HW 5 KEY

E 7.1a $2H_2O \rightleftharpoons 2H_2 + O_2$

	H_2O	H_2	O_2
Equil	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
mol. frac.	$\frac{1-\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$
Pressure	$\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\frac{\alpha p}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$

$$K = \frac{\left(\frac{p_{H_2}}{p^\circ}\right)^2\left(\frac{p_{O_2}}{p^\circ}\right)}{\left(\frac{p_{H_2O}}{p^\circ}\right)^2}$$

a) $K = \prod_J a_J^{\nu_J}$ $a_J = \frac{p_J}{p^\circ}$ (assume ideal gases)

$$K = \frac{\left(\frac{\alpha p}{p^\circ(1+\frac{\alpha}{2})}\right)^2\left(\frac{\alpha p/2}{(1+\frac{\alpha}{2})p^\circ}\right)}{\left(\frac{(1-\alpha)p}{(1+\frac{1}{2}\alpha)p^\circ}\right)^2} = \frac{\alpha^3 p}{2(1-\alpha)^2(1+\frac{\alpha}{2})p^\circ}$$

$$= \cancel{\frac{(0.01773)^3}{2(1-0.01773)}} = \frac{(0.0177)^3}{2(1-0.0177)^2(1+\frac{0.0177}{2})}$$

$K = 2.85\times10^{-6}$

b) $\Delta_r G^\circ = -RT\ln K = -(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})(2257\ \mathrm{K})\ln(2.85\times10^{-6})$

$= 240\ \mathrm{kJ\,mol^{-1}}$

c) $\Delta_r G = 0$ because at equilibrium

E7.3a

$\Delta_r G^\circ = \sum_J \nu_J \Delta_f G$

$\nu(Pb)=1$ $\nu(CO_2)=1$ $\nu(PbO)=-1$ $\nu(CO)=-1$

$\Delta_r G^\circ = (-394.36)-(-188.93)-(-137.17) = -68.26\ \mathrm{kJ\,mol^{-1}}$

E7.3a

~~[illegible]~~ $\exp[-\Delta_r G/RT] = K = 9.2\times10^{11}$ (at 298 K)

b) $\Delta_r H^\circ = (-393.51) - (-218.99) - (-110.53) = -63.99\ kJ\,mol^{-1}$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K(400) = \ln K(298) - \left(\frac{-63.99\,(10^3)}{8.314}\right)\left(\frac{1}{400} - \frac{1}{298}\right)$$

$$= 20.96$$

$$K(400\,K) = 1.3\times10^9$$

At 400K: $\Delta_r G^\circ = -RT\ln K(400K) = -8.314(400)\ln(1.3\times10^9)$

$$= -69.7\ kJ\,mol^{-1}$$

E7.12a $CaCO_3 \rightleftharpoons CaO(s) + CO_2(g)$

Assume K=1, for purpose of exercise (which really means we are assuming that the process is occurring at some temperature, T)

$\therefore\ \Delta_r G^\circ = 0$

when K=1, $\frac{\Delta H}{\Delta S} = T$ (equilibrium)

$\Delta_r H^\circ = -635.09 - 393.51 + 1206.9 = 178.3\ kJ\,mol^{-1}$

$\Delta_r S^\circ = 39.75 + 213.74 - 92.9 = 160.6\ JK^{-1}mol^{-1}$

$$T = \frac{178.3\cdot10^3\ J\,mol^{-1}}{160.6\ JK^{-1}mol^{-1}} = 1110\ K$$

E 7.14a

Standard potentials from table

a) $Zn | ZnSO_4 || AgNO_3(aq) | Ag$

Reduction $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ $E^\circ = 0.80V$

Oxidation $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^\circ = -0.76V$

Total $2Ag^+ + Zn(s) \rightarrow Zn^{2+} + 2Ag(s)$

$$E^\circ_{tot} = E_{cat} - E_{anode} = 0.80 - (-0.76) = 1.56V$$

b) $Cd | CdCl_2(aq) || HNO_3(aq) | H_2(g) | Pt$

$2H^+ + 2e^- \rightarrow H_2(g)$ $E^\circ = 0V$ Red (cathode)

$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $E^\circ = -0.40V$ Oxid (Anode)

