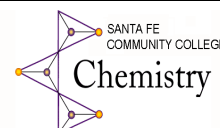


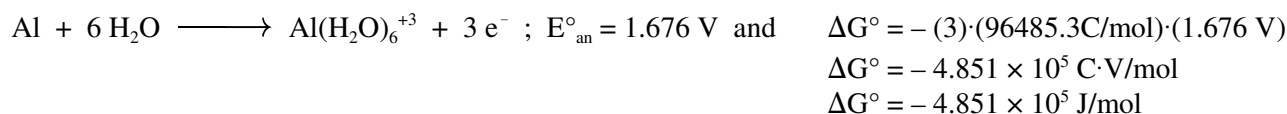


## Quantitative Redox Chemistry

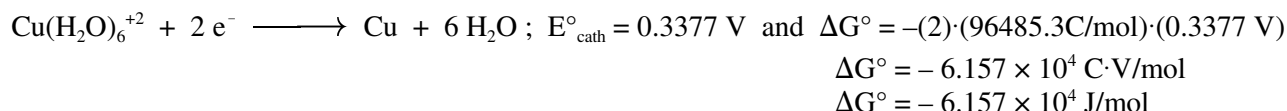


As developed in class,  $\Delta G = -n \cdot F \cdot E$ , where  $\Delta G$  is the free energy change for some process,  $n$  is the number of moles of electron involved in the overall process,  $F$  is the Faraday (96485.3383 C/mole), and  $E$  is the cell potential for the process. Under standard conditions this equation becomes,  $\Delta G^\circ = -n \cdot F \cdot E^\circ$ , the superscript  $^\circ$  denotes that the system is under standard conditions. Upon rearrangement one gets,  $\Delta G^\circ / n = -F \cdot E^\circ$ . Thus,  $E^\circ$  is proportional to  $-\Delta G^\circ / n$ . That is the  $E^\circ$  is the negative free energy change **PER** mole of electron involved. Let's see what the consequences of this relationship are in the handling of  $E^\circ$  values.

Consider the reaction of Al with  $\text{Cu}(\text{H}_2\text{O})_6^{+2}$  to form Cu and  $\text{Al}(\text{H}_2\text{O})_6^{+3}$  under standard conditions. The two half-reaction involved with their  $E^\circ$  and  $\Delta G^\circ$  are as follows.



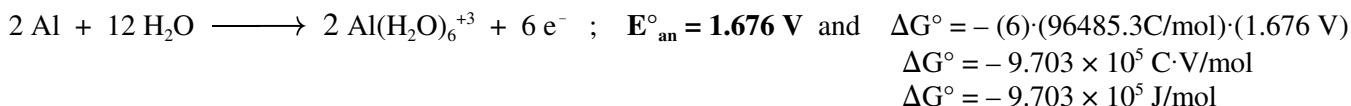
and



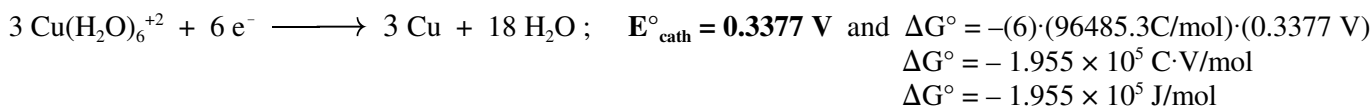
Now, there are two things to note,

- 1) for any complete redox reaction, the number of electrons lost in the oxidation step **MUST** equal the number of electrons gained in the reduction step and therefore the oxidation step must be multiplied by 2 and the reduction step must be multiplied by 3.
- 2)  $\Delta G^\circ$  values are additive in accord with the first law of thermodynamics.

Thus the two equations become:



and



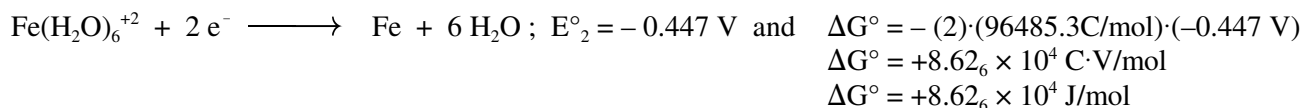
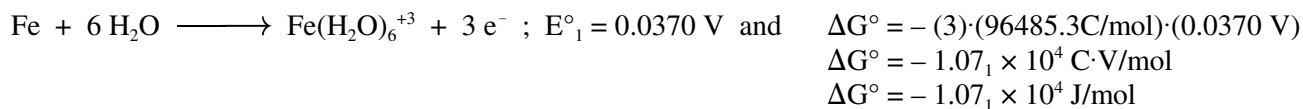
Because,  $E^\circ$  is equal to  $-\Delta G^\circ / n \cdot F$

