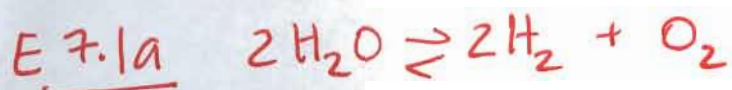


HW 5 KEY



	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			
Pressure	$\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\frac{\alpha p}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$

$$K = \frac{\left(\frac{P_{\text{H}_2}}{P^\circ}\right)^2 \left(\frac{P_{\text{O}_2}}{P^\circ}\right)}{\left(\frac{P_{\text{H}_2\text{O}}}{P^\circ}\right)^2}$$

a) $K = \prod_j a_j^{\nu_j}$ $a_j = \frac{P_j}{P^\circ}$ (assume ideal gases)

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

$$= \frac{(0.0177)^3}{2(1-0.0177)^2 \left(1+\frac{0.0177}{2}\right)} = \frac{(0.0177)^3}{2(1-0.0177)^2 \left(1+\frac{0.0177}{2}\right)}$$

$$K = 2.85 \times 10^{-6}$$

b) $\Delta_r G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(2257 \text{ K}) \ln(2.85 \times 10^{-6})$
 $= 240 \text{ kJ mol}^{-1}$

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

E7.3a

$$\Delta_r G^\circ = \sum_j \nu_j \Delta_f G^\circ$$

$$\nu(\text{Pb}) = 1 \quad \nu(\text{CO}_2) = 1 \quad \nu(\text{PbO}) = -1 \quad \nu(\text{CO}) = -1$$

$$\Delta_r G^\circ = (-394.34) - (-188.93) - (-137.17) = -68.26 \text{ kJ mol}^{-1}$$

E7.3a
~~100%~~ $\exp[-\Delta_r G^\circ / RT] = K = 9.2 \times 10^{11}$ (at 298 K)

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

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

$$\begin{aligned} \ln K(400) &= \ln K(298) - \left(\frac{-63.99 (10^3)}{8.314}\right) \left(\frac{1}{400} - \frac{1}{298}\right) \\ &= 20.96 \end{aligned}$$

$$K(400 \text{ K}) = 1.3 \times 10^9$$

At 400 K: $\Delta_r G^\circ = -RT \ln K(400 \text{ K}) = -8.314 (400) \ln(1.3 \times 10^9)$
 $= -69.7 \text{ kJ mol}^{-1}$



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 $K=1$, $\frac{\Delta_r H^\circ}{\Delta_r S^\circ} = T$ (equilibrium)

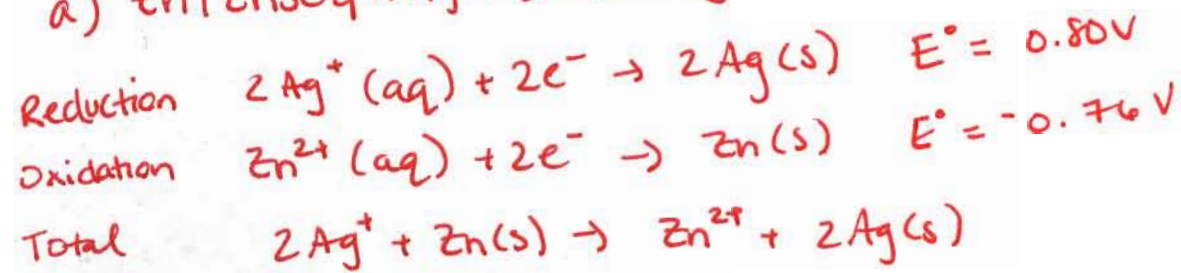
$$\Delta_r H^\circ = -635.09 - 393.51 + 1206.9 = 178.3 \text{ kJ mol}^{-1}$$

