

Chapter 13

13-3, 13-5, 13-10, 13-14, 13-15, 13-17, 13-20, 13.21,
13-22, 13-26, 13-29, 13.35, 13.47

13-3

a)

$$(16 \text{ mol O}_2) * ((4 \text{ mol e}^-) / (\text{mol O}_2)) * ((9.649 * 10^4 \text{ C}) / (\text{mol e}^-)) = 6.2 * 10^6 \text{ C}$$

$$I = (6.2 * 10^6 \text{ C}) / ((1 \text{ day}) * (24 \text{ hr/day}) * (3600 \text{ s/hr})) = 71 \text{ A}$$

b)

$$I = P/E = (5.00 * 10^2 \text{ W}) / (115 \text{ V}) = 4.35 \text{ A}$$

c)

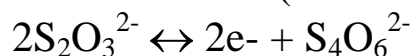
$$P = EI = (1.1 \text{ V})(71 \text{ A}) = 78 \text{ W}$$

13-5

To find the re-dox pairs for a given reaction, You must look for species that contain the same element in different oxidation states. In this case S(+2) in $\text{S}_2\text{O}_3^{2-}$ is being oxidized to S(+1) in $\text{S}_4\text{O}_6^{2-}$. I(0) in I_2 is being reduced to I(-1) in I^- .

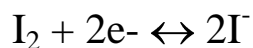
a)

Lose Electrons (Oxidation)



b)

Gain Electrons Reduction



I_2 is the oxidant and $\text{S}_2\text{O}_3^{2-}$ is the reductant

c)

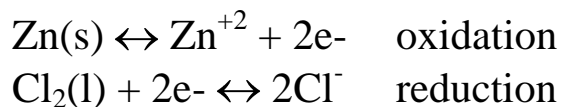
$$(1.00 \text{ g S}_2\text{O}_3^{2-}) * (112.12 \text{ g/mol}) = 8.92 \text{ mmol S}_2\text{O}_3^{2-} = 8.92 \text{ mmol e}^-$$

$$d) \quad [(8.92 * 10^{-3} \text{ mol e}^-) * (9.649 * 10^4 \text{ C}) / (\text{mol e}^-)] / (60\text{s}) = 14.3 \text{ A}$$

13.10

a)

By convention the oxidation is always written on the left side of the cell notation and the reduction is written on the right side.



Electrons flow from the Zn electrode.

b)

$$(1.00 \times 10^3 \text{ C/s}) \times (3600 \text{ s/hr}) \times (1 \text{ mol e}^- / 9.649 \times 10^4 \text{ C}) \times (1 \text{ mol Cl}_2 / 2 \text{ mol e}^-)$$

$$(70.90 \text{ g Cl}_2 / 1 \text{ mol Cl}_2) (1 \text{ kg} / 1000 \text{ g}) = 1.32 \text{ kg Cl}_2 \text{ consumed}$$

13-13

The larger the E^0 , the greater the equilibrium constant.

$$E^0 = (0.05916/n) \log K$$

With the reaction, $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \leftrightarrow \text{Fe}(\text{CN})_6^{4-}$, you still have Fe^{+2} going to Fe^{+3} because the each CN^- carries one negative charge.

Since E^0 for this reaction is less than that for the uncomplexed reaction, the equilibrium constant must be smaller and Fe^{+3} (the reactant) must be stabilized to a greater extent by CN^- complexation relative to Fe^{2+} .

The E^0 for the phenathroline complex reaction is greater than that for the uncomplexed reaction. Therefore, the equilibrium

constant is greater and Fe^{2+} (the product) must be stabilized to a greater extent by CN^- complexation relative to Fe^{3+} .

13-14

E is the cell potential under any given set of conditions. At equilibrium $E = 0$.

E^0 is the cell potential only under the special case where all activities of all species that make up the cell are at unity. This is a constant at standard pressure and temperature.

13-16

The half reaction is already written as a reduction. So...

a)

$$E = E^0 - (0.05914/3) \log\{P_{\text{AsH}_3}/[\text{H}^+]^3\}$$

b)

$$\begin{aligned} &= -0.238 - (0.05914/3) \log\{(1 \text{ torr}/760)/(10^{-3})^3\} \\ &= -0.36 \text{ V} \end{aligned}$$

13-18

The only aqueous specie that participates in the reaction is $[\text{OH}^-]$, and it is both consumed and produced in the overall redox reaction. Also, because both reactants are solids, there is no need for separate anode and cathode compartments. Therefore, the $[\text{OH}^-]$ remains constant.