$$\text{then } E^\circ = \frac{-(-11.658 \times 10^5 \text{ C} \cdot \text{V/mol})}{6 \text{ mol} \times 96485.3 \text{ C/mol}} = 2.013_7 \text{ V} = 2.014 \text{ V} \text{ which is merely the SUM of } E^\circ_{\text{an}} \text{ and } E^\circ_{\text{cath}}$$

$$E^\circ_{\text{overall}} = E^\circ_{\text{an}} + E^\circ_{\text{cath}} = 1.676 \text{ V} + 0.3377 \text{ V} = 2.013_7 \text{ V} = 2.014 \text{ V}.$$

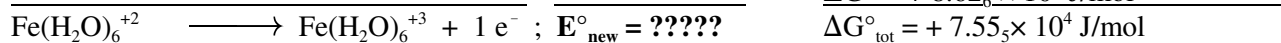
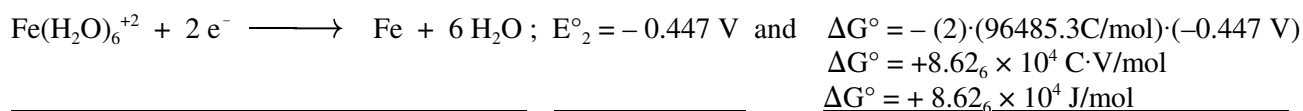
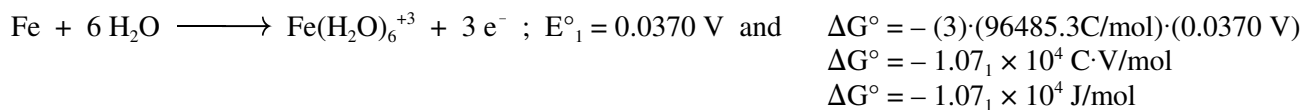
**Thus, the  $E^\circ$  for a redox reaction is simply the SUM of the  $E^\circ$ 's for the oxidation and reduction half-reactions.**

Let's consider another situation where we are adding two half-cell reactions together to determine a third half-cell reaction .



Again, there are two things to note,

- 1) the number of electrons lost in step 1 **IS NOT** equal the number of electrons gained in the step 2 and therefore the electrons **DO NOT** completely cancel in the final equation.
- 2)  $\Delta G^\circ$  values are additive in accord with the first law of thermodynamics.



Because,  $E^\circ$  is equal to  $-\Delta G^\circ/n \cdot F$

$$\text{then } E^\circ = \frac{- (+7.55_5 \times 10^4 \text{ C} \cdot \text{V/mol})}{1 \text{ mol} \times 96485.3 \text{ C/mol}} = -0.783_0 \text{ V} = -0.783 \text{ V} \quad \text{This is **NOT** merely the SUM of } E^\circ_{\text{an}}$$

and  $E^\circ_{\text{cath}}$  which would give,  $E^\circ_{\text{overall}} = 0.0370 \text{ V} + (-0.447 \text{ V}) = -0.410_0 \text{ V} = -0.410 \text{ V}$ .

**Thus, the  $E^\circ$  for a new half-reaction is NOT simply the SUM of the  $E^\circ$ 's for the oxidation and reduction half-reactions.**

Since the factor 96485.3 C/mol appears in each step of the  $\Delta G^\circ$  calculation it can be eliminated by division leaving the equation:

$$(E^\circ_{\text{an}} \times n_{\text{an}}) + (E^\circ_{\text{cath}} \times n_{\text{cath}}) = E^\circ_{\text{tot}} \times n_{\text{tot}} \quad \text{or} \quad E^\circ_{\text{tot}} = \frac{(E^\circ_{\text{an}} \times n_{\text{an}}) + (E^\circ_{\text{cath}} \times n_{\text{cath}})}{n_{\text{tot}}}$$

In our example,

$$E^\circ_{\text{tot}} = \frac{(E^\circ_{\text{an}} \times n_{\text{an}}) + (E^\circ_{\text{cath}} \times n_{\text{cath}})}{n_{\text{tot}}} = \frac{(0.0370 \text{ V} \times 3) + (-0.447 \text{ V} \times 2)}{1} = -0.783 \text{ V}$$

Notice that when  $n_{\text{an}} = n_{\text{cath}} = n_{\text{tot}}$  (as in the previous example), then the above equation reduces to,

$$(E^\circ_{\text{an}} \times n) + (E^\circ_{\text{cath}} \times n) = E^\circ_{\text{tot}} \times n \quad \text{or} \quad E^\circ_{\text{tot}} = \frac{(E^\circ_{\text{an}} \times n) + (E^\circ_{\text{cath}} \times n)}{n} = E^\circ_{\text{an}} + E^\circ_{\text{cath}}$$

which is the manner in which we calculated the cell potential previously.