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

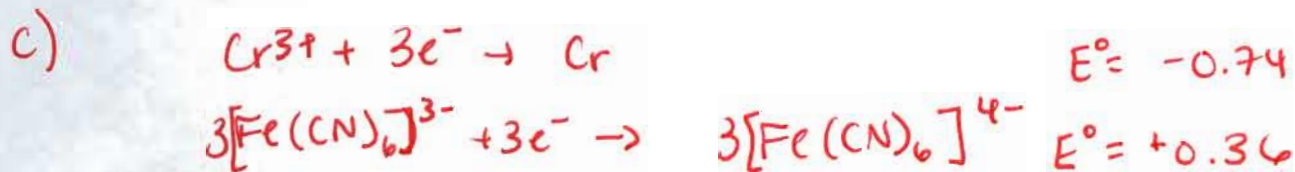
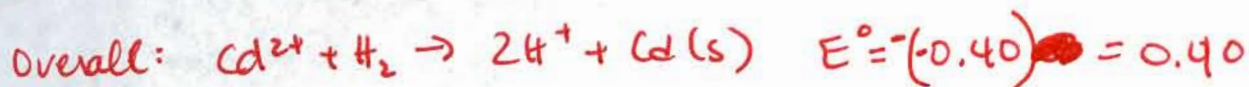
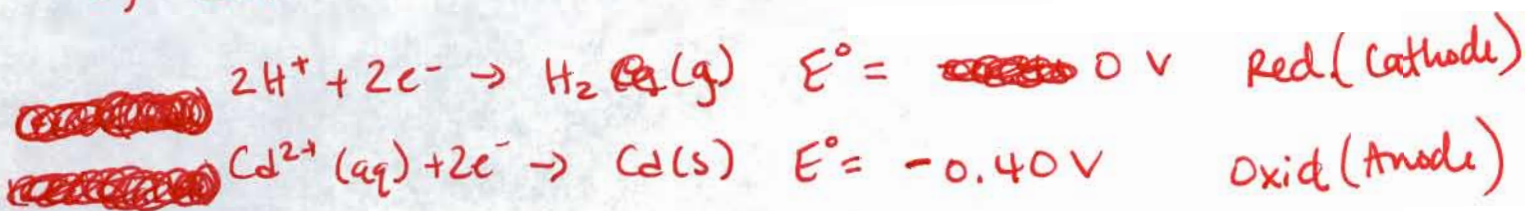
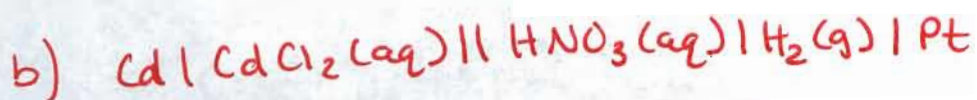
$$T = \frac{178.3 \cdot 10^3 \text{ J mol}^{-1}}{160.6 \text{ J K}^{-1} \text{ mol}^{-1}} = 1110 \text{ K}$$

E 7.14a

Standard potentials from table



$$E_{\text{tot}}^\circ = E_{\text{cat}}^\circ - E_{\text{node}}^\circ = 0.80 - (-0.76) = 1.56\text{V}$$



$$E_{\text{tot}}^\circ = E_{\text{cat}}^\circ - E_{\text{an}}^\circ = 0.36 - (-0.74) = 1.10\text{V}$$

Under standard conditions

$E^\circ > 0$ spontaneous galvanic

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

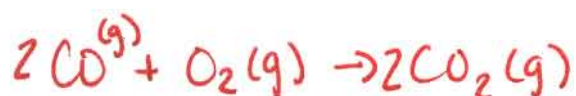
DR. VPB's Questions:



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

$$\begin{aligned} \Delta_r G^\circ &= (1) \Delta_f G^\circ(\text{PCl}_3) + (1) \Delta_f G^\circ(\text{Cl}_2) - (1) \Delta_f G^\circ(\text{PCl}_5) \\ &= -267.8 - (-305) \text{ kJ mol}^{-1} = 37.2 \text{ kJ mol}^{-1} \end{aligned}$$

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



$$\Delta_r G^\circ = 2 \Delta_f G^\circ(\text{CO}_2) - \Delta_f G^\circ(\text{O}_2) - 2 \Delta_f G^\circ(\text{CO})$$

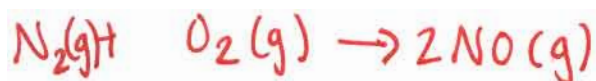
$$\Delta_r G^\circ = 2(-394.36) - (0) - 2(-137.17) = -514.38 \text{ kJ mol}^{-1}$$

$$K = 1.47 \times 10^9 \text{ favors products}$$



$$\Delta_r G^\circ = 2 \Delta_f G^\circ(\text{O}_3) - 3 \Delta_f G^\circ(\text{O}_2) = 2(163.2) - 0 = 326.4 \text{ kJ/mol}$$

$$K = 4.1 \times 10^{-58} \text{ Reactants favored (Ozone very rare, O}_2 \text{ very abundant)}$$



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

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

$\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ 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).



