/V][n\{Cl_2(g)\}RT/V]}{[n\{BrCl(g)\}RT/V]^2} = \frac{n\{Br_2(g)\}n\{Cl_2(g)\}}{n\{BrCl(g)\}^2}$$

$$= \frac{x^2}{(1.00-2x)^2} = (0.361)^2 \qquad \frac{x}{1.00-2x} = 0.361 \qquad x = 0.361 - 0.722\,x$$

$$x = \frac{0.361}{1.722} = 0.210\,\text{mol}\,Br_2 = 0.210\,\text{mol}\,Cl_2 \qquad 1.00-2x = 0.580\,\text{mol}\,BrCl$$

74. (M) First we determine the value of K_p for the dissociation reaction. If $I_2(g)$ is 50% dissociated, then for every mole of undissociated $I_2(g)$, one mole of $I_2(g)$ has dissociated, producing two moles of I(g). Thus, the partial pressure of I(g) is twice the partial pressure of $I_2(g)$ ($I_2(g) \rightleftharpoons 2\,I(g)$).

$$P_{total} = 1.00\,\text{atm} = P_{I_2(g)} + P_{I(g)} = P_{I_2(g)} + 2\times P_{I_2(g)} = 3\,P_{I_2(g)} \qquad P_{I_2(g)} = 0.333\,\text{atm}$$

$$K_p = \frac{P_{I(g)}{}^2}{P_{I_2(g)}} = \frac{(0.667)^2}{0.333} = 1.34 \qquad \ln K_p = 0.293$$

$$\Delta H° = 2\,\Delta H°_f\,[I(g)] - \Delta H°_f\,[I_2(g)] = 2\times106.8\,\text{kJ/mol} - 62.44\,\text{kJ/mol} = 151.2\,\text{kJ/mol}$$

$$\Delta S° = 2\,S°[I(g)] - S°[I_2(g)] = 2\times180.8\,\text{J mol}^{-1}\,\text{K}^{-1} - 260.7\,\text{J mol}^{-1}\,\text{K}^{-1} = 100.9\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Now we equate two expressions for $\Delta G°$ and solve for T.

$$\Delta G° = \Delta H° - T\,\Delta S° = -RT\,\ln K_p = 151.2\times10^3 - 100.9T = -8.3145\times T\times 0.293$$

$$151.2\times10^3 = 100.9T - 2.44T = 98.4T \qquad T = \frac{151.2\times10^3}{98.5} = 1535\,\text{K} \approx 1.5\times10^3\,\text{K}$$

75. **(M)** **(a)** The oxide with the most positive (least negative) value of $\Delta G°_f$ is the one that most readily decomposes to the free metal and O_2(g), since the decomposition is the reverse of the formation reaction. Thus the oxide that decomposes most readily is Ag_2O(s).

(b) The decomposition reaction is $2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$ For this reaction $K_p = P_{O_2(g)}$. Thus, we need to find the temperature where $K_p = 1.00$.Since $\Delta G° = -RT\ln K_p$ and $\ln(1.00) = 0$, we wish to know the temperature where $\Delta G° = 0$. Note also that the decomposition is the reverse of the formation reaction. Thus, the following values are valid for the decomposition reaction at 298 K.

$\Delta H° = +31.05$ kJ/mol $\qquad$ $\Delta G° = +11.20$ kJ/mol

We use these values to determine the value of $\Delta S°$ for the reaction.

$$\Delta G° = \Delta H° - T\,\Delta S° \quad T\,\Delta S° = \Delta H° - \Delta G° \quad \Delta S° = \frac{\Delta H° - \Delta G°}{T}$$

$$\Delta S° = \frac{31.05\times10^3\ \text{J/mol} - 11.20\times10^3\ \text{J/mol}}{298\,\text{K}} = +66.6\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Now we determine the value of T where $\Delta G° = 0$.

$$T = \frac{\Delta H° - \Delta G°}{\Delta S°} = \frac{31.05\times10^3\ \text{J/mol} - 0.0\,\text{J/mol}}{+66.6\,\text{J mol}^{-1}\,\text{K}^{-1}} = 466\,\text{K} = 193\,°\text{C}$$

76. **(M)** At 127 °C = 400 K, the two phases are in equilibrium, meaning that

$$\Delta G°_{rxn} = 0 = \Delta H°_{rxn} - T\Delta S°_{rxn} = [\Delta H°_f\,(\text{yellow}) - \Delta H°_f\,(\text{red})] - T[S°(\text{yellow}) - S°(\text{red})]$$

$$= [-102.9 - (-105.4)]\times10^3\ \text{J} - 400\,\text{K}\times[S°(\text{yellow}) - 180\,\text{J mol}^{-1}\,\text{K}^{-1}]$$

$$= 2.5\times10^3\ \text{J/mol} - 400\,\text{K}\times S°(\text{yellow}) + 7.20\times10^4\ \text{J/mol}$$

$$S°(\text{yellow}) = \frac{(7.20\times10^4 + 2.5\times10^3)\,\text{J/mol}}{400\,\text{K}} = 186\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Then we compute the value of the “entropy of formation” of the yellow form at 298 K.

$$\Delta S°_f = S°[HgI_2] - S°[Hg(l)] - S°[I_2(s)] = [186 - 76.02 - 116.1]\ \text{J mol}^{-1}\,\text{K}^{-1} = -6\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Now we can determine the value of the free energy of formation for the yellow form.

$$\Delta G°_f = \Delta H°_f - T\Delta S°_f = -102.9\frac{\text{kJ}}{\text{mol}} - [298\,\text{K}\times(-6\frac{\text{J}}{\text{K mol}})\times\frac{1\,\text{kJ}}{1000\,\text{J}}] = -101.1\frac{\text{kJ}}{\text{mol}}$$

77. **(M)** First we need a value for the equilibrium constant. 1% conversion means that 0.99 mol N_2(g) are present at equilibrium for every 1.00 mole present initially.

$$K = K_p = \frac{{P_{NO(g)}}^2}{P_{N_2(g)}\,P_{O_2(g)}} = \frac{[n\{NO(g)\}RT/V]^2}{[n\{N_2(g)\}RT/V][n\{O_2(g)\}RT/V]} = \frac{n\{NO(g)\}^2}{n\{N_2(g)\}\ n\{O_2(g)\}}$$

Reaction:	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\,NO(g)$
Initial:	1.00 mol		1.00 mol		0 mol
Changes(1% rxn):	−0.010 mol		−0.010 mol		+0.020 mol
Equil:	0.99 mol		0.99 mol		0.020 mol

$$K = \frac{(0.020)^2}{(0.99)(0.99)} = 4.1\times10^{-4}$$

The cited reaction is twice the formation reaction of NO(g), and thus

$\Delta H° = 2\Delta H°_f\,[NO(g)] = 2\times 90.25\,kJ/mol = 180.50\,kJ/mol$

$\Delta S° = 2\,S°[NO(g)] - S°[N_2(g)] - S°[O_2(g)]$

$\quad = 2\,(210.7\,J\,mol^{-1}\,K) - 191.5\,J\,mol^{-1}\,K^{-1} - 205.0\,J\,mol^{-1}\,K^{-1} = 24.9\,J\,mol^{-1}\,K^{-1}$

$\Delta G° = -RT\ln K = -8.31447\,JK^{-1}mol^{-1}(T)\ln(4.1\times10^{-4}) = 64.85(T)$

$\Delta G° = \Delta H° - T\Delta S° = 64.85(T) = 180.5\,kJ/mol - (T)24.9\,J\,mol^{-1}\,K^{-1}$

