Chapter 6 Homework Solutions

6.1 (a) $Q = 0.01$ [same equation used for (b)-(e)]

$$\Delta G = \Delta G^o + RT \ln Q = -32.9\,kJ/mol + (8.31x10^{-3}\,kJ/mol \cdot K)(298\,K)\ln(0.01) = -44.3\,kJ/mol$$

	Q	ΔG
(a)	0.01	-44.3 kJ/mol
(b)	1.0	-32.9
(c)	10.0	-27.2
(d)	$1x10^5$	-4.4
(e)	$1x10^6$	+1.3

One can see from the table that K is between $1x10^5$ and $1x10^6$.

We can calculate K easily by using the fact that $\Delta G = 0$ at equilibrium, yielding:

$$\ln K = -\frac{\Delta G^o}{RT} = \frac{-(-32.9\,kJ/mol)}{(8.31x10^{-3}\,kJ/mol \cdot K)(298\,K)} = +13.29$$

$$K = e^{13.29} = 5.9x10^5$$

6.2 $2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g)$

$\alpha = 0.0177 \quad T = 2257\,K \quad p = 2.0\,bar$

	$H_2O(g)$	$H_2(g)$	$O_2(g)$
Amt. at Equil.	$(1-\alpha)n$	αn	$\tfrac{1}{2}\alpha n$
Mole Fraction*	$\dfrac{1-\alpha}{1+(1/2)\alpha}$	$\dfrac{\alpha}{1+(1/2)\alpha}$	$\dfrac{(1/2)\alpha}{1+(1/2)\alpha}$
Pressure	$\dfrac{1-\alpha}{1+(1/2)\alpha}p$	$\dfrac{\alpha}{1+(1/2)\alpha}p$	$\dfrac{(1/2)\alpha}{1+(1/2)\alpha}p$
Pressure (numerical)	1.948 bar	0.0352 bar	0.0175 bar

*Using $n_{tot} = (1-\alpha)n + \alpha n + \tfrac{1}{2}\alpha n = (1+\tfrac{1}{2}\alpha)n$

$$K = \frac{p_{H_2}^2 p_{O_2}}{p_{H_2O}^2} = \frac{(0.0352)^2(0.0175)}{(1.948)^2} = 5.7x10^{-6}$$

6.3 **Reaction:** $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$
$\Delta G° = 2\Delta_f G°(NH_3) = -33.0$ kJ/mol
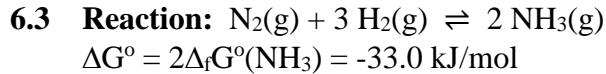
$T = 25 °C = 298$ K , $p_{N2} = 3.0$ bar , $p_{H2} = 1.0$ bar , $p_{NH3} = 0.50$ bar

$$Q = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3} = \frac{(4.0)^2}{(3.0)(0.50)^3} = 42.67$$

$\Delta G = \Delta G° + RT \ln Q$

`` $= -33.0 \, kJ/mol + (0.00831 \, kJ/mol \cdot K)(298 \, K) \ln(42.67)$

$= -33.0 \, kJ/mol + 9.29 \, kJ/mol \approx -23.7 \, kJ/mol$

Because $\Delta G < 0$ under these conditions, the reaction will proceed spontaneously to the right (towards more products).
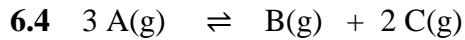
6.4 $3 A(g) \rightleftharpoons B(g) + 2 C(g)$
$T = 50 °C = 323$ K , $\Delta G = -2.50$ kJ/mol , $P_A = 2.0$ bar , $P_B = 4.0$ bar, $P_C - 0.50$ barn

$$Q = \frac{P_B P_C^2}{P_A^3} = \frac{(4.0)(0.50)^2}{(2.0)^3} = 0.125$$

$\Delta G = \Delta G° + RT \ln(Q)$

$\Delta G° = \Delta G - RT \ln(Q)$

$= -2.50 \, kJ/mol - (0.00831 \, kJ/mol \cdot K)(323 \, K) \ln(0.125)$

$= +3.08 \, kJ/mol$

$\Delta G° = -RT \ln(K)$

$$\ln(K) = -\frac{\Delta G°}{RT} = -\frac{3.08 \, kJ/mol}{(0.00831 \, kJ/mol \cdot K)(323 \, K)} = -1.147$$

