FREE ENERGY BOOK QUESTIONS
#19.56, 19.63, 19.66, 19.78, 19.81, 19.107

19.56 (a) Data for $CrBr_3$ does not appear in Appendix C.
Consider the reaction $4Cr(s) + 3O_2(g) \rightarrow 2Cr_2O_3(s)$

$\Delta H° = 2(-1139.7) - 4(0) + 3(0)$ = **-2279.4 kJ**
$\Delta S° = 2(81.2) - 4(23.6) - 3(205.0)$ = **-547.0 J/K**
$\Delta G° = 2(-1058.1) - 4(0) + 3(0)$ = **-2116.2 kJ**

4 pt

$\Delta G°$ = $\Delta H° - T\Delta S°$
= (-2279.4 kJ) - (298K (-0.547 kJ/K))
= **-2116.4 kJ**

(b) $\Delta H° = -553.5 - 393.5 - (-1216.3)$ = **+269.3.4 kJ**
$\Delta S° = 70.42 + 213.6 - 112.1$ = **+171.9 J/K**
$\Delta G° = -525.1 - 394.4 - (-1137.6)$ = **+218.1 kJ**

4 pt

$\Delta G°$ = $\Delta H° - T\Delta S°$
= (+269.3.4 kJ) - (298K (+0.1719 kJ/K))
= **+218.1 kJ**

(c) Assume the reactant is P(g) not P(s)

$\Delta H° = 2(-1594.4) + 5(0) - 2(316.4) - 10(-268.61)$ = **-1135.5 kJ**
$\Delta S° = 2(300.8) + 5(130.58) - 2(163.2) - 10(173.51)$ =**-807.0 J/K**
$\Delta G° = 2(-1520.7) + 5(0) - 2(280.0) - 10(-270.70)$ = **-894.4 kJ**

4 pt

$\Delta G°$ = $\Delta H° - T\Delta S°$
= (-1135.5 kJ) - (298K (-0.8070 kJ/K))
= **-895.0 kJ**

(d) $\Delta H° = -284.5 - 0 - 0$ = **-284.5 kJ**
$\Delta S° = 122.5 - 64.67 - 205.0$ = **-147.2 J/K**
$\Delta G° = -240.6 - 0 - 0$ = **-240.6 kJ**

4 pt

$\Delta G°$ = $\Delta H° - T\Delta S°$
= (-284.5 kJ) - (298K (+0.8070 kJ/K))
= **-240.6 kJ**

19.63 At 450 K $\Delta G < 0$; $\Delta G = \Delta H - T\Delta S < 0$

$34.5kJ - 450K(\Delta S) < 0$
$34.5\ kJ < 450K\ (\Delta S)$

3 pt

$\Delta S > 34.5\ kJ / 450\ K$

$\Delta S > 0.0767$ kJ/K or

$\Delta S > 76.7$ J/K

19.66 ΔG is negative when $T\Delta S > \Delta H$ or $T > \Delta H/\Delta S$

$\Delta H^\circ = \Delta H^\circ_{(CH3OH)} + \Delta H^\circ_{(CO,g)} - \Delta H^\circ_{(CH3COOH)}$
$= -201.2 - 110.5 - (-487.0)$
$= +175.3$

$\Delta S^\circ = S^\circ_{(CH3OH)} + S^\circ_{(CO,g)} - S^\circ_{(CH3COOH)}$
$= 237.6 + 197.9 - 159.8$
$= +275.7$ J/K

4 pt

$$T > \frac{175.3kJ}{0.2757\,kJ/K} = 635.8K$$

The reaction is spontaneous above 635.8K (363°C)

19.78

(a) $\Delta G = -RT \ln K$; $\ln K = -\Delta G^\circ / RT$; at 298K, $RT = 2.4776 = 2.478$ kJ

$\Delta G^\circ = \Delta G^\circ (NaOH) + \Delta G^\circ (CO_2) - \Delta G^\circ(NaHCO_3)$
$= -379.5 + (-394.4) - (-851.8) =$ **+77.9kJ**