$180.5 \times 10\,J/mol = 64.85(T) + (T)24.9\,J\,mol^{-1}\,K^{-1} = 89.75(T)$ $\qquad T = 2.01 \times 10^3\ K$

78. **(E)** $Sr(IO_3)_2(s) \rightleftharpoons Sr^{2+}(aq) + 2\ IO_3^-(aq)$

$\Delta G° = (2\ mol\times(-128.0\ kJ/mol) + (1\ mol \times -500.5\ kJ/mol)) - (1\ mol \times -855.1\ kJ/mol) = -0.4\ kJ$

$\Delta G° = -RT\ln K = -8.31447\ JK^{-1}mol^{-1}(298.15\ K)\ln K = -0.4\ kJ = -400\ J$

$\ln K = 0.16$ and $K = 1.\underline{175} = [Sr^{2+}][IO_3^-]^2$ $\qquad$ Let x = solubility of $Sr(IO_3)_2$

$[Sr^{2+}][IO_3^-]^2 = 1.\underline{175} = x(2x)^2 = 4x^3$ $\ x = 0.6\underline{65}$ M for a saturated solution of $Sr(IO_3)_2$.

79. **(M)** P_{H2O} = 75 torr or $0.098\underline{7}$ atm. $\qquad K = (P_{H2O})^2 = (0.098\underline{7})^2 = 9.7\underline{4} \times 10^{-3}$

$\Delta G° = (2\ mol\times(-228.6\ kJ/mol) + (1\ mol)\times -918.1\ kJ/mol) - (1\ mol)\times -1400.0\ kJ/mol = 309.0\ kJ$

$\Delta H° = (2\ mol\times(-241.8\ kJ/mol) + (1\ mol)\times -1085.8.1\ kJ/mol) - (1\ mol)\times -1684.3\ kJ/mol = 114.9\ kJ$

$\Delta S° = (2\ mol\times(188.J/K\ mol) + (1\ mol\times 146.J/K\ mol) + (1\ mol)\times 221.3.J/K\ mol = 302.3\ J/K\ mol$

$\Delta G° = -RT\ln K_{eq} = -8.3145\,J\,mol^{-1}\,K^{-1}\times T\times\ln(9.74\times10^{-3}) = 38.\underline{5}(T)$

$\Delta G° = 38.\underline{5}(T) = \Delta H° - T\Delta S° = 114{,}900\,J\,mol^{-1} - (T)\times 302.3\,J\,K^{-1}\,mol^{-1}$

$114{,}900 = 340.8\,K^{-1}(T)$ $\quad$ Hence: $T = 337\,K = 64\,°C$

80. **(D) (a)** $\quad \Delta G° = -RT\ln K \qquad \ln K = -\dfrac{\Delta G°}{RT} = -\dfrac{131\times10^3\ J/mol}{8.3145\,J\,mol^{-1}\,K^{-1}\times 298.15\,K} = -52.8$

$$K = e^{-52.8} = 1.2\times10^{-23}\ atm\times\frac{760\,mmHg}{1\,atm} = 8.9\times10^{-21}\ mmHg$$

Since the system cannot produce a vacuum lower than 10^{-9} mmHg, this partial pressure of $CO_2(g)$ won't be detected in the system.

(b) Since we have the value of ΔG° for the decomposition reaction at a specified temperature (298.15 K), and we need ΔH° and ΔS° for this same reaction to determine $P\{CO_2(g)\}$ as a function of temperature, obtaining either ΔH° or ΔS° will enable us to determine the other.

(c) $\Delta H^\circ = \Delta H^\circ_f\,[\text{CaO(s)}] + \Delta H^\circ_f\,[\text{CO}_2\text{(g)}] - \Delta H^\circ_f\,[\text{CaCO}_3\text{(s)}]$

$= -635.1\,\text{kJ/mol} - 393.5\,\text{kJ/mol} - (-1207\,\text{kJ/mol}) = +178\,\text{kJ/mol}$

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

$$\Delta S^\circ = \frac{178\ \ \text{kJ/mol} - 131\ \ \text{kJ/mol}}{298.\ \ \text{K}} \times \frac{1000\ \ \text{J}}{1\ \ \text{kJ}} = 1.6\times10^2\ \ \text{J}\ \ \text{mol}^{-1}\ \ \text{K}^{-1}$$

$$K = 1.0\times10^{-9}\ \ \text{mmHg} \times \frac{1\ \ \text{atm}}{760\ \ \text{mmHg}} = 1.3\times10^{-12}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = -RT\ln K_{eq} \qquad \Delta H^\circ = T\,\Delta S^\circ - RT\ln K$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K} = \frac{178\times10^3\ \text{J/mol}}{1.6\times10^2\ \text{J mol}^{-1}\ \text{K}^{-1} - 8.3145\,\text{J mol}^{-1}\ \text{K}^{-1}\ \ln(1.3\times10^{-12})} = 4.6\times10^2\ \text{K}$$

<u>81</u>. (D) $\Delta H^\circ = \Delta H^\circ_f\,[\text{PCl}_3\text{(g)}] + \Delta H^\circ_f\,[\text{Cl}_2\text{(g)}] - \Delta H^\circ_f\,[\text{PCl}_5\text{(g)}]$

$= -287.0\ \ \text{kJ/mol} + 0.00\ \ \text{kJ/mol} - (-374.9\ \ \text{kJ/mol}) = 87.9\ \ \text{kJ/mol}$

$\Delta S^\circ = S^\circ[\text{PCl}_3\text{(g)}] + S^\circ[\text{Cl}_2\text{(g)}] - S^\circ[\text{PCl}_5\text{(g)}]$

$= 311.8\ \text{J mol}^{-1}\ \text{K}^{-1} + 223.1\ \text{J mol}^{-1}\ \text{K}^{-1} - 364.6\ \text{J mol}^{-1}\ \text{K}^{-1} = +170.3\ \text{J mol}^{-1}\ \text{K}^{-1}$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = 87.9\times10^3\ \text{J/mol} - 500\,\text{K} \times 170.3\,\text{J mol}^{-1}\ \text{K}^{-1}$$

$$\Delta G^\circ = 2.8\times10^3\ \text{J/mol} = -RT\ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-2.8\times10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\ \text{K}^{-1}\times500\,\text{K}} = -0.67 \qquad K_p = e^{-0.67} = 0.51$$

$$P_i[\text{PCl}_5] = \frac{nRT}{V} = \frac{0.100\,\text{mol}\times0.08206\,\text{L atm mol}^{-1}\ \text{K}^{-1}\times500\,\text{K}}{1.50\,\text{L}} = 2.74\,\text{atm}$$

Reaction:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$ +		$Cl_2(g)$
Initial:	$2.74\,\text{atm}$		$0\ \text{atm}$		$0\ \text{atm}$
Changes:	$-x\,\text{atm}$		$+x\,\text{atm}$		$+x\,\text{atm}$
Equil:	$(2.74-x)\,\text{atm}$		$x\,\text{atm}$		$x\,\text{atm}$

$$K_p = \frac{P[PCl_3]P[Cl_2]}{P[PCl_5]} = 0.51 = \frac{x \cdot x}{2.74 - x}$$

$$x^2 = 0.51(2.74 - x) = 1.4 - 0.51x \quad x^2 + 0.51x - 1.4 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.51 \pm \sqrt{0.26 + 5.6}}{2} = 0.96\,\text{atm}, -1.47\,\text{atm}$$

$$P_{\text{total}} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = (2.74 - x) + x + x = 2.74 + x = 2.74 + 0.96 = 3.70\,\text{atm}$$

82. **(M)** The value of $\Delta H°$ determined in Exercise 64 is $\Delta H° = +128\,\text{kJ/mol}$. We use any one of the values of $K_p = K_{eq}$ to determine a value of $\Delta G°$. At 30 °C = 303 K,

$$\Delta G° = -RT \ln K_{eq} = -(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})(303\,\text{K}) \ln(1.66 \times 10^{-5}) = +2.77 \times 10^4\ \text{J/mol}$$

Now we determine $\Delta S°$. $\Delta G° = \Delta H - T\,\Delta S°$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} = \frac{128 \times 10^3\ \text{J/mol} - 2.77 \times 10^4\ \text{J/mol}}{303\,\text{K}} = +331\,\text{J mol}^{-1}\ \text{K}^{-1}$$

By using the appropriate $S°$ values in Appendix D, we calculate $\Delta S° = +334\,\text{J mol}^{-1}\,\text{K}^{-1}$.