$K = e^{-1.147} = 0.317 \approx 0.32$

6.5 $\alpha = 0.30$

$\begin{array}{ccc} A(g) & \rightleftharpoons & B(g) + 3 C(g) \end{array}$
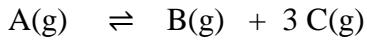
$n_o(1-\alpha) \qquad n_o\alpha \qquad 3n_o\alpha$

$n_{tot} = n_o(1-\alpha) + n_o\alpha + 3n_o\alpha = n_o(1+3\alpha)$

$$p_A = X_A p = \frac{n_o(1-\alpha)}{n_o(1+3\alpha)} p = \frac{1-0.30}{1+3(0.30)} \cdot 2.0 \, bar = 0.737 \, bar$$

$$p_B = X_B p = \frac{n_o\alpha}{n_o(1+3\alpha)} p = \frac{0.30}{1+3(0.30)} \cdot 2.0 \, bar = 0.316 \, bar$$

$$p_C = X_C p = \frac{3n_o\alpha}{n_o(1+3\alpha)} p = \frac{3(0.30)}{1+3(0.30)} \cdot 2.0 \, bar = 0.947 \, bar$$

$$K = \frac{p_B p_C^3}{p_A} = \frac{(0.316)(0.947)^3}{0.737} = 0.364 \approx 0.36$$

6.6 $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ $\quad \alpha = 0.1846$ at 25 °C and p = 1.0 bar
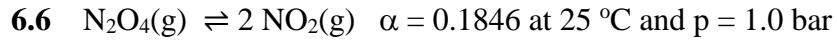
(a) K at 25 °C

	$N_2O_4(g)$	$NO_2(g)$
Amt. at Equil.	$(1-\alpha)n$	$2\alpha n$
Mole Fraction*	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Pressure	$\dfrac{1-\alpha}{1+\alpha}p$	$\dfrac{2\alpha}{1+\alpha}p$
Pressure (numerical)**	0.688 bar	0.312 bar

*Using $n_{tot} = (1-\alpha)n + 2\alpha n = (1+\alpha)n$
**Using $\alpha = 0.1846$ and p = 1.0 bar

$$K = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{(0.312)^2}{(0.688)} = 0.141$$

(b) K at 100 °C: $K_1 = 0.141$ at $T_1 = 298$ K, $K_2 = ??$ at $T_2 = 373$ K, $\Delta_{vap}H° = 56.2$ kJ/mol

$$\ln(K_2 / K_1) = -\frac{\Delta_r H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln(K_2 / 0.141) = -\frac{56.2\,kJ/mol}{8.31x10^{-3}\,J/mol \cdot K}\left[\frac{1}{373\,K} - \frac{1}{298\,K}\right] = +4.56$$

$$K_2 = (0.141)e^{+4.56} = 13.5$$

6.7 $2A + B \rightleftharpoons 3C + 2D.$ p =4.00 bar

	A	B	C	D
Initial Moles	1.00	2.00	0.00	1.00
Final Moles	1.00-2x	2.00-x	3x	1.00+2x
Final Moles (numerical)*	0.40	1.70	0.90	1.60
Mole Fraction**	0.087	0.370	0.196	0.348
Pressure***	0.348	1.478	0.783	1.391

*Using from D: $3x = 0.90 \rightarrow x = 0.30$
**Using n(tot) = 0.4 + 1.7 + 0.9 + 1.6 = 4.6
***$p_i = X_i p$

K: $K = \dfrac{p_C^3 p_D^2}{p_A^2 p_B} = \dfrac{(0.783)^3 (1.391)^2}{(0.348)^2 (1.478)} = 5.19$

Δ$_r$G°: $\Delta_r G^o = -RT \ln K = -(8.31 x 10^{-3}\, kJ\,/\,mol \cdot K)(298\,K)\ln(5.19)$
$$= -4.08\, kJ\,/\,mol \approx 4.1 kJ\,/\,mol$$

6.8 $\Delta G^o = -RT \ln K_1 \;\rightarrow\; K_1 = e^{-\frac{\Delta G^o}{RT_1}} = e^{-\frac{33 kJ/mol}{(8.31 x10^{-3}\, kJ/mol \cdot K)(1280 K)}} = e^{-3.10} = 0.045$