The Nernst equation for the cathode reaction is

$$E_{\text{R}} = E^0 - 0.05916 \log[\text{OH}^-]$$

$$E_{\text{O}} = E^0 - 0.05916 \log\{1/[\text{OH}^-]\}$$

As a result, the E_{cell} is independent of the concentrations of the reactants or products

13-19

This problem is designed to illustrate that many times a given half-cell can be written correctly as more than one half reaction.

a)



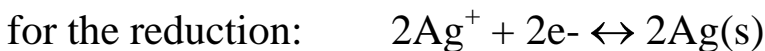
$$\begin{aligned} E_{+} &= E^0 - (0.05914) \log[\text{Cl}^-] \\ &= 0.222 - (0.05914) \log(0.10) = 0.281 \text{ V} \end{aligned}$$



$$\begin{aligned} E_{-} &= E^0 - (0.05914/2) \log([\text{F}^-]^2) \\ &= -0.350 - (0.05914/2) \log((0.10)^2) = -0.291 \text{ V} \end{aligned}$$

$$E_{\text{cell}} = E_{+} - E_{-} = 0.281 - (-0.291) = 0.572 \text{ V}$$

b)



$$E_{+} = E^0 - (0.05914) \log(1/[\text{Ag}^{+}])$$

$$[\text{Ag}^{+}] = K_{\text{sp}(\text{AgCl})}/[\text{Cl}^-]$$

$$\begin{aligned} E_{+} &= E^0 - (0.05914) \log([\text{Cl}^-]/(1.8 \times 10^{-10})) \\ &= 0.7993 - (0.05914) \log((0.1)/(1.8 \times 10^{-10})) = 0.281 \text{ V} \end{aligned}$$



$$E_{-} = E^0 - (0.05914) \log(1/[\text{Pb}^{+2}])$$

$$[\text{Pb}^{+2}] = K_{\text{sp}\text{PbF}_2}/[\text{F}^-]^2$$

$$= -0.126 - (0.05914/2) \log([F^-]^2/K_{spPbF_2})$$

$$= -0.126 - (0.05914/2) \log([0.10]^2/(3.6 \cdot 10^{-8})) = -0.287 \text{ V}$$

$$E_{\text{cell}} = E^+ - E^- = 0.281 - (-0.287) = 0.568 \text{ V}$$

The two calculations are in reasonable agreement!!!!

Whether you write the half reaction in terms of AgCl, Ag, and Cl- or just in terms of Ag, and Ag⁺, you obtain a E⁺ of 0.281 V. If you look at the difference between the two Nernst equations for E-, you will see that the only difference is the K_{sp} factor in the log term. This K_{sp} factor is built into E⁰(AgCl).

13.20

Dr. Harris has already written out the Nernst equation for the whole reaction for you. It is truly a chug and plug type of problem. But you must first find the ionic strength and the activity coefficients.

μ in each half-cell = $\frac{1}{2} (.01 + .01) = .01 \text{ M}$
by interpolation

$$\gamma_{(H^+ @ m=0.01)} = 0.914$$

$$\gamma_{(Ag^+ @ m=0.01)} = 0.898$$

$$0.7983 = E^0 -$$

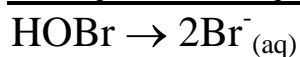
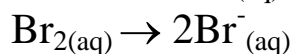
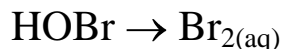
$$0.05916 \log\{((0.01) \cdot .914)/((727.2/760)^5 \cdot (.01 \cdot .898))\}$$

$$= E^0 - 0.00102$$

$$E^0 = 0.7993 \text{ V}$$

13.21

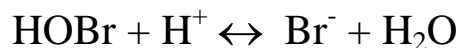
You must determine which reactions you must to add together to obtain the reaction in question.



balanced reaction between HOBr and Br^- in an acidic solution

balancing the half-cell reaction:

step 1: add H^+ to the reactant side and water to the product side



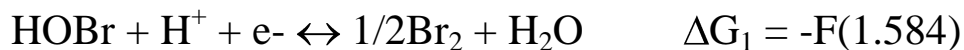
Step 2: Stoichiometrically balance the reaction.

It already is in this case!

Step 3: balance the charge by adding electrons



Repeat for the reactions that you must add to obtain the above rxn. When you add to half-rxns to obtain a third half-rxn, the safe thing to do is to add the ΔG s.



$$-F(1.584) + -F(1.098) = -2FE^0$$

$$E^0 = (1.584 + 1.098)/2 = 1.341 \text{ V}$$

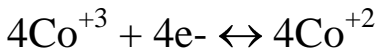
13.25

a)

Break the reaction into two half-cell reactions

When adding a reduction rxn to an oxidation rxn to obtain a whole cell reaction, E^0 s are simply additive.