83. **(M)** In this problem we are asked to estimate the temperature at which the vapor pressure of cyclohexane is 100 mmHg. We begin by using Trouton's rule to determine the value of ΔH_{vap} for cyclohexane. The temperature at which the vapor pressure is 100.00 mmHg can then be determined using Clausius–Clapeyron equation.

Stepwise approach:

Use Trouton's rule to find the value of ΔH_{vap}:

$$\Delta H_{\text{vap}} = T_{\text{nbp}}\,\Delta S_{\text{vap}} = 353.9\,\text{K} \times 87\,\text{J mol}^{-1}\ \text{K}^{-1} = 31 \times 10^3\ \text{J/mol}$$

Next, use Clausius–Clapeyron equation to find the required temperature:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln\frac{100\,\text{mmHg}}{760\,\text{mmHg}}$$

$$= \frac{31 \times 10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}}\left(\frac{1}{353.9\,\text{K}} - \frac{1}{T}\right) = -2.028$$

$$\frac{1}{353.9} - \frac{1}{T} = \frac{-2.028 \times 8.3145}{31 \times 10^3} = -5.4 \times 10^{-4} =$$

$$2.826 \times 10^{-3} - \frac{1}{T} \qquad \frac{1}{T} = 3.37 \times 10^{-3} K^{-1}$$

$$T = 297\,\text{K} = 24\,°\text{C}$$

Conversion pathway approach:

$$\ln\frac{P_2}{P_1}=\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{T_{\text{nbp}}\,\Delta S_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{R}{T_{\text{nbp}}\,\Delta S_{\text{vap}}}\ln\frac{P_2}{P_1}\Rightarrow\frac{1}{T_2}=\frac{1}{T_1}-\frac{R}{T_{\text{nbp}}\,\Delta S_{\text{vap}}}\ln\frac{P_2}{P_1}$$

$$\frac{1}{T_2}=\frac{1}{353.9\text{K}}-\frac{8.314\text{JK}^{-1}\text{mol}^{-1}}{353.9K\times 87\text{JK}^{-1}\text{mol}^{-1}}\ln\frac{100\text{mmHg}}{760\text{mmHg}}=3.37\times 10^{-3}$$

$$T_2=297\text{K}=24^{o}C$$

84. (M)**(a)** $2\text{Ag(s)}+\frac{1}{2}\text{O}_2\text{(g)}\rightarrow \text{Ag}_2\text{O}$

$$\Delta\text{G}_\text{f}^\text{o}=\Delta\text{G}_\text{f}^\text{o}(\text{Ag}_2\text{O(s)})\text{-}\{2\Delta\text{G}_\text{f}^\text{o}(Ag(s))+\frac{1}{2}\Delta\text{G}_\text{f}^\text{o}(O_2)\}$$

$$\Delta\text{G}_\text{f}^\text{o}=\ \text{-11.2 kJ-}\{2(0)\ +\frac{1}{2}(0)\}=-11.2\ kJ\Rightarrow \text{Ag}_2\text{O is thermodynamically stable at }25^\text{o}\text{C}$$

(b) Assuming ΔH^o, ΔS^o are constant from 25-200°C (not so, but a reasonable assumption !)

$$\Delta\text{S}^\text{o}=\text{S}^\text{o}(\text{Ag}_2\text{O})\text{-}\{2\ \text{S}^\text{o}(\text{Ag(s)})+\frac{1}{2}\ \text{S}^\text{o}(\text{O}_2)\}=121.3-(2(42.6)+\frac{1}{2}(205.1))=-66.5\text{ J/K}$$

$$\Delta\text{G}^\text{o}=-31.0\text{ kJ}-\frac{(473\text{ K})(\text{-}66.5\text{ J/K})}{1000\text{ J/kJ}}=\Delta H^\text{o}-T\Delta S^\text{o}=+0.45\text{ kJ}$$

$\Rightarrow$ thermodynamically *unstable* at 200°C

85. **(M)** ΔG = 0 since the system is at equilibrium. As well, ΔG° = 0 because this process is under standard conditions. Since ΔG° = ΔH° - TΔS° = 0. = ΔH° = TΔS° =273.15 K×21.99 J $\text{K}^{-1}\ \text{mol}^{-1}$ = 6.007 kJ mol^{-1}. Since we are dealing with 2 moles of ice melting, the values of ΔH° and ΔS° are doubled. Hence, ΔH° = 12.01 kJ and ΔS° = 43.98 J K^{-1}.
Note: The densities are not necessary for the calculations required for this question.

86. **(D)** First we determine the value of K_p that corresponds to 15% dissociation. We represent the initial pressure of phosgene as *x* atm.

Reaction:	$\text{COCl}_2\text{(g)}$	$\rightleftharpoons$	CO(g)	+	$\text{Cl}_2\text{(g)}$
Initial:	x atm		0 atm		0 atm
Changes:	$-0.15x$ atm		$+0.15x$ atm		$+0.15x$ atm
Equil:	$0.85x$ atm		$0.15x$ atm		$0.15x$ atm

$$P_{\text{total}} = 0.85\,x\,\text{atm} + 0.15\,x\,\text{atm} + 0.15\,x\,\text{atm} = 1.15\,x\,\text{atm} = 1.00\,\text{atm} \qquad x = \frac{1.00}{1.15} = 0.870\,\text{atm}$$

$$K_p = \frac{P_{\text{CO}}\,P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{(0.15\times 0.870)^2}{0.85\times 0.870} = 0.0230$$

Next we find the value of $\Delta H°$ for the decomposition reaction.

$$\ln\frac{K_1}{K_2} = \frac{\Delta H°}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \ln\frac{6.7\times 10^{-9}}{4.44\times 10^{-2}} = -15.71 = \frac{\Delta H°}{R}\left(\frac{1}{668}-\frac{1}{373.0}\right) = \frac{\Delta H°}{R}(-1.18\times 10^{-3})$$

$$\frac{\Delta H°}{R} = \frac{-15.71}{-1.18\times 10^{-3}} = 1.33\times 10^{4},$$

$$\Delta H° = 1.33\times 10^{4} \times 8.3145 = 111\times 10^{3}\ \text{J/mol} = 111\,\text{kJ/mol}$$

And finally we find the temperature at which $K = 0.0230$.