Overall: $Cd^{2+} + H_2 \rightarrow 2H^+ + Cd(s)$ $E^\circ = -(-0.40) = 0.40$

c) $Cr^{3+} + 3e^- \rightarrow Cr$ $E^\circ = -0.74$

$3[Fe(CN)_6]^{3-} + 3e^- \rightarrow 3[Fe(CN)_6]^{4-}$ $E^\circ = +0.36$

$$E^\circ_{tot} = E^\circ_{cat} - E^\circ_{an} = 0.36 - (-0.74) = 1.10V$$

Under standard conditions

$E^\circ > 0$ spontaneous galvanic

$E^\circ < 0$ non-spontaneous electrolytic

DR. VDB's Questions:

① $PCl_5 \rightarrow PCl_3 + Cl_2$

$\Delta_r G^\circ = \sum_{prod} \nu_i \Delta G_i - \sum_{reactants} \nu_i \Delta_r G_i$ $\quad \Delta G = -RT \ln K \quad K = e^{-\Delta G/RT}$

$\Delta_r G = (1)\Delta_f G^\circ(PCl_3) + (1)\Delta_r G^{\circ(Cl_2)} - (1)\Delta_r G^\circ(PCl_5)$

$= -267.8 - (-305)\ kJ\,mol^{-1} = 37.2\ kJ\,mol^{-1}$

$K = \exp\left[-37.2(10^3)/[8.314(298)]\right] = 3\times 10^{-7}$ favors reactants

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$\Delta_r G^\circ = 2\Delta_r G^\circ(CO_2) - \Delta_r G^\circ(O_2) - 2\Delta_r G^\circ(CO)$

$\Delta_r G^\circ = 2(-394.36) - (-137.17)2 = -514.38\ kJ\,mol^{-1}$

$K = 1.47\times 10^9$ favors products

$3O_2(g) \rightarrow 2O_3(g)$

$\Delta_r G^\circ = 2\Delta_r G^\circ(O_3) - 3\Delta_r G^\circ(O_2) = 2(163.2) - 0 = 326.4\ kJ/mol$

$K = 4.1\times 10^{-58}$ Reactants favored (Ozone very rare, O_2 very abundant)

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

$\Delta_r G^\circ = 2(86.55) - 0 = 173.1\ kJ\,mol^{-1}$

$K = 4.54\times 10^{-31}$ favors reactants

$N_2(g)$ and $O_2(g)$ comprise ~90% of gases in earth's atmosphere, so if this rxn was heavily favored, we would see the atmosphere being composed of NO (a pollutant).

(4) $I_2(s) + H_2(g) \rightarrow 2HI(g)$ $T = 300\,K$

$y_{HI} = 0.39$ $y_{H_2} = 0.61$ $P_o = 1\,bar$ $y_i = \frac{P_i}{P_o}$

$$K = \frac{a_{HI}^2}{a_{I_2} a_{H_2}} = \frac{(0.39)^2}{(1)(0.61)} = 0.25$$

$$\Delta_r G^0 = -RT\ln K = -(8.314\,J\,K^{-1}mol^{-1})(300K)\ln(0.25)$$

$$\Delta_r G^\circ = 3.5\,kJ\,mol^{-1}$$

	I_2	H_2	HI	total gas
Init:	0.5	0.5	0	0.5
Equil:	0.5-x	0.5-x	+2x	0.5 + x
Pressure:	—	$\frac{0.5-x}{0.5+x}P$	$\frac{2x}{0.5+x}P$	

$$K = \frac{P_{HI}^2}{P_{H_2}} = \frac{\left(\frac{2x}{0.5+x}\right)^2 P^2}{\left(\frac{0.5-x}{0.5+x}\right)P}$$ $P = 1\,bar$

$$K = \frac{4x^2}{(0.5+x)(0.5-x)} = \frac{4x^2}{0.25-x^2} = 0.25$$

$\Delta H = 6.62\,kJ$

$\Delta H = n\Delta_r H^\circ$

$\Delta H = 55.2\,kJ\,mol^{-1}$

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

$$4x^2 = 0.25(0.25 - x^2)$$

$$x^2 = 0.015$$

$$x = 0.12 \text{ (or n)}$$

$$\Delta S^\circ = \frac{\Delta G^\circ - \Delta H^\circ}{-T} = \frac{3.5 - 55.2}{-300} = 172\,J\,K^{-1}mol^{-1}$$

③ $H_2(g) + CO_2(g) \rightarrow H_2O(g) + CO(g)$

$$\Delta_r H^\circ = {}^-241.8 + {}^-110.53 - 0 - ({}^-393.5) = 41.17 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = {}^-137.17 + {}^-228.57 - 0 - ({}^-394.36) = 28.62 \text{ kJ mol}^{-1}$$