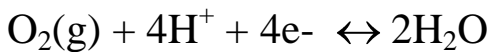
Reduction



from Appendix H

$$E_+^0 = 1.92$$

Oxidation



$$E_-^0 = 1.229$$

$$E^0 = E_+^0 + E_-^0 = 0.69 \text{ V}$$

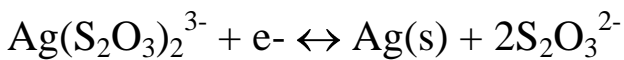
$$\Delta G^0 = -nFE^0 = -4(9.649 \times 10^4 \text{ C/mol})(0.69 \text{ V}) = -2.7 \times 10^5 \text{ J}$$

$$K = 10^{(nE^0/0.05916)} = 10^{(4(.69)/0.05916)} = 10^{46.653} = 10^{47}$$

b)

Break the reaction into 2 half-cell reaction

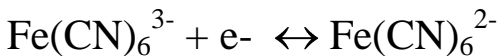
Reduction



from Appendix H

$$E_+^0 = 0.017 \text{ V}$$

Oxidation



$$E_-^0 = 0.356$$

$$E^0 = E_+^0 + E_-^0 = -0.339 \text{ V}$$

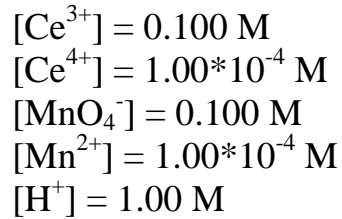
$$\Delta G^0 = -nFE^0 = -(1)(9.649 \times 10^4 \text{ C/mol})(-0.339 \text{ V}) = 3.27 \times 10^4 \text{ J}$$

$$K = 10^{(nE^0/0.05916)} = 10^{(4(-.339)/0.05916)} = 1.9 \times 10^{-6}$$

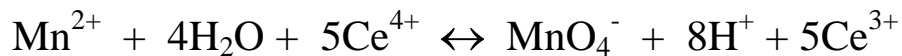
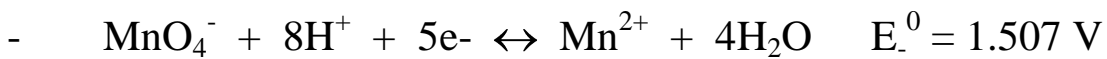
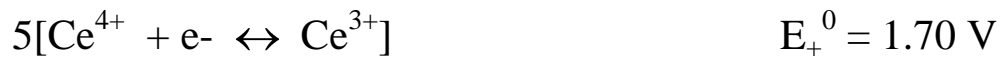
13-26

14-26

You got a solution containing



a)



$$E = (E_+^0 - E_-^0) - 0.05916/5 \log \{ [\text{H}^+]^8 [\text{MnO}_4^-] [\text{Ce}^{3+}]^5 / [\text{Mn}^{2+}] [\text{Ce}^{4+}]^5 \}$$

b)

At equilibrium $E = 0$ and $Q = K$

$$\begin{aligned}(E_+^0 - E_-^0) &= 0.05916/5 \log K \\ 5(1.70 - 1.507)/0.05916 &= \log K \\ K &= 10^{16.3117} = 2 \cdot 10^{16}\end{aligned}$$

$$\begin{aligned}\Delta G^0 &= -RT \ln K = -(8.314 \text{ J/Kmol})(298 \text{ K}) \ln(2 \cdot 10^{16}) \\ &= -9.3 \cdot 10^4 \text{ J/mol or } 93 \text{ kJ/mol}\end{aligned}$$

c)

$$E = 0.193 - 0.05916/5 \log\{[1.00]^8[0.1][0.1]^5/[10^{-4}][10^{-4}]^5\}$$

$$E = 0.193 - 0.05916/5 \log\{[10^3]^6\} = 0.02 \text{ V}$$

d)

$$\begin{aligned}\Delta G &= -nFE = -(5)(9.649 \times 10^4 \text{ C/mol e}^-)(0.02 \text{ V}) \\ &= 9649 \text{ J or } 10 \text{ kJ}\end{aligned}$$