$$\ln\frac{K_1}{K_2} = \frac{\Delta H°}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \ln\frac{0.0230}{0.0444} = \frac{111\times 10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}}\left(\frac{1}{668\,\text{K}}-\frac{1}{T}\right) = -0.658$$

$$\frac{1}{668}-\frac{1}{T} = \frac{-0.658\times 8.3145}{111\times 10^3} = -4.93\times 10^{-5} = 1.497\times 10^{-3} - \frac{1}{T} \qquad \frac{1}{T} = 1.546\times 10^{-3}$$

$$T = 647\,\text{K} = 374\,°\text{C}$$

87. **(D)** First we write the solubility reaction for AgBr. Then we calculate values of $\Delta H°$ and $\Delta S°$ for the reaction: $\text{AgBr(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Br}^-\text{(aq)} \quad K_{\text{eq}} = K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = s^2$

$$\Delta H° = \Delta H°_f\,[\text{Ag}^+\text{(aq)}] + \Delta H°_f\,[\text{Br}^-\text{(aq)}] - \Delta H°_f\,[\text{AgBr(s)}]$$
$$= +105.6\,\text{kJ/mol} - 121.6\,\text{kJ/mol} - (-100.4\,\text{kJ/mol}) = +84.4\,\text{kJ/mol}$$

$$\Delta S° = S°[\text{Ag}^+\text{(aq)}] + S°[\text{Br}^-\text{(aq)}] - S°[\text{AgBr(s)}]$$
$$= +72.68\,\text{J mol}^{-1}\,\text{K}^{-1} + 82.4\,\text{J mol}^{-1}\,\text{K}^{-1} - 107.1\,\text{J mol}^{-1}\,\text{K}^{-1} = +48.0\,\text{J mol}^{-1}\,\text{K}^{-1}$$

These values are then used to determine the value of $\Delta G°$ for the solubility reaction, and the standard free energy change, in turn, is used to obtain the value of K.

$$\Delta G° = \Delta H° - T\Delta S° = 84.4\times 10^3\ \text{J mol}^{-1} - (100+273)\,\text{K}\times 48.0\,\text{J mol}^{-1}\,\text{K}^{-1} = 66.5\times 10^3\ \text{J/mol}$$

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-66._5\times 10^3}{\frac{8.3145\,\text{J}}{\text{mol K}}\times 373\,\text{K}} = -21.4 \qquad K = K_{\text{sp}} = e^{-21.4} = 5.0\times 10^{-10} = s^2$$

And now we compute the solubility of AgBr in mg/L.

$$s = \sqrt{5.0\times 10^{-10}} \times \frac{187.77\,\text{g AgBr}}{1\,\text{mol AgBr}} \times \frac{1000\,\text{mg}}{1\,\text{g}} = 4.2\,\text{mg AgBr/L}$$

88. **(M)** $S°_{298.15} = S°_{274.68} + \Delta S_{fusion} + \Delta S_{heating}$

$$S°_{298.15} = 67.15 \text{ J K}^{-} \text{ mol}^{-1} + \frac{12{,}660 \text{ J mol}^{-1}}{274.68 \text{ K}} + \int_{274.68}^{298.15} 97.78 \frac{\text{J}}{\text{mol K}} + 0.0586 \frac{\text{J}}{\text{mol K}^2} \times (T - 274.68)$$

$$S°_{298.15} = 67.15 \text{ J K}^{-1} \text{ mol}^{-1} + 46.09 \text{ J K}^{-1} \text{ mol}^{-1} + 8.07 \text{ J K}^{-1} \text{ mol}^{-1} = 121.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

89. **(M)** $S° = S°_{solid} + \Delta S_{fusion} + \Delta S_{heating} + \Delta S_{vaporization} + \Delta S_{pressure\ change}$

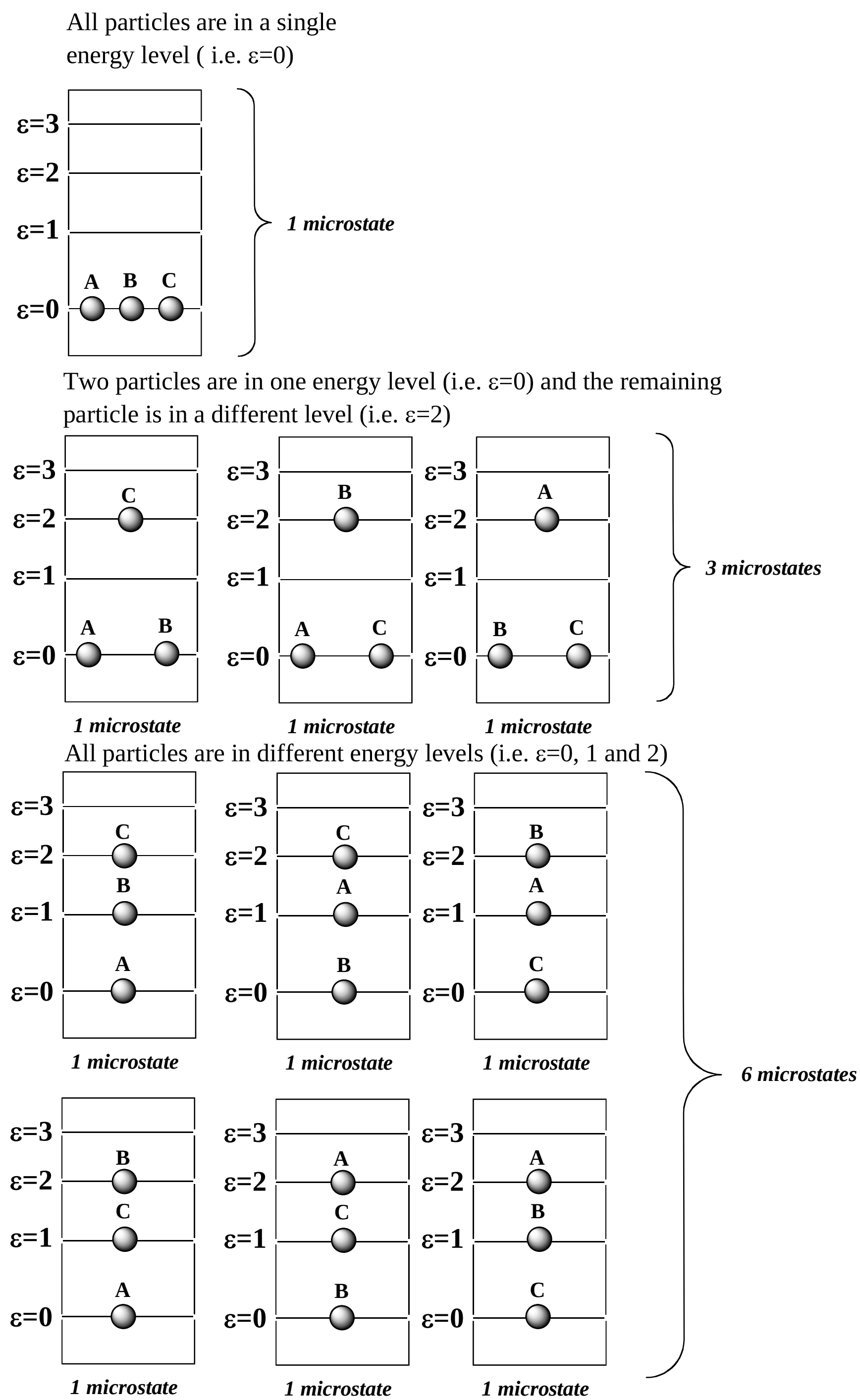
$$S° = 128.82 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{9866 \text{ J mol}^{-1}}{278.68 \text{ K}} + \int_{278.68}^{298.15} \frac{134.0 \frac{\text{J}}{\text{mol K}} dT}{\text{T}} + \frac{33{,}850 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

$$+ 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\left(\frac{95.13 \text{ torr}}{760 \text{ torr}}\right)$$

$$S° = 128.82 \text{ J K}^{-1} \text{ mol}^{-1} + 35.40 \text{ J K}^{-1} \text{ mol}^{-1} + 9.05 \text{ J K}^{-1} \text{ mol}^{-1} + 113.5 \text{ J K}^{-1} \text{ mol}^{-1} + (-17.28 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$S° = 269.53 \text{ J K}^{-1} \text{ mol}^{-1}$$

