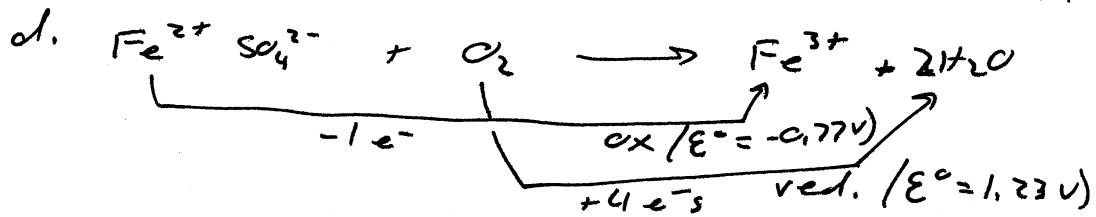


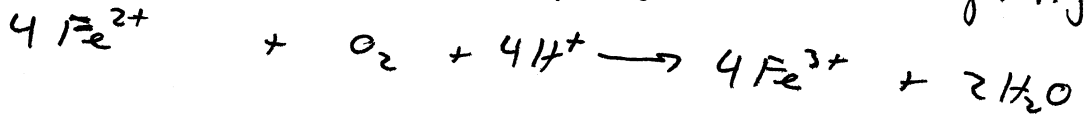
1. Ch 11, 34.c. $Ag + CuCl_2$ rxn?

Ag metal can be oxidized to Ag^+ ($E^\circ = -0.80V$)
 Cu^{2+} can be reduced to Cu^+ ($E^\circ = +0.16V$)
 or to Cu metal ($E^\circ = +0.34V$)

neither option provides a positive E°_{cell} , so no rxn.



let's balance this first... (dropping the SO_4^{2-} for simplicity)



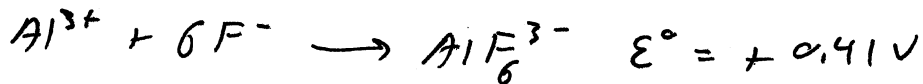
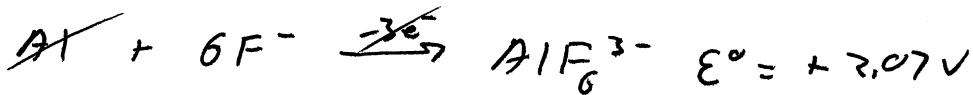
$$E^\circ_{cell} = \underset{Fe^{2+} \text{ ox}}{-0.77V} + \underset{O_2 \text{ red}}{1.23V} = +0.46V$$

as shown in non-graded part...

$$\Delta G^\circ = -178 \text{ kJ/mol}$$

$$K = 1.32 \times 10^{31}$$

43.



$$\Delta G^\circ = -nFE^\circ$$

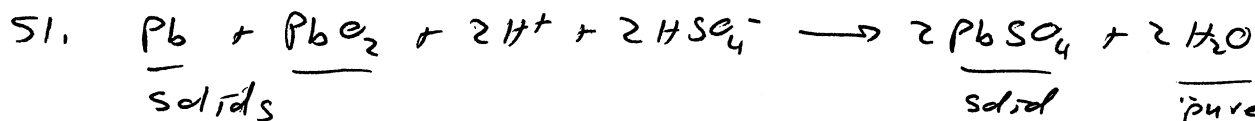
$$= -(3)(96,485 \text{ J/Vmol})(0.41V)$$

$$= -119 \text{ kJ/mol}$$

$$K = e^{-\Delta G^\circ / RT}$$

$$= e^{-(-119,000 \text{ J/mol}) / (8.314 \text{ J/molK})(298K)}$$

$$= 6.35 \times 10^{20}$$



$$E = 2.04 \text{ V} - \frac{0.0591 \text{ V}}{2} \log \left(\frac{1}{[\text{H}^+]^2 [\text{HSO}_4^-]^2} \right)$$

a. $[\text{H}^+] = [\text{HSO}_4^-] = 4.5 \text{ M}$

$$E = 2.04 \text{ V} + 0.077 \text{ V} = 2.12 \text{ V}$$

(For 6 cells in series, 12.7 V)

b. $\Delta G^\circ = -315.9 \text{ (kJ/mol)} - (253 \text{ K})(203.5 \text{ (J/K)})$