$\Delta H^o = +224$ kJ/mol , $K_1 = 0.045$ at $T_1 = 1280$ K , $K_2 = 1.00$ at $T_2 = ??$

$$\ln\left(K_2 / K_1\right) = -\frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \;\rightarrow\; \frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta H^o}\ln\left(K_2 / K_1\right)$$

$$\frac{1}{T_2} = \frac{1}{1280\,K} - \frac{8.31 x 10^{-3}\, kJ\,/\,mol \cdot K}{224\, kJ\,/\,mol}\ln\left(1\,/\,0.045\right) = 6.662 x10^{-4}\, K^{-1}$$

$$T_2 = \frac{1}{6.662 x10^{-4}\, K^{-1}} = 1501\,K \approx 1500\,K$$

Because ΔH° > 0, the equilibrium constant will rise above 1 at higher temperatures.

6.9   T = 180 °C = 453 K

$$\ln K = A + \frac{B}{T} + \frac{C}{T^2} \ , \ \ A = -1.0 \ , \ B = -1100 \text{ K} \ , \ C = 1.5 \text{x} 10^5 \text{ K}^2$$

(a) ΔH°

$$\frac{d \ln K}{dT} = -\frac{B}{T^2} - \frac{2C}{T^3}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \ \rightarrow \ \Delta H^\circ = RT^2 \cdot \frac{d \ln K}{dT}$$

$$\Delta H^\circ = RT^2 \left(-\frac{B}{T^2} - \frac{2C}{T^3} \right) = -RB - \frac{2RC}{T}$$

$$= -(0.00831 \text{ J / mol} \cdot \text{K})(-1100 \text{ K}) - \frac{2(.00831 \text{ J / mol} \cdot \text{K})(1.5 \text{x} 10^5 \text{ K}^2)}{453 \text{ K}}$$

$$= 9.14 - 5.50 = +3.64 \text{ kJ} \approx +3.6 \text{ kJ}$$

(b) ΔS° (Note: We'll determine ΔG° first)

$$\ln K = A + \frac{B}{T} + \frac{C}{T^2} = -1.0 + \frac{-1100 \text{ K}}{453 \text{ K}} + \frac{1.5 \text{x} 10^5 \text{ K}^2}{(453 \text{ K})^2} = -2.697$$

$$\Delta G^\circ = -RT \ln K = -(0.00831 \text{ kJ / mol} \cdot \text{K})(453 \text{ K})(-2.697) = +10.15 \text{ kJ / mol}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \ \rightarrow \ \Delta H^\circ = \Delta G^\circ + T \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{3.64 \text{ kJ / mol} - 10.15 \text{ kJ / mol}}{453 \text{ K}}$$

$$= -0.0144 \text{ kJ / mol} \cdot \text{K} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}} = -14.4 \text{ J / mol} \cdot \text{K}$$

6.10 (a) $p_o = 3.0$ bar. For simplicity, $PCl_5 = A$, $PCl_3 = B$, $Cl_2 = C$

$$A \rightleftharpoons B + C$$

Equil. Press: $(1-x)p_o$ xp_o xp_o

$$K = \frac{p_B p_C}{p_A} = \frac{(xp_o)(xp_o)}{(1-x)p_o} = \frac{x^2 p_o}{1-x} \rightarrow p_o x^2 + Kx - K = 0 = ax^2 + bx - c$$

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = \frac{-K + \sqrt{K^2 - 4p_o(-K)}}{2p_o} = \frac{-4.5 + \sqrt{(4.5)^2 - 4(3.0)(-4.5)}}{2(3.0)}$$

$$x = \frac{-4.5 + \sqrt{74.25}}{6.0} = 0.686$$

$$p_A = p_{PCl_5} = (1-x)p_o = (1-0.686)(3.0) = 0.942\,bar \approx 0.94\,bar$$

$$p_B = p_{PCl_3} = xp_o = (0.686)(3.0) = 2.058\,bar \approx 2.06\,bar$$

$$p_C = p_{Cl_2} = xp_o = (0.686)(3.0) = 2.058\,bar \approx 2.06\,bar$$

(b) $T = 150\ °C = 423$ K

$\Delta G° = -RT\ln(K) = -8.31$ J/mol-K(423 K)ln(4.5) = -5290 J

$$\Delta G = \Delta G° + RT\ln(Q) = \Delta G° + RT\ln\left(\frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}\right)$$

$$\Delta G = \Delta G° + RT\ln(Q) = -5290 + (8.31)(423)\ln\left(\frac{(2.2)(2.2)}{0.8}\right) = -5290 + 6330 = +1040\,J = +10.4\,kJ$$