90. **(D)** Start by labeling the particles A, B and C. Now arrange the particles among the states. One possibility includes A, B, and C occupying one energy state (ε=0,1,2 or 3). This counts as one microstate. Another possibility is two of the particles occupying one energy state with the remaining one being in a different state. This possibility includes a total of three microstates. The final set of combinations is one with each particle being in different energy state. This combination includes a total of six microstates. Therefore, the total number of microstates in the system is 10. See pictorial representation on the following page illustrating the three different cases.



91. **(M)** **(a)** In the solid as the temperature increases, so do the translational, rotational, and vibrational degrees of freedom. In the liquid, most of the vibrational degrees of freedom are saturated and only translational and rotational degrees of freedom can increase. In the gas phase, all degrees of freedom are saturated. **(b)** The increase in translation and rotation on going from solid to liquid is much less than on going from liquid to gas. This is where most of the change in entropy is derived.

92. (D) Because KNO_3 is a strong electrolyte, its solution reaction will be:

$$KNO_3(s) + H_2O \rightleftharpoons K^+(aq) + NO_3^-(aq)$$

This reaction can be considered to be at equilibrium when the solid is in contact with a saturated solution, i.e. the conditions when crystallization begins. The solubility, s, of the salt, in moles per liter, can be calculated from the amount of salt weighted out and the volume of the solution. The equilibrium constant K for the reaction will be:

$$\text{K}=[\text{K}^+(\text{aq})][\text{NO}_3^-(\text{aq})]=(\text{s})(\text{s})=\text{s}^2$$

In the case of 25.0 mL solution at 340 K, the equilibrium constant K is:

$$n(KNO_3) = \frac{m}{M} = \frac{20.2\text{g}}{101.103\text{gmol}^{-1}} = 0.200\text{mol} \Rightarrow \text{s}=\frac{n}{V} = \frac{0.200\text{mol}}{0.0250\text{L}} = 8.0\text{molL}^{-1}$$

$$K = s^2 = 8^2 = 64$$

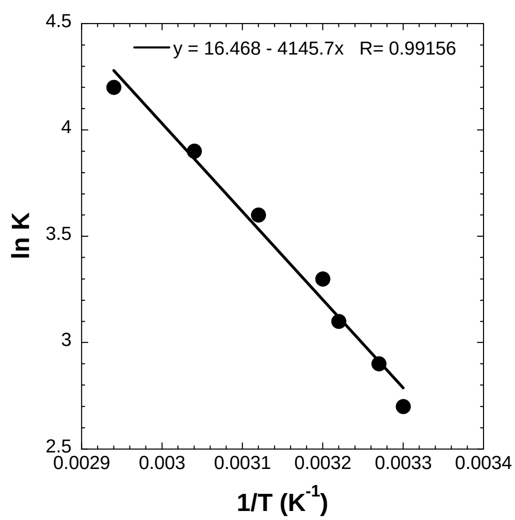
The equilibrium constant K can be used to calculate ΔG for the reaction using ΔG=-RTlnK:

$$\Delta G = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 340\text{K} \times \ln 64 = -12\text{kJmol}^{-1}$$

The values for K and ΔG at all other temperatures are summarized in the table below.

Volume (mL)	T/(K)	1/T (K^{-1})	s ($molL^{-1}$)	K	lnK	ΔG ($kJmol^{-1}$)
25.0	340	0.00294	8.0	64	4.2	-12
29.2	329	0.00304	6.9	48	3.9	-11
33.4	320	0.00312	6.0	36	3.6	-9.6
37.6	313	0.00320	5.3	28	3.3	-8.6
41.8	310	0.00322	4.8	23	3.1	-8.0
46.0	306	0.00327	4.3	18.5	2.9	-7.4
51.0	303	0.00330	3.9	15	2.7	-6.8

The plot of lnK v.s. 1/T provides ΔH (slope=-ΔH/R) and ΔS (y-intercept=ΔS/R) for the reaction:



$$\Delta H = -slope \times R = 4145.7 \times 8.314\text{JK}^{-1}\text{mol}^{-1} = 34.5\text{kJmol}^{-1}$$

$$\Delta S = y-\text{int}ercept \times R = 16.468 \times 8.314\text{JK}^{-1}\text{mol}^{-1} = 136.9\text{JK}^{-1}\text{mol}^{-1}$$

ΔH for the crystallization process is -35.4 kJmol^{-1}. It is negative as expected because crystallization is an exothermic process. Furthermore, the positive value for ΔS shows that crystallization is a process that decreases the entropy of a system.

FEATURE PROBLEMS

93. **(M) (a)** The first method involves combining the values of ΔG_f^o. The second uses

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

$$\Delta G^o = \Delta G_f^\circ\left[H_2O(g)\right] - \Delta G_f^\circ\left[H_2O(l)\right]$$

$$= -228.572\ \text{kJ/mol} - (-237.129\ \text{kJ/mol}) = +8.557\ \text{kJ/mol}$$

$$\Delta H^o = \Delta H_f^\circ\left[H_2O(g)\right] - \Delta H_f^\circ\left[H_2O(l)\right]$$

$$= -241.818\ \text{kJ/mol} - (-285.830\ \text{kJ/mol}) = +44.012\ \text{kJ/mol}$$

$$\Delta S^o = S^o\left[H_2O(g)\right] - S^o\left[H_2O(l)\right]$$

$$= 188.825\ \text{J mol}^{-1}\ \text{K}^{-1} - 69.91\ \text{J mol}^{-1}\ \text{K}^{-1} = +118.92\ \text{J mol}^{-1}\ \text{K}^{-1}$$

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

$$= 44.012\ \text{kJ/mol} - 298.15\ \text{K} \times 118.92 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1} = +8.556\ \text{kJ/mol}$$

(b) We use the average value: $\Delta G^o = +8.558 \times 10^3$ J/mol $= -RT \ln K$

$$\ln K = -\frac{8558\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}} = -3.452; \quad K = e^{-3.452} = 0.0317\ \text{bar}$$

(c) $$P\{H_2O\} = 0.0317\ \text{bar} \times \frac{1\ \text{atm}}{1.01325\ \text{bar}} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 23.8\ \text{mmHg}$$

(d) $$\ln K = -\frac{8590\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}} = -3.465;$$

$$K = e^{-3.465} = 0.0312_7\ \text{atm};$$

$$P\{H_2O\} = 0.0313\ \text{atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 23.8\ \text{mmHg}$$