$$y_{\text{HI}} = 0.39 \quad y_{\text{H}_2} = 0.61 \quad P_0 = 1 \text{ bar} \quad y_i = \frac{P_i}{P_0}$$

$$K = \frac{a_{\text{HI}}^2}{a_{\text{I}_2} a_{\text{H}_2}} = \frac{(0.39)^2}{(1)(0.61)} = 0.25$$

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

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

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

$$K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}} = \frac{\left(\frac{2x}{0.5+x}\right)^2 P^2}{\left(\frac{0.5-x}{0.5+x}\right) P} \quad P = 1 \text{ bar}$$

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

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

$$x^2 = 0.015$$

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

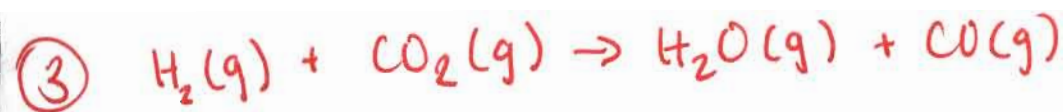
$$\Delta S^\circ = \frac{\Delta G^\circ - \Delta H^\circ}{-T} = \frac{3.5 - 55.2}{-300} = 172 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = 6.62 \text{ kJ}$$

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

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

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



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

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

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

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

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

At 1000 K

$$\Delta C_p = 33.58 \text{ J K}^{-1} \text{ mol}^{-1} + 29.14 - (37.11 + 29.824) = -3.214 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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

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

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

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

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

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

Assume ΔH is T independent:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right); \quad \ln K_2 = \frac{-38.9(10^3)}{8.314} \left(\frac{1}{1259} - \frac{1}{1000}\right) + \ln K_1$$

$$\ln K_2 = 0.879$$

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



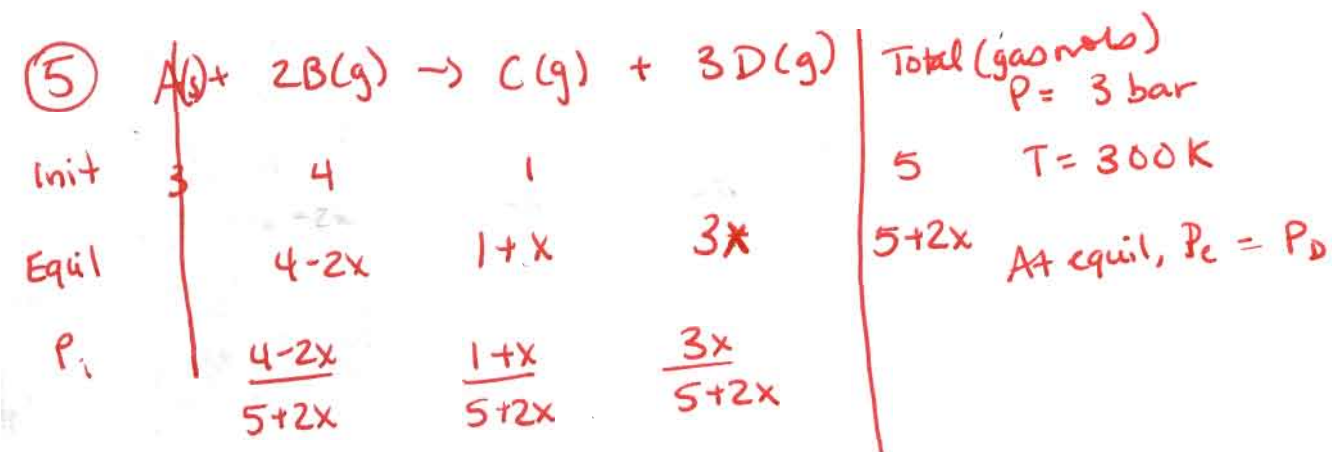
$$\Delta G^\circ = 0 + 2(0) - 2(-58.54) = 117.1 \text{ kJ/mol}$$

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

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

$$Q = \frac{a_{\text{H}_2(g)}^{27} a_{\text{O}_2(g)}}{a_{\text{H}_2\text{O}(s)}^{27}} = a_{\text{O}_2(g)} = \frac{P_{\text{O}_2}}{P^\circ} = P_{\text{O}_2}$$

Since 20% of air is $\text{O}_2(g)$, $Q \approx 0.20$ and $Q > K$
 so the reaction favors the reactants unless it was
 done with much less $\text{O}_2(g)$ or at higher T.



Find K

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

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

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

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

$$\Delta G_r = -RT \ln K$$

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

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

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

$$w = -\Delta n R T = 2 \times (8.314)(300) = -2.49 \text{ kJ}$$

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