↑ Note the units! ↑
+ convert before adding!

$$= -382.6 \text{ kJ/mol}$$

$$E^\circ = -\frac{\Delta G^\circ}{nF}$$

$$= 1.98 \text{ V}$$

c. now we need to use the "proper" version of the Nernst eqn with all the parameters

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$T = 253 \text{ K} :$$

$$E = 1.98 \text{ V} - \frac{(8.314 \text{ J/mol K})(253 \text{ K})}{(2)(96,485 \text{ J/V mol})} \ln \left(\frac{1}{(4.5)^2 (4.5)^2} \right)$$

$$= 2.05 \text{ V}$$

(For 6 of these in series, 12.3 V)

d. That's almost half a volt less overall.

(Of course oil viscosity is a problem also.)

2. Ch 10, 25. a. 1 mol gas, 1.0 L, 5.0 atm

expands isothermally to 2.0 L against no external pressure, so

$$w = 0 \quad \therefore q = 0$$

$$q_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= PV \ln\frac{V_2}{V_1}$$

$$= 5 \text{ Latm} \ln\left(\frac{2}{1}\right)$$

$$= 3.47 \text{ Latm} \times \frac{101.3 \text{ J}}{1 \text{ Latm}}$$

$$= 351 \text{ J}$$

we could calculate T
($T = \frac{PV}{nR}$) but

$PV = nRT$ & we already have PV !

$$T = \frac{(5 \text{ atm})(1 \text{ L})}{(1 \text{ mol})(0.082 \text{ Latm/molK})} = 61 \text{ K}$$

$$\Delta S = q_{rev}/T = 5.76 \text{ J/K}$$

$$\Delta S = nR \ln\frac{V_2}{V_1} = 5.76 \text{ J/K}$$

\uparrow
8.314 J/molK

b. $P_i = 2 \text{ atm} \Rightarrow T = 24 \text{ K}$ (brrrrr...)

ΔS is the same! 5.76 J/K

$$q_{rev} = 140 \text{ J}$$

c. $P_i = 15 \text{ atm} \Rightarrow T = 183 \text{ K}$

ΔS is the same! 5.76 J/K

$$q_{rev} = 1053 \text{ J}$$

same inc. in "disorder" results from less heat input at low T & more at high T

3. 50. See non-graded parts -

$$\begin{array}{l} \text{a. } \Delta H^\circ = -802.5 \text{ kJ/mol} \\ \Delta S^\circ = -4 \text{ J/K} \end{array} \quad \xrightarrow{T=298\text{K}} \quad \Delta G^\circ = -801 \text{ kJ/mol}$$

50. (cont'd)

$$d. \quad \begin{array}{l} \Delta H^\circ = -176 \text{ kJ/mol} \\ \Delta S^\circ = -284 \text{ J/K} \end{array} \xrightarrow{T=298\text{K}} \Delta G^\circ = -91 \text{ kJ/mol}$$

4. 52. ΔH° & ΔS° are normally assumed to be ~ temp-independent
 ΔG° , of course, depends on T —

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

— how strongly T-dep it is depends on the magnitude of ΔS° .

$$53. \quad T = 298\text{K} : \Delta G^\circ = -58.03 \text{ (kJ/mol)} - (298\text{K})(-176.6 \text{ (J/K)})$$

↑
watch the units! →

$$\Delta G^\circ = -5.40 \text{ kJ/mol}$$

$$\Delta G^\circ = 0 \text{ when } \Delta H^\circ = T\Delta S^\circ$$

$$\therefore T = 328.6\text{K} = 55.4^\circ\text{C} -$$

above this temp, $-T\Delta S^\circ$ term dominates, so ΔG° is pos; below this temp ΔH° dominates, ΔG° is neg.