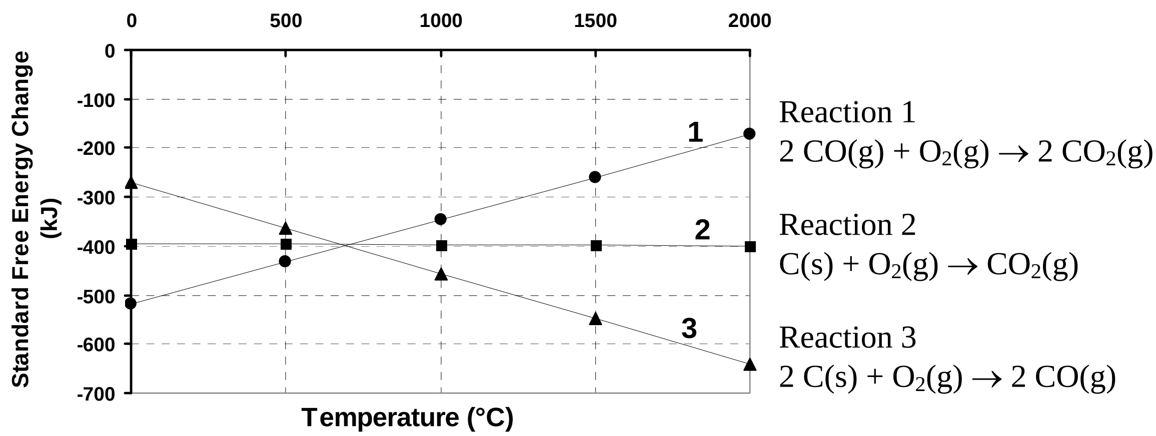
94. **(D) (a)** When we combine two reactions and obtain the overall value of ΔG^o, we subtract the value on the plot of the reaction that becomes a reduction from the value on the plot of the reaction that is an oxidation. Thus, to reduce ZnO with elemental Mg, we subtract the values on the line labeled "$2Zn + O_2 \rightarrow 2ZnO$" from those on the line labeled "$2Mg + O_2 \rightarrow 2MgO$". The result for the overall ΔG^o will always be negative because every point on the "zinc" line is above the corresponding point on the "magnesium" line

(b) In contrast, the "carbon" line is only below the "zinc" line at temperatures above about $1000^\circ C$. Thus, only at these elevated temperatures can ZnO be reduced by carbon.

(c) The decomposition of zinc oxide to its elements is the reverse of the plotted reaction, the value of ΔG° for the decomposition becomes negative, and the reaction becomes spontaneous, where the value of ΔG° for the plotted reaction becomes positive. This occurs above about $1850^{\circ}\mathrm{C}$.

(d) The "carbon" line has a negative slope, indicating that carbon monoxide becomes more stable as temperature rises. The point where CO(g) would become less stable than 2C(s) and O_2(g) looks to be below $-1000^{\circ}\mathrm{C}$ (by extrapolating the line to lower temperatures). Based on this plot, it is not possible to decompose CO(g) to C(s) and $O_2(g)$ in a spontaneous reaction.

(e)



All three lines are straight-line plots of $\Delta G°$ vs. T following the equation $\Delta G° = \Delta H° - T\Delta S°$.

The general equation for a straight line is given below with the slightly modified Gibbs Free-Energy equation as a reference: $\Delta G° = -\Delta S° T + \Delta H°$ (here $\Delta H°$ assumed constant)

$y = mx + b$ (m = $-\Delta S°$ = slope of the line)

Thus, the slope of each line multiplied by minus one is equal to the $\Delta S°$ for the oxide formation reaction. It is hardly surprising, therefore, that the slopes for these lines differ so markedly because these three reactions have quite different $\Delta S°$ values ($\Delta S°$ for Reaction 1 = -173 J K^{-1}, $\Delta S°$ for Reaction 2 = 2.86 J K^{-1}, $\Delta S°$ for Reaction 3 = 178.8 J K^{-1})

(f) Since other metal oxides apparently have positive slopes similar to Mg and Zn, we can conclude that in general, the stability of metal oxides decreases as the temperature increases. Put another way, the decomposition of metal oxides to their elements becomes more spontaneous as the temperature is increased. By contrast, the two reactions involving elemental carbon, namely Reaction 2 and Reaction 3, have negative slopes, indicating that the formation of CO_2(g) and CO(g) from graphite becomes more favorable as the temperature rises. This means that the $\Delta G°$ for the reduction of metal oxides by carbon becomes more and more negative with increasing temperature. Moreover, there must exist a threshold temperature for each metal oxide above which the reaction with carbon will occur spontaneously. Carbon would appear to be an excellent reducing agent, therefore, because it will reduce virtually <u>any</u> metal oxide to its corresponding metal as long as the temperature chosen for the reaction is higher than the threshold temperature (the threshold temperature is commonly referred to as the transition temperature).

Consider for instance the reaction of MgO(s) with graphite to give CO_2(g) and Mg metal:
2 MgO(s) + C(s) $\rightarrow$ 2 Mg(s) + CO_2(g) $\Delta S°_{rxn}$ = 219.4 J/K and $\Delta H°_{rxn}$ = 809.9 kJ

$$T_{transition} = \frac{\Delta H^{o}_{rxn}}{\Delta S^{o}_{rxn}} = \frac{809.9 \text{ kJ}}{0.2194 \text{ kJ K}^{-1}} = 3691 \text{ K} = T_{threshold}$$

Consequently, above 3691 K, carbon will spontaneously reduce MgO to Mg metal.

95. (D) (a) With a 36% efficiency and a condenser temperature (T_l) of 41 °C = 314 K,

$$\text{efficiency} = \frac{T_h - T_l}{T_h} \times 100\% = 36\% \qquad \frac{T_h - 314}{T_h} = 0.36\,;$$

$T_h = (0.36 \times T_h) + 314$ K; $0.64\, T_h = 314$ K; $T_h = 4.9 \times 10^2$ K

(b) The overall efficiency of the power plant is affected by factors other than the thermodynamic efficiency. For example, a portion of the heat of combustion of the fuel is lost to parts of the surroundings other than the steam boiler; there are frictional losses of energy in moving parts in the engine; and so on. To compensate for these losses, the thermodynamic efficiency must be greater than 36%. To obtain this higher thermodynamic efficiency, T_h must be greater than 4.9×10^2 K.

(c) The steam pressure we are seeking is the vapor pressure of water at 4.9×10^2 K. We also know that the vapor pressure of water at 373 K (100 °C) is 1 atm. The enthalpy of vaporization of water at 298 K is $\Delta H° = \Delta H_f°[H_2O(g) - \Delta H_f°[H_2O(l)]$ = −241.8 kJ/mol − (−285.8 kJ/mol) = 44.0 kJ/mol. Although the enthalpy of vaporization is somewhat temperature dependent, we will assume that this value holds from 298 K to 4.9×10^2 K, and make appropriate substitutions into the Clausius-Clapeyron equation.

$$\ln\left(\frac{P_2}{1 \text{ atm}}\right) = \frac{44.0 \text{ kJ mol}^{-1}}{8.3145\times10^{-3} \text{ kJ mol}^{-1}}\left(\frac{1}{373 \text{ K}} - \frac{1}{490 \text{ K}}\right) = 5.29\times10^{-3}\left(2.68\times10^{-3} - 2.04\times10^{-3}\right)$$

$$\ln\left(\frac{P_2}{1 \text{ atm}}\right) = 3.39\,; \quad \left(\frac{P_2}{1 \text{ atm}}\right) = 29.7\,; \quad P_2 \approx 30 \text{ atm}$$

The answer cannot be given with greater certainty because of the weakness of the assumption of a constant $H°_{vapn}$.