6.11 $p_{init}(A) = p_{init}(B) = 3.0$ bar $p_{init}(C) = 0.0$ bar

$$2A + B \rightleftharpoons 2C$$

Equil. Press: $3.0-2x$ $3-x$ $2x$

$$K = 1x10^{-3} = \frac{p_C^2}{p_A^2 p_B} = \frac{(2x)^2}{(3-2x)^2(3-x)} \approx \frac{4x^2}{(3)^2(3)} = \frac{4x^2}{27}$$

$$x = \sqrt{\frac{27}{4}(1x10^{-3})} = 0.082$$

$p_C = 2x = 0.164$ bar ≈ 0.16 bar

6.12 $K_1 = 337$ at $T_1 = 100\ °C = 373\ K$ $\qquad$ $K_2 = 7.1 \times 10^{-5}$ at $T_2 = 500\ °C = 773\ K$

(a) $\ln(K_2 / K_1) = -\dfrac{\Delta H^o}{R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$

$$\Delta H^o = \dfrac{-R\ln(K_2/K_1)}{\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]} = \dfrac{-8.31\ln(7.1 \times 10^{-5}/337)}{\left[\dfrac{1}{773} - \dfrac{1}{373}\right]} = -92,080\ J/mol = -92.1\ kJ/mol$$

$$\ln(K_1) = -\dfrac{\Delta H^o}{RT_1} + \dfrac{\Delta S^o}{R}$$

Therefore, $\Delta S^o = R\left[\ln(K_1) + \dfrac{\Delta H^o}{RT_1}\right] = 8.31\left[\ln(337) + \dfrac{-92,080}{(8.31)(373)}\right]$

$$= 8.31(-23.9) = -198.5\ J/mol \cdot K$$

(b) $\Delta H^o = -92,080\ J/mol$, $K_1 = 337$ at $T_1 = 100\ °C = 373\ K$, $K_3 = ??$ at $T_3 = 300\ °C = 573\ K$

$$\ln(K_3 / K_1) = -\dfrac{\Delta H^o}{R}\left[\dfrac{1}{T_3} - \dfrac{1}{T_1}\right]$$

$$\ln(K_3 / 337) = -\dfrac{(-92,080)}{8.31}\left[\dfrac{1}{573} - \dfrac{1}{373}\right] = -10.37$$

$$\dfrac{K_3}{337} = e^{-10.37} = 3.14 \times 10^{-5} \rightarrow K_3 = 0.0106 \approx 0.011$$

(c) $\qquad\qquad$ N$_2$ $\ +\ $ 3H$_2$ $\ \rightleftharpoons\ $ 2NH$_3$

Equil. Press: $\quad$ 3.0-x $\qquad$ 2.0-3x $\qquad$ 2x

$$K = 7.1 \times 10^{-5} = \dfrac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \dfrac{(2x)^2}{(3.0 - x)(2.0 - 3x)^3} \approx \dfrac{4x^2}{(3.0)(2.0)^3} = \dfrac{4x^2}{24}$$

$$x = \sqrt{\dfrac{24}{4}(7.1 \times 10^{-5})} = 0.0206 \rightarrow P_{NH3} = 2x = 0.0412\ bar \approx 0.041\ bar$$

(d) T = 500 °C = 773 K $\qquad$ K = 7.1×10^{-5}

$$\Delta G^o = -RT \ln K = -(8.31 \, J \, / \, mol \cdot K)(773 \, K) \ln(7.1 x 10^{-5}) = +61,360 \, J \, / \, mol$$

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(2.5)^2}{(0.2)(0.2)^3} = 3910$$

$$\Delta G = \Delta G^o + RT \ln Q = 61360 \, J \, / \, mol + (8.31 \, J \, / \, mol)(773 \, K) \ln(3910)$$
$$= 114500 \, J \, / \, mol = 114.5 \, kJ \, / \, mol \approx 115 \, kJ \, / \, mol$$