$$90^\circ\text{C} \Rightarrow 363\text{K} \quad \Delta G^\circ = +6.08 \text{ kJ/mol}$$

$$-50^\circ\text{C} \Rightarrow 223\text{K} \quad \Delta G^\circ = -18.65 \text{ kJ/mol}$$

$$5. 68. \quad \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HO}^- \quad K_w = 1.00 \times 10^{-14}$$

$$a. \quad \Delta G^\circ = -RT \ln K$$

$$= -(8.314 \text{ J/mol K})(298\text{K}) \ln(1.00 \times 10^{-14})$$

$$= +79.9 \text{ kJ/mol}$$

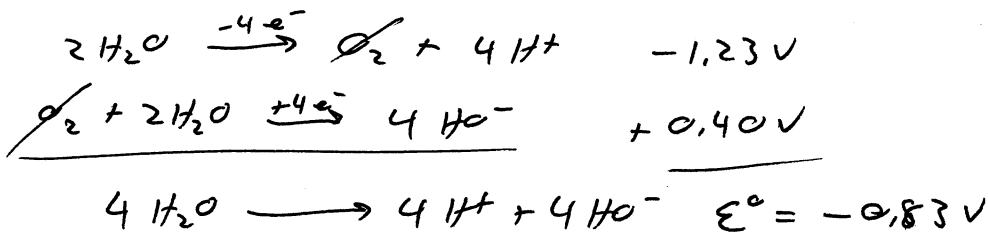
$$b. \quad T = 40^\circ\text{C}$$

$$K = 2.92 \times 10^{-14}$$

↓

$$\Delta G_{40}^\circ = 81.1 \text{ kJ/mol}$$

5. (cont'd) - didn't we do this in class?



Note that one can also combine $2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{HO}^-$ and $\text{H}_2 \rightarrow 2\text{H}^+$ to get the same result!

$$\begin{aligned}
 \Delta G^\circ &= -(4)(96,485 \text{ J/molV})(-0.83\text{V}) \\
 &= +320 \text{ J/mol} \quad \text{for the rxn as written!}
 \end{aligned}$$

$$\text{for } \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HO}^-, \quad \frac{320}{4} = +80 \text{ kJ/mol}$$

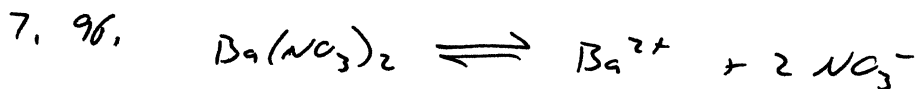
same as above!

6. 91. see non-sv. part for set-up.

a. $\Delta G = \Delta G^\circ!$ $\Delta G = +18 \text{ kJ/mol} \Rightarrow$ rxn shifts left, i.e. toward HF, to reach equilibrium.

c. $\Delta G = -10.5 \text{ kJ/mol}$ - rxn shifts right - HF dissociates to make more H^+ & F^-

e. $\Delta G = +1.5 \text{ kJ/mol}$ - rxn shifts left to reach equilib.



$$\begin{aligned}
 \Delta G^\circ &= +18 \text{ kJ/mol} \Rightarrow K_{sp} = e^{-\frac{(18,000 \text{ J/mol})}{(8.314 \text{ J/molK})(298\text{K})}} \\
 &= 7.0 \times 10^{-4}
 \end{aligned}$$



$$T_b = 35^\circ\text{C} = 308\text{K}$$

$$\Delta H_{\text{vap}}^\circ = 27.5 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}}^\circ = \frac{\Delta H_{\text{vap}}^\circ}{T} = \frac{27500 \text{ J/mol}}{308\text{K}} = 89.3 \text{ J/molK}$$