at equilibrium

$$(1.70-1.507) = -0.05916/5 \log\{[H^+]^8[0.1][0.1]^5/[10^{-4}][10^{-4}]^5\}$$

$$10^{5(1.70-1.507)/.05916} = \{[H^+]^8[0.1][0.1]^5/[10^{-4}][10^{-4}]^5\}$$

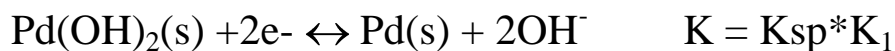
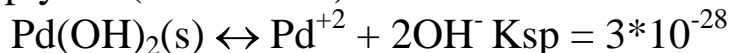
$$(10^{5(1.70-1.507)/.05916})/10^{18} = [H^+]^8$$

$$\{(10^{5(1.70-1.507)/.05916})/10^{18}\}^{1/8} = [H^+] = 0.62 \text{ M}$$

$$\text{pH} = -\log[H^+] = 0.21$$

13-28

You are forming a half-reaction. It is safest to add together multiply Ks (or add ΔG s).



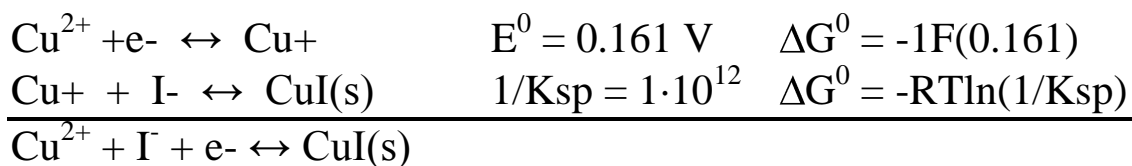
$$K = 3 \times 10^3$$

$$\text{Log } K = -nE^0/0.05916$$

$$E^0 = -(0.05916/2)\log(3 \cdot 10^3) = 0.103 \text{ V}$$

13-32

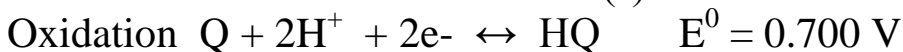
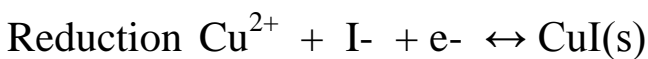
The following two equations add to give the overall reduction reaction. You add the ΔG^0 , when adding equations to form half reactions.



$$\Delta G^0 = -1(0.161) - RT\ln(1/K_{\text{sp}}) = -84000 \text{ J/mol}$$

$$E^0 = \Delta G^0 / -nF = 0.870 \text{ V}$$

Now use the E^0 for the half reactions to calculate E_{cell} .

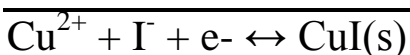
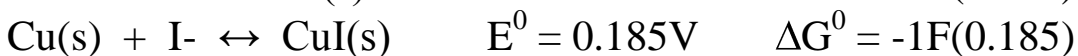
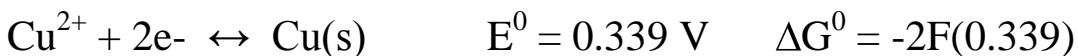


$$E^0_{\text{cell}} = 0.870 - 0.700 = 0.170 \text{ V}$$

$$\Delta G^0_{\text{cell}} = -(2)FE^0_{\text{cell}} = -32900 \text{ J/mol} = -32.9 \text{ kJ/mol}$$

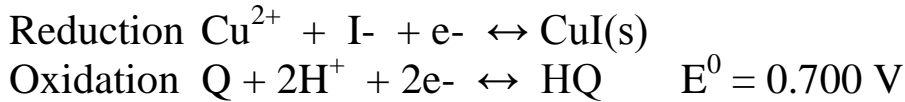
$$K = e^{-\Delta G^0/RT} = 6 \cdot 10^5$$

OR



$$E^0 = 2(.339) + 0.185 = 0.863 \text{ V}$$

Now use the E^0 for the half reactions to calculate E_{cell} .



$$E^0_{\text{cell}} = 0.863 - 0.700 = 0.163 \text{ V}$$

$$\Delta G^0_{\text{cell}} = -(2)FE^0_{\text{cell}} = -31500 \text{ J/mol} = -31.5 \text{ kJ/mol}$$

$$K = e^{-\Delta G^0/RT} = 3 \cdot 10^5$$

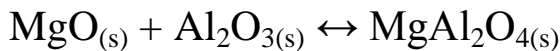
The difference between the two answers is just a reflection of the precision in which the E^0 's and K_{sp} 's are known.