(d) It is not possible to devise a heat engine with 100% efficiency or greater. For 100% efficiency, T_l = 0 K, which is unattainable. To have an efficiency greater than 100 % would require a *negative* T_l, which is also unattainable.

96. **(D) (a)** Under biological standard conditions:

$ADP^{3-} + HPO_4^{2-} + H^+ \rightarrow ATP^{4-} + H_2O \quad \Delta G^{o'} = 32.4$ kJ/mol

If all of the energy of combustion of 1 mole of glucose is employed in the conversion of ADP to ATP, then the maximum number of moles ATP produced is

$$\text{Maximum number} = \frac{2870 \text{ kJ mol}^{-1}}{32.4 \text{ kJ mol}^{-1}} = 88.6 \text{ moles ATP}$$

(b) In an actual cell the number of ATP moles produced is 38, so that the efficiency is:

$$\text{Efficiency} = \frac{\text{number of ATP's actually produced}}{\text{Maximum number of ATP's that can be produced}} = \frac{38}{88.6} = 0.43$$

Thus, the cell's efficiency is about 43%.

(c) The previously calculated efficiency is based upon the biological standard state. We now calculate the Gibbs energies involved under the actual conditions in the cell. To do this we require the relationship between ΔG and $\Delta G^{\circ'}$ for the two coupled reactions. For the combustion of glucose we have

$$\Delta G = \Delta G^{\circ'} + RT \ln\left(\frac{a_{CO_2}^6 a_{H_2O}^6}{a_{glu} a_{O_2}^6}\right)$$

For the conversion of ADP to ATP we have

$$\Delta G = \Delta G^{\circ'} + RT \ln\left(\frac{a_{ATP} a_{H_2O}}{a_{ADP} a_{P_i} \left(\left[H^+\right]/10^{-7}\right)}\right)$$

Using the concentrations and pressures provided we can calculate the Gibbs energy for the combustion of glucose under biological conditions. First, we need to replace the activities by the appropriate effective concentrations. That is,

$$\Delta G = \Delta G^{\circ'} + RT \ln\left(\frac{\left(p/p^o\right)_{CO_2}^6 a_{H_2O}^6}{\left[glu\right]/\left[glu\right]^o \left(p/p^o\right)_{O_2}^6}\right)$$

using $a_{H_2O} \approx 1$ for a dilute solution we obtain

$$\Delta G = \Delta G^{\circ'} + RT \ln\left(\frac{\left(0.050 \text{ bar}/1 \text{ bar}\right)^6 \times 1^6}{\left[glu\right]/1 \times \left(0.132 \text{ bar}/1 \text{ bar}\right)^6}\right)$$

The concentration of glucose is given in mg/mL and this has to be converted to molarity as follows:

$$[glu] = \frac{1.0 \text{ mg}}{\text{mL}} \times \frac{\text{g}}{1000 \text{ mg}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1}{180.16 \text{ g mol}^{-1}} = 0.00555 \text{ mol L}^{-1},$$

where the molar mass of glucose is 180.16 g mol^{-1}.
Assuming a temperature of 37 ^{o}C for a biological system we have, for one mole of glucose:

$$\Delta G = -2870\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\text{K}\times\ln\left(\frac{(0.050\ )^6\times1^6}{0.00555/1\times(0.132)^6}\right)$$

$$\Delta G = -2870\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\text{K}\times\ln\left(\frac{2.954\times10^{-3}}{0.00555}\right)$$

$$\Delta G = -2870\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\,\text{K}\times\ln(0.5323)$$

$$\Delta G = -2870\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\text{K}\times(-0.6305)$$

$$\Delta G = -2870\times10^3\,\text{J} - 1.625\times10^3\,\text{J}$$

$$\Delta G = -2872\times10^3\,\text{J}$$

In a similar manner we calculate the Gibbs free energy change for the conversion of ADP to ATP:

$$\Delta G = \Delta G^{o} + RT\ln\left(\frac{[ATP]/1\times1}{[ADP]/1\times[P_i]/1\times([H^+]/10^{-7})}\right)$$

$$\Delta G = 32.4\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\,\text{K}\times\ln\left(\frac{0.0001}{0.0001\times0.0001\times(10^{-7}/10^{-7})}\right)$$

$$\Delta G = 32.4\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\,\text{K}\times\ln(10^4)$$

$$\Delta G = 32.4\times10^3\,\text{J} + 8.314\,\text{JK}^{-1}\times310\,\text{K}\times(9.2103)) = 32.4\times10^3\,\text{J} + 23.738\times10^3\,\text{J} = 56.2\times10^3\,\text{J}$$

(d) The efficiency under biological conditions is

$$\text{Efficiency} = \frac{\text{number of ATP's actually produced}}{\text{Maximum number of ATP's that can be produced}} = \frac{38}{2872/56.2} = 0.744$$

Thus, the cell's efficiency is about 74%.

The theoretical efficiency of the diesel engine is:

$$\text{Efficiency} = \frac{T_\text{h} - T_\text{l}}{T_\text{h}}\times100\% = \frac{1923-873}{1923}\times100\% = 55\%$$

Thus, the diesel's actual efficiency is 0.78 × 55 % = 43 %.
The cell's efficiency is 74% whereas that of the diesel engine is only 43 %. Why is there such a large discrepancy? The diesel engine supplies heat to the surroundings, which is at a lower temperature than the engine. This dissipation of energy raises the temperature of the surroundings and the entropy of the surroundings. A cell operates under isothermal conditions and the energy not utilized goes only towards changing the entropy of the cell's surroundings. The cell is more efficient since it does not heat the surroundings.

97. **(E) (a)** In this case CO can exist in two states, therefore, W=2. There are N of these states in the crystal, and so we have

$S = k \ln 2^N = 1.381 \times 10^{-23} \text{JK}^{-1} \times 6.022 \times 10^{23} \text{mol}^{-1} \ln 2 = 5.8 \text{JK}^{-1}\text{mol}^{-1}$

(b) For water, W=3/2, which leads to

$S = k \ln(\frac{3}{2})^N = 1.381 \times 10^{-23} \text{JK}^{-1} \times 6.022 \times 10^{23} \text{mol}^{-1} \ln 1.5 = 3.4 \text{JK}^{-1}\text{mol}^{-1}$

SELF-ASSESSMENT EXERCISES

98. **(E) (a)** ΔS_{univ} or total entropy contains contributions from the entropy change of the system (ΔS_{sys}) and the surroundings (ΔS_{surr}). According to the second law of thermodynamics, ΔS_{univ} is always greater then zero.

(b) ΔG_f^o or standard free energy of formation is the free energy change for a reaction in which a substances in its standard state is formed from its elements in their reference forms in their standard states.

(c) For a hypothetical chemical reaction $\text{aA+bB} \rightleftharpoons \text{cC+dD}$, the equilibrium constant K is defined as $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.

99. **(E) (a)** Absolute molar entropy is the entropy at zero-point energy (lowest possible energy state) and it is equal to zero.

(b) Coupled reactions are spontaneous reactions (ΔG<0) that are obtained by pairing reactions with positive ΔG with the reactions with negative ΔG.

(c) Trouton's rule states that for many liquids at their normal boiling points, the standard molar entropy of vaporization has a value of approximately 87 $\text{Jmol}^{-1}\text{K}^{-1}$.

(d) Equilibrium constant K for a certain chemical reaction can be evaluated using either ΔG_f^o or ΔH_f^o in conjunction with S^o (which are often tabulated). The relationship used to calculate K is $\Delta G^o = -RT \ln K$.