At 298 K, $\Delta G^\circ = -(8.314 \text{ J K}^{-1}\text{mol}^{-1})(298 \text{ K})(\ln K)$

$$K = \exp[-28.62 \overset{(10^{3})}{/} (298)(8.314)] = 9.6 \times 10^{-6}$$

$$\Delta_r S^\circ = 188.8 + 197.7 - (130.68 + 213.74) = \overset{42.08}{\cancel{41.28}} \text{ J K}^{-1}\text{mol}^{-1}$$

At 1000 K

$$\Delta C_p = 33.58 \text{ J K}^{-1}\text{mol} + 29.14 - (37.11 + 28.824) = -3.214 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ \, dT$$

$$\Delta_r H^\circ(1000 \text{ K}) = 41.17 + 3.214(10^{-3})(1000 - 298) = 38.9 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_r S^\circ(1000 \text{K}) = \Delta S^\circ(298 \text{K}) + \int_{T_1}^{T_2} \frac{\Delta C_p^\circ}{T} dT =$$

$$= 42.08 \text{ J K}^{-1}\text{mol}^{-1} + -3.214 \text{ J K}^{-1}\text{mol}^{-1} \ln\left(\frac{1000}{298}\right)$$

$$\Delta_r S(1000 \text{K}) = 38.2 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta_r G^\circ(1000 \text{ K}) = 38.9 \times 10^3 - 1000(38.2) = 700 \text{ J mol}^{-1}$$

$$K_{1000 K} = \exp(-700/(8.314)(1000)) = 0.92$$

Assume ΔH is T independent: $\ln\left(\frac{K_2}{K_1}\right) = -\frac{\overset{\text{at } 1000\text{K}}{\Delta H^\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$; $\ln K_2 = \frac{-38.9(10^3)}{8.314}\left(\frac{1}{1259} - \frac{1}{1000}\right) + \ln K_1$

$$\ln K_2 = 0.879$$

$$K(1259 \text{ K}) = 2.4$$

④ $2HgO(s) \rightarrow 2Hg(l) + O_2(g)$

$$\Delta G^\circ = 0 + 2(0) - 2(-58.54) = 117.1 \text{ kJ/mol}$$

$$K = \exp(-117.1(1000)/[8.314(298)]) =$$

$$K = 2.98 \times 10^{-21}$$

$$Q = \frac{\cancel{a^2_{Hg(l)}} \, a_{O_2(g)}}{\cancel{a^2_{HgO(s)}}} = a_{O_2(g)} = \frac{P_{O_2}}{P^\circ} = P_{O_2}$$

Since 20% of air is $O_2(g)$, $Q \cong 0.20$ and $Q > K$ so the reaction favors the reactants unless it was done with much less $O_2(g)$ or at higher T.

⑤ $A(s) + 2B(g) \rightarrow C(g) + 3D(g)$ | Total (gas mols) $P = 3$ bar

	A(s)	2B(g)	C(g)	3D(g)	Total (gas mols)
Init	3	4	1		5
Equil		$4-2x$	$1+x$	$3x$	$5+2x$
P_i		$\frac{4-2x}{5+2x}$	$\frac{1+x}{5+2x}$	$\frac{3x}{5+2x}$	

$T = 300$ K

At equil, $P_C = P_D$

Find K

$$P_C = P_D \quad 3x = 1 + x \qquad x = 0.5$$

$$P_B = \frac{4-1}{5+1} = \frac{1}{2}$$

$$P_C = P_D = \frac{1}{4}$$

$$K = \frac{\frac{P_C}{P^\circ} \cdot \frac{P_D^3}{P^{\circ 3}}}{P_B^2 / P^{\circ 2}} = \frac{P_C P_D^3}{P_B^2 \, P^{\circ 2}} = \frac{\frac{1}{4} \cdot \frac{1}{64}}{\frac{1}{4} \cdot 3^2} = 1.74 \times 10^{-3}$$

$\Delta_R G^\circ = -RT\ln K$

$= -8.314 \cdot 300 \cdot \ln(1.74 \times 10^{-3})$

$= 15.9\ kJ\,mol^{-1}$

$q = \Delta_r H \cdot x = 1\ kJ \quad (x = 0.5)$

$w = -\Delta n RT = 2x\,(8.314)(300) = -2.49\ kJ$

$\Delta U = q + w = 1 + -2.49 = -1.49\ kJ$