13-33

$$E_{\text{left}} = E^0_{(\text{MgF}_2)} - 0.05916/2 \log\{[\text{F}^-]^2/p\text{O}_2^{1/2}\}$$

$$E_{\text{right}} = E^0_{(\text{MgF}_2)} - 0.05916/2 \log\{[\text{F}^-]^2/p\text{O}_2^{1/2}\}$$

Net Rxn



$E = E^0$ because all reactants and products in the Nernst Eq are solids (in std state)

$$\Delta G^0 = -2F(0.1529) = 2.951 \cdot 10^4 \text{ J/mol} = 29.51 \text{ kJ/mol}$$

Use the formula given to calculate E^0 at 900 and 1250. Convert the E^0 to ΔG^0 ($\Delta G^0 = -nFE^0$). Plot E^0 as a function of T. The negative of the slope give ΔS^0 and the intercept gives ΔH^0 .

	E^0	ΔG^0				
900	1.50E-01	-2.89E+04	slope	-5.90519	5.905188	ΔS^0
1250	1.61E-01	-3.10E+04	intercept	-23601.5		ΔH^0

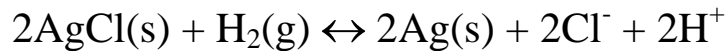
13.35

a)

Reduction



Oxidation



$$E_{\text{cell}}^0 = E_+^0 - E_-^0 = 0.222 \text{ V} - 0 \text{ V} = 0.222 \text{ V}$$

Nerst eq for this cell

$$E_{\text{cell}} = E_{\text{cell}}^0 - 0.05916/n \log K$$

$$0.485 = 0.222 - 0.05916/n \log \{ [\text{Cl}^-]^2 [\text{H}^+]^2 / p_{\text{H}_2} \}$$

$$0.263 = -0.05916/2 \log \{ [\text{Cl}^-]^2 [10^{-3.60}]^2 / 1.00 \text{ atm} \}$$

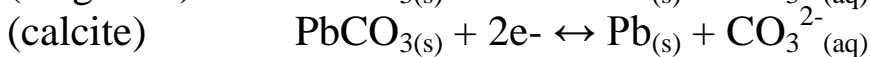
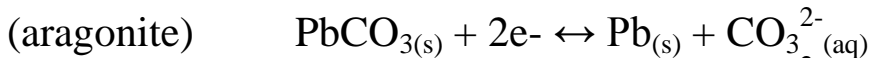
$$-(0.263)(2)/(0.05916) = \log \{ [\text{Cl}^-]^2 [10^{-3.60}]^2 / 1.00 \text{ atm} \}$$

$$10^{-(0.263*2/0.05916)} = [\text{Cl}^-]^2 [10^{-3.60}]^2 / 1.00$$

$$[\text{Cl}^-]^2 = \{ 1/10^{-3.6} \}^2 10^{-(0.263*2/0.05916)} = 0.0204$$

$$[\text{Cl}^-] = 0.143 \text{ M}$$

13-39



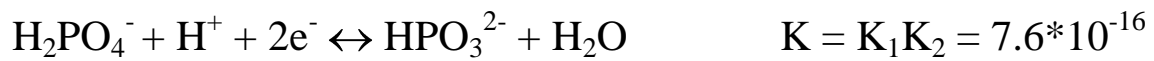
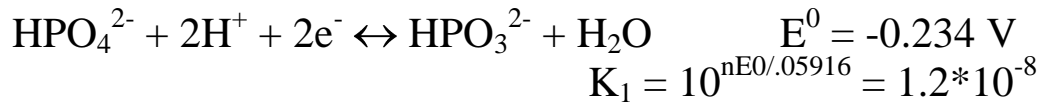
$$E = E^0_{\text{cell}} - 0.05916 \log \{ [\text{CO}_3^{2-}]_{\text{arg}} / [\text{CO}_3^{2-}]_{\text{cal}} \}$$

$$-0.0018 = 0.000 - 0.05916/2 \log \{ [\text{CO}_3^{2-}]_{\text{arg}} / [\text{CO}_3^{2-}]_{\text{cal}} \}$$

$$\begin{aligned}
[\text{CO}_3^{2-}]_{\text{arg}}/[\text{CO}_3^{2-}]_{\text{cal}} &= 1.15 \\
[\text{CO}_3^{2-}]_{\text{cal}}/[\text{CO}_3^{2-}]_{\text{arg}} &= 0.869 \\
[\text{Ca}^{2+}]_{\text{cal}}/[\text{Ca}^{2+}]_{\text{arg}} &= 0.869
\end{aligned}$$

$$K_{\text{sp}}(\text{CaCO}_3)_{\text{calc}}/K_{\text{sp}}(\text{CaCO}_3)_{\text{arg}} = (0.869)(.869) = 0.76$$

13.47



$$E^0 = 0.05914/2 \log K = -0.447 \text{ V}$$