2 pt

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-77.9kJ}{2.478kJ} = -31.442 = -31.4$$

$$K = 2\times10^{-14}$$

$$K = P_{CO_2} = 2\times10^{-14}$$

(b) $\Delta G^\circ = 2\Delta G^\circ (HCl) + \Delta G^\circ (Br_2) - 2\Delta G^\circ(HBr) - \Delta G^\circ(Cl_2)$
$= 2(-95.27) + 3.14 - 2(-53.22) - 0 =$ **-80.96 kJ**

2 pt

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-80.96)kJ}{2.478\,kJ} = +32.68$$

$$K = 1.6\times10^{14}$$

$$K = \frac{P^2_{HCl}\times P_{Br_2}}{P^2_{HBr}\times P_{Cl_2}} = 1.6\times10^{14}$$

(c) $\Delta G^\circ =$ **-140.0 kJ**

2 pt

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-140.0)kJ}{2.478kJ} = +56.51$$

$$K = 3.5\times10^{24}$$

$$K = \frac{P^2_{SO3}}{P^2_{SO2}\times P_{O_2}} = 3.5\times10^{24}$$

19.81 (a) $HNO_2(aq) \rightleftharpoons H^{+1}(aq) + NO_2^{-1}(aq)$ 1 pt

(b) $\Delta G° = -RT \ln K_a = -(8.314 \times 10^{-3}\ kJ/mol\ K)(298K) \ln (4.5 \times 10^{-4})$
$= +19.0928$
$= \mathbf{19.1\ kJ}$ 2 pt

(c) $\Delta G = 0$ at equilibrium 1 pt

(d) $\Delta G = \Delta G° + RT \ln Q$

$$\Delta G = 19.09kJ + (8.314\times10^{-3}\ \tfrac{kJ}{molK})(298K)\ln\left(\frac{(5.0\times10^{-2})(6.0\times10^{-4})}{(0.20)}\right)$$ 2 pt

$$\Delta G = -2.72kJ = \boxed{-3kJ}$$

19.107 (a)
$$\Delta G° = 3\Delta G°_f(S(s)) + 2\Delta G°_f(H_2O) - \Delta G°_f(SO_2) - 2\Delta G°_f(H_2S)$$
$$\Delta G° = 3(0) + 2(-228.57) - (-300.4) - 2(-33.01)$$
$$\Delta G° = -90.72 = -90.7kJ$$ 3 pt

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-(-90.72kJ)}{(8.314\times10^{-3}\ \tfrac{kJ}{molK})(298K)} = 36.6165 = 36.6$$
$$K = e^{36.6} = 7.99\times10^{15} = \boxed{8\times10^{15}}$$

(b) The reaction is highly spontaneous at 298K and feasible in principle. However, use of $H_2S(g)$ produces a severe safety hazard for workers and the surrounding community. 1 pt

(c)
$$P_{H_2O} = \frac{25torr}{760torr/atm} = 0.033\,atm$$

$$K = \frac{P^2_{H_2O}}{P_{SO_2}P^2_{H_2S}};\ P_{SO_2} = P_{H_2S}$$

$$K = 7.99\times10^{25} = \frac{(0.033)^2}{x(x)^2}$$ 3 pt

$$x^3 = \frac{(0.033)^2}{7.99\times10^{15}} = \boxed{5\times10^{-7}\,atm}$$

(d)
$$\Delta H° = 3\Delta H°_f(S(s)) + 2\Delta H°_f(H_2O(l)) - \Delta H°_f(SO_2) - 2\Delta H°_f(H_2S)$$
$$\Delta H° = 3(0) + 2(-241.82) - (296.9) - 2(-20.17) = \boxed{-146.4kJ}$$
$$\Delta S° = 3S°(S(s)) + 2S°(H_2O(l)) - S°(SO_2) - 2S°(H_2S)$$ 3 pt
$$\Delta S° = 3(31.88) + 2(188.83) - 248.5 - 2(205.6) = \boxed{-186.4J/K}$$

The reaction is exothermic so the value of K_{eq} will decrease with increasing temperature. The negative change in entropy means that the reaction will become nonspontaneous at some higher T. The process will be less effective at elevated T