100. **(E) (a)** A spontaneous process is a process that occurs in a system left to itself; once started, no external action form outsize the system is necessary to make the process continue. A nonspontaneous process is a process that will not occur unless some external action is continuously applied.

(b) Second law of thermodynamics states that the entropy of universe is always greater than zero or in other words that all spontaneous processes produce an increase in the entropy of the universe. The third law of thermodynamics states that the entropy of perfect pure crystal at 0K is zero.

(c) ΔG is the Gibbs free energy defined as ΔG=ΔH-TΔS. ΔG^0 is the standard free energy change.

101. **(E)** Second law of thermodynamics states that all spontaneous processes produce an increase in the entropy of the universe. In other words, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$. Therefore, the correct answer is (d).

102. **(E)** The Gibbs free energy is a function of ΔH, ΔS and temperature T. It cannot be used to determine how much heat is absorbed from the surroundings or how much work the system does on the surroundings. Furthermore, it also cannot be used to determine the proportion of the heat evolved in an exothermic reaction that can be converted to various forms of work. Since Gibbs free energy is related to the equilibrium constant of a chemical reaction ($\Delta G = -RT \ln K$) its value can be used to access the net direction in which the reaction occurs to reach equilibrium. Therefore, the correct answer is (c).

103. **(M)** In order to answer this question, we must first determine whether the entropy change for the given reaction is positive or negative. The reaction produces three moles of gas from two moles, therefore there is an increase in randomness of the system, i.e. entropy change for the reaction is positive. Gibbs free energy is a function of enthalpy, entropy and temperature ($\Delta G = \Delta H - T\Delta S$). Since $\Delta H < 0$ and $\Delta S > 0$, this reaction will be spontaneous at any temperature. The correct answer is (a).

104. **(M)** Recall that $\Delta G^o = -RT \ln K$. If $\Delta G^o = 0$, then it follows that $\Delta G^o = -RT \ln K = 0$. Solving for K yields: $\ln K = 0 \Rightarrow K = e^0 = 1$. Therefore, the correct answer is (b).

105. **(E)** In this reaction, the number of moles of reactants equals the number of moles of products. Therefore, K is equal to K_p and K_c. The correct answers are (a) and (d).

106. **(M)** **(a)** The two lines will intersect at the normal melting point of $I_2(s)$ which is 113.6 ^oC. **(b)** ΔG^o for this process must be equal to zero because solid and liquid are at equilibrium and also in their standard states.

107. **(M)** **(a)** No reaction is expected because of the decrease in entropy and the expectation that the reaction is endothermic. As a check with data from Appendix D, ΔG^o=326.4 $kJmol^{-1}$ for the reaction as written-a very large value. **(b)** Based on the increase in entropy, the forward reaction should occur, at least to some extent. For this reaction ΔG^o=75.21 $kJmol^{-1}$. **(c)** ΔS is probably small, and ΔH is probably also small (one Cl-Cl bond and one Br-Br bonds are broken and two Br-Cl bonds are formed). ΔG^o should be small and the forward reaction should occur to a significant extent. For this reaction ΔG^o=-5.07 $kJmol^{-1}$.

108. **(M)** **(a)** Entropy change must be accessed for the system and its surroundings (ΔS_{univ}), not just for the system alone. **(b)** Equilibrium constant can be calculated from ΔG^o ($\Delta G^o = -RT \ln K$), and K permits equilibrium calculations for nonstandard conditions.

109. **(D)** **(a)** First we need to determine ΔH^o_{vap} which is simply equal to: $\Delta H^o_{vap} = \Delta H^o_f[(C_5H_{10}(g)] - \Delta H^o_f[(C_5H_{10}(l)] = -77.2\text{kJ/mol} - (-105.9\text{kJ/mol}) = 28.7\text{kJ/mol}$. Now we use Trouton's rule to calculate the boiling point of cyclopentane:

$$\Delta S^o_{vap} = \frac{\Delta H^o_{vap}}{T_{bp}} = 87\,\text{Jmol}^{-1}\text{K}^{-1} \Rightarrow T_{bp} = \frac{\Delta H^o_{vap}}{87\,\text{Jmol}^{-1}\text{K}^{-1}} = \frac{28.7 \times 1000\,\text{Jmol}^{-1}}{87\,\text{Jmol}^{-1}\text{K}^{-1}} = 330K$$

$$T_{bp} = 330K - 273.15K = 57^oC$$

(b) If we assume that ΔH^o_{vap} and ΔS^o_{vap} are independent of T we can calculate ΔG^o_{vap}:

$$\Delta G^o_{vap,298K} = \Delta H^o_{vap} - T\Delta S^o_{vap} = 28.7\text{kJmol}^{-1} - 298.15K \times \frac{87}{1000}\text{kJK}^{-1}\text{mol}^{-1} = 2.8\text{kJmol}^{-1}$$

(c) Because $\Delta G^o_{vap,298K}$ >0, the vapor pressure is less than 1 atm at 298 K, consistent with T_{bp}=57 ^{o}C.

110. **(M)** **(a)** We can use the data from Appendix D to determine the change in enthalpy and entropy for the reaction:

$$\Delta H^o = \Delta H^o_f(N_2O(g)) + 2\Delta H^o_f(H_2O(l)) - \Delta H^o_f(NH_4NO_3(s))$$

$$\Delta H^o = 82.05\text{kJmol}^{-1} + 2 \times (-285.8\text{kJmol}^{-1}) - (-365.6\text{kJmol}^{-1}) = -124\text{kJmol}^{-1}$$

$$\Delta S^o = S^o(N_2O(g)) + 2S^o(H_2O(l)) - S^o(NH_4NO_3(s))$$

$$\Delta S^o = 219.9\text{JK}^{-1}\text{mol}^{-1} + 2 \times 69.91\text{JK}^{-1}\text{mol}^{-1} - 151.1\text{JK}^{-1}\text{mol}^{-1} = 208.6\text{JK}^{-1}\text{mol}^{-1}$$

(b) From the values of ΔH^o and ΔS^o determined in part (a) we can calculate ΔG^o at 298K:

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

$$\Delta G^o = -124\text{kJmol}^{-1} - 298K \times \frac{208.6\text{kJmol}^{-1}\text{K}^{-1}}{1000} = -186.1\text{kJmol}^{-1}$$

Alternatively, ΔG^o can also be calculated directly using ΔG^o_f values tabulated in Appendix D.

(c) The equilibrium constant for the reaction is calculated using $\Delta G^o = -RT\ln K$:

$$\Delta G^o = -RT\ln K \Rightarrow -186.1 \times 1000\text{Jmol}^{-1} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298K \times \ln K$$

$$-186100\text{Jmol}^{-1} = -2477.6\ln K \Rightarrow \ln K = 75.1 \Rightarrow K = e^{75.1} = 4.1 \times 10^{32}$$

(d) The reaction has $\Delta H^o < 0$ and $\Delta S^o > 0$. Because $\Delta G^o = \Delta H^o - T\Delta S^o$, the reaction will be spontaneous at all temperatures.

111. **(M)** Recall from exercise 104 that $\Delta G^o = 0$ when K=1. Therefore, we are looking for the diagram with smallest change in Gibbs free energy between the products and the reactants. The correct answer is diagram (a). Notice that diagrams (b) and (c) represent chemical reactions with small and large values of equilibrium constants, respectively.

112. **(M)** Carbon dioxide is a gas at room temperature. The melting point of carbon dioxide is expected to be very low. At room temperature and normal atmospheric pressure this process is spontaneous. The entropy of the universe if positive.