6.13 Reduction Potentials are taken from Resource Section Table 6.2 (pg. 929)

(a) **Sn(s) + Sn⁴⁺(aq) ⇌ 2 Sn²⁺(aq)**

Reduction: $Sn^{4+}(aq) + 2 \, e^- \rightarrow Sn^{2+}(aq)$ $\qquad$ $E^o_{Red}(Sn^{4+}) = +0.15 \, v$
Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2 \, e^-$ $\qquad$ $E^o_{Oxid}(Sn) = -E^o_{Red}(Sn^{2+}) = +0.14 \, V$
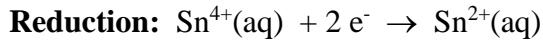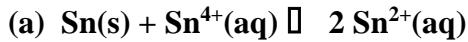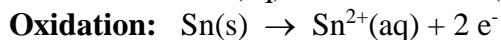
$E^o_{Cell} = +0.15 \, V + 0.14 \, V = +0.29 \, V$

$$E^o_{Cell} = \frac{RT}{nF} \ln K \;\; \rightarrow \;\; \ln K = \frac{nF}{RT} E^o_{Cell}$$

$$\ln K = \frac{(2)(96,500)}{(8.31)(298)}(+0.29) = +22.60 \;\; \rightarrow \;\; K = e^{+22.60} = 6.5 x 10^9$$

(b) **Sn(s) + 2 AgCl(s) ⇌ Sn²⁺(aq) + 2 Cl⁻(aq) + 2 Ag(s)**

Reduction: $2 \, AgCl(s) + 2 \, e^- \rightarrow 2 \, Ag(s) + 2 \, Cl^-(aq)$ $E^o_{Red}(Sn^{4+}) = +0.22 \, v$
Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2 \, e^-$ $\qquad$ $E^o_{Oxid}(Sn) = -E^o_{Red}(Sn^{2+}) = +0.14 \, V$
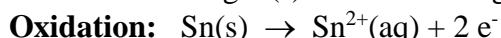
$E^o_{Cell} = +0.22 \, V + 0.14 \, V = +0.36 \, V$

$$E^o_{Cell} = \frac{RT}{nF} \ln K \;\; \rightarrow \;\; \ln K = \frac{nF}{RT} E^o_{Cell}$$

$$\ln K = \frac{(2)(96,500)}{(8.31)(298)}(+0.36) = +28.06 \;\; \rightarrow \;\; K = e^{+28.06} = 1.5 x 10^{12}$$

6.14. The procedure will be to determine the Ion Product, Q, for each salt. If $Q > K_{sp}$, then the salt will precipitate. If $Q \leq K_{sp}$, the salt will not precipitate.

AgBr: $[Ag^+] = 5.0 \times 10^{-5}$ M , $[Br^-] = 2.0 \times 10^{-8}$ M
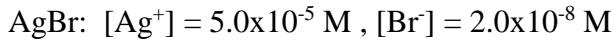
$Q = [Ag^+][Br^-] = (5.0 x 10^{-5})(2.0 x 10^{-8}) = 1.0 x 10^{-12} > K_{sp}(5.4 x 10^{-14})$

Because $Q > K_{sp}$, AgBr(s) will precipitate from solution.

HgBr$_2$: $[Hg^{2+}] = 5.0 \times 10^{-5}$ M , $[Br^-] = 2.0 \times 10^{-8}$ M
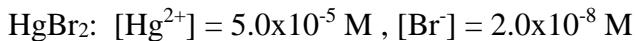
$Q = [Hg^{2+}][Br^-]^2 = (5.0 x 10^{-5})(2.0 x 10^{-8})^2 = 2.0 x 10^{-20} < K_{sp}(6.2 x 10^{-20})$

Because $Q < K_{sp}$, HgBr$_2$(s) will **not** precipitate from solution.

6.15. We will first calculate the concentrations, $[Hg^+]$ and $[SO_4^{2-}]$
We will then calculate the Ion Product, Q, and compare it to K_{sp}
$V_{tot} = 1200$ mL + 800 mL = 2000 mL = 2.0 L

Calculation of $[Hg^+]$:

$n_{Hg^+} = M_{Hg^+} \cdot V_{Hg^+} = (0.02 \, mol \, / \, L)(0.80 \, L) = 1.6 x 10^{-2} \, mol$

$[Hg^+] = \dfrac{n_{Hg^+}}{V_{tot}} = \dfrac{1.6 x 10^{-2} \, mol}{2.0 \, L} = 8.0 x 10^{-3} \, M$

Calculation of $[SO_4^{2+}]$:

$n_{SO_4^{2-}} = M_{SO_4^{2-}} \cdot V_{SO_4^{2-}} = (0.01 \, mol \, / \, L)(1.20 \, L) = 1.2 x 10^{-2} \, mol$

$[SO_4^{2-}] = \dfrac{n_{SO_4^{2-}}}{V_{tot}} = \dfrac{1.2 x 10^{-2} \, mol}{2.0 \, L} = 6.0 x 10^{-3} \, M$

Calculate of Q and comparison to K_{sp}

$Q = \left[Hg^+\right]^2\left[SO_4^{2-}\right] = (8.0 x 10^{-3})^2(6.0 x 10^{-3}) = 3.84 x 10^{-7} < K_{sp}(6.5 x 10^{-7})$

Because $Q < K_{sp}$, Hg$_2$SO$_4$(s) will **not** precipitate from solution.

6.16 (a) Oxidation: 2 Br$^-$(0.005 M) → Br$_2$(l) + 2 e$^-$
    Reduction: Hg^{2+}(2.5 M) + 2 e$^-$ → Hg(l)
    Overall: 2 Br$^-$(0.005 M) + Hg^{2+}(2.5 M) → Br$_2$(l) + Hg(l) , n = 2 electrons transfered
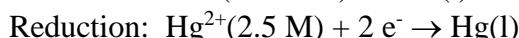
(b) $E^o_{cell} = E^o_{red}\left(Hg^{2+}\right) + E^o_{oxid}\left(Br^-\right) = E^o_{red}\left(Hg^{2+}\right) - E^o_{red}\left(Br_2\right) = +0.86V - (1.07V) = -0.21V$

(c) $E^o_{cell} = \dfrac{RT}{nF}\ln K \rightarrow \ln K = \dfrac{nF}{RT}E^o_{cell} = \dfrac{2(96,500 \, C \, / \, mol)}{(8.31 C \cdot V \, / \, mol \cdot K)(298 \, K)}(-0.21V) = -16.37$

$K = e^{-16.37} = 7.8 x 10^{-8}$

(d) $E_{cell} = E^o_{cell} - \dfrac{RT}{nF} \ln\left(\dfrac{1}{[Br^-]^2[Hg]^{2+}}\right) = -0.21V - \dfrac{(8.31)(298)}{2(96,500)} \ln\left(\dfrac{1}{(0.005)^2(2.5)}\right)$

$= -0.21V - 0.124V \approx -0.33V$

6.17 (a) Oxidation: $Mg(s) \rightarrow Mg^{2+}(1.8\ M) + 2\ e^-$

Reduction: $Al^{3+}(0.001\ M) + 3\ e^- \rightarrow Al(s)$

Overall: $3\ Mg(s) + 2\ Al^{3+}(0.001\ M) \rightarrow 3\ Mg^{2+}(1.8\ M) + 2\ Al(s)$, n = 6 electrons transfered
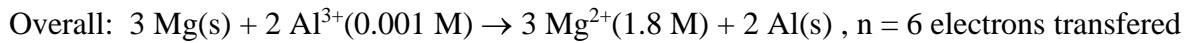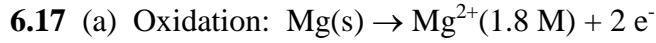
(b) $E^o_{cell} = E^o_{red}\left(Al^{3+}\right) + E^o_{oxid}\left(Mg\right) = E^o_{red}\left(Al^{3+}\right) - E^o_{red}\left(Mg^{2+}\right) = -1.66 + (+2.37V) = +0.71V$

(c) $E^o_{cell} = \dfrac{RT}{nF} \ln K \rightarrow \ln K = \dfrac{nF}{RT} E^o_{cell} = \dfrac{6(96,500\,C/mol)}{(8.31\,C\cdot V/mol\cdot K)(298\,K)}(+0.71V) = +166$

$K = e^{+166} = 1.2x10^{+72}$

(d) $E_{cell} = E^o_{cell} - \dfrac{RT}{nF} \ln\left(\dfrac{[Mg^{2+}]^3}{[Al^{3+}]^2}\right) = +0.71V - \dfrac{(8.31)(298)}{6(96,500)} \ln\left(\dfrac{(1.8)^3}{(0.001)^2}\right)$

$= +0.71V - 0.067V \approx +0.64V$

6.18 **Reaction:** $Zn^{2+}(0.20\ M) \rightarrow Zn^{2+}(xx\ M)$
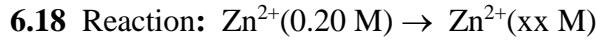
$E_{cell} = 0.078 = 0 - \dfrac{0.0592}{2} \log\left(\dfrac{xx}{0.20}\right) \rightarrow \log\left(\dfrac{xx}{0.20}\right) = -\dfrac{2}{0.0592}(0.078) = -2.64$

$\dfrac{xx}{0.20\,M} = 10^{-2.64} = 0.00232 \rightarrow xx = [Zn^{2+}] = 0.20(0.00232) = 4.63x10^{-4}\ M$

$4.63x10^{-4}\ mol/L \cdot \dfrac{65.4\,g}{1\,mol} = 0.0303\,g/L \cdot \dfrac{1mg}{10^{-3}\,g} = 30.3\,mg/L$

6.19 **Reaction:** $Pb^{2+}(0.50\ M) \rightarrow Pb^{2+}(xx\ M)$
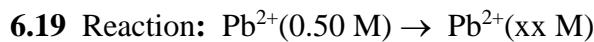
$E_{cell} = 0.120 = 0 - \dfrac{0.0592}{2} \log\left(\dfrac{xx}{0.50}\right) \rightarrow \log\left(\dfrac{xx}{0.50}\right) = -\dfrac{2}{0.0592}(0.120) = -4.054$

$\dfrac{xx}{0.50\,M} = 10^{-4.054} = 8.83x10^{-5} \rightarrow xx = [Pb^{2+}] = 0.50(8.83x10^{-5}) = 4.41x10^{-5}\ M$

$[Pb^{2+}] = s = 4.41x10^{-5} \qquad [IO_3^-] = 2s = 8.82x10^{-5}$

$K_{sp} = [Pb^{2+}]\cdot[IO_3^-]^2 = \left(4.41x10^{-5}\right)\cdot\left(8.82x10^{-5}\right)^2 = 3.4x10^{-13}$

6.20 Reaction: $Ag^+(0.25 \text{ M}) \rightarrow Ag^+(xx \text{ M})$

$$E_{cell} = 0.195 = 0 - \frac{0.0592}{1}\log\left(\frac{xx}{0.25}\right) \rightarrow \log\left(\frac{xx}{0.25}\right) = -\frac{1}{0.0592}(0.195) = -3.294$$

$$\frac{xx}{0.25\,M} = 10^{-3.294} = 5.092x10^{-4} \rightarrow xx = [Ag^+] = (0.25)\cdot(5.092x10^{-4}) = 1.27x10^{-4}\,M$$

$$[Ag^+] = 3s = 1.27x10^{-4} \qquad [PO_4^{3-}] = s = 1.27x10^{-4}/3 = 4.24x10^{-5}$$

$$K_{sp} = [Ag^+]^3 \cdot [PO_4^{3-}] = \left(1.27x10^{-4}\right)^3 \cdot \left(4.24x10^{-5}\right) = 8.7x10^{-17}$$

6.21 (a) Δ_rG^o

Note: For this reaction, n = 2 electrons transfered.

$$E_{cell}^o = a - bT^2 = 0.313V - \left(5.1x10^{-7}\,V\,/\,K^2\right)(298\,K)^2 = 0.268V$$

$$\Delta_rG^o = -nFE_{cell}^0 = -(2)(96,500\,C\,/\,mol)(0.268V) = -51720\,C\cdot V\,/\,mol$$

$$= -51720\,J\,/\,mol = -51.7\,kJ\,/\,mol$$

(b) Δ_rS^o

$$\Delta_rS^o = nF\frac{dE_{cell}^o}{dT} = nF[0 - 2bT] = 2(96,500\,C\,/\,mol)[(-2)(5.1x10^{-7}\,V\,/\,K^2)(298\,K)]$$

$$= -58.7\,C\cdot V\,/\,mol\cdot K) = -58.7J\,/\,mol\cdot K$$

(c) Δ_rH^o

$$\Delta_rH^o = \Delta_rG^o + T\Delta_rS^o = -51720\,J\,/\,mol + (298\,K)(-51.7\,J\,/\,mol\cdot K)$$

$$= -67130\,J\,/\,mol \approx -67.1kJ\,/\,mol$$

X