Next, let's consider what changes in the potentials that occur if the system is not under standard conditions. This is easily determined. We already know what changes occur in the free energy when the system is under non-standard conditions.

$$\Delta G = \Delta G^\circ + R \cdot T \cdot \ln(Q); \text{ where } Q, \text{ of course, is the reaction quotient.}$$

Recall that  $Q$  has the same form as  $K_{eq}$  (products over reactants omitting solids, pure liquids and solvents) except the concentrations used are the initial concentrations not the equilibrium values.

In addition,  $\Delta G = -n \cdot F \cdot E$  and therefore by substitution;

$$\Delta G = -n \cdot F \cdot E = \Delta G^\circ + R \cdot T \cdot \ln(Q). \text{ But, } \Delta G^\circ = -n \cdot F \cdot E^\circ. \text{ Therefore,}$$

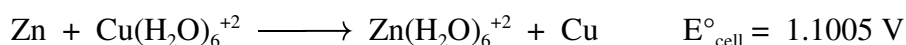
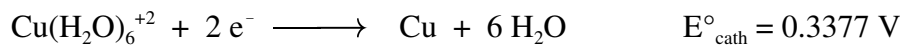
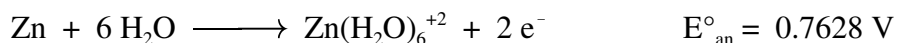
$$-n \cdot F \cdot E = -n \cdot F \cdot E^\circ + R \cdot T \cdot \ln(Q). \text{ Finally, dividing everything by } (-n \cdot F) \text{ gives}$$

$$E = E^\circ - \frac{R \cdot T}{n \cdot F} \times \ln(Q) \text{ or using } \log_{10}; E = E^\circ - \frac{2.303 \cdot R \cdot T}{n \cdot F} \times \log(Q)$$

One final simplification can be made by recognizing that most standard table are at 298.15 K. Substituting this temperature along with the values for  $R$  and  $F$  gives the **Nernst equation**

$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \times \log(Q)$$

Consider the "Daniell" cell which uses Zn and Cu as electrodes and  $\text{Zn}(\text{H}_2\text{O})_6^{+2}$  and  $\text{Cu}(\text{H}_2\text{O})_6^{+2}$  as electrolytes. Under standard conditions the cell voltage is,



What happens to the voltage as the cell operates? We can use the Nernst equation to find out.

$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \times \log(Q); \text{ where } n=2 \text{ and } Q = \frac{[\text{Zn}(\text{H}_2\text{O})_6^{+2}]}{[\text{Cu}(\text{H}_2\text{O})_6^{+2}]}$$

As the cell operates the  $[\text{Zn}(\text{H}_2\text{O})_6^{+2}]$  will increase to values above 1 M and the  $[\text{Cu}(\text{H}_2\text{O})_6^{+2}]$  will decrease to values below 1M. Thus, the value of  $Q$  will increase during operation of the cell to values above 1.

The logarithm of a number larger than 1 will be a positive number. Thus, the term  $-\frac{0.05916 \text{ V}}{n} \times \log(Q)$

will become progressively more negative as  $Q$  increases, making the cell potential **DECREASE**. Eventually, the potential will reach zero and the battery is "dead".

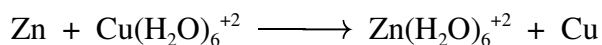
Let's reconsider this "dead" battery. At this point, the potential,  $E$ , is zero volts and there is no net tendency for the reaction to move forward or backwards. That is, the system is at equilibrium and the value of  $Q = K_{eq}$ . Using the Nernst equation and substituting in these values, we see that;

$$E = E^\circ - \frac{0.05916\text{V}}{n} \times \log(Q) = E^\circ - \frac{0.05916\text{V}}{n} \times \log(K_{eq}) = 0\text{V}$$

Rearranging gives the important relationship:

$$E^\circ = \frac{0.05916\text{V}}{n} \times \log(K_{eq})$$

Thus, we can determine the  $K_{eq}$  for our "Daniell" cell where  $E^\circ = 1.005\text{ V}$ . The cell reaction is



$$\therefore K_{eq} = \frac{[\text{Zn}(\text{H}_2\text{O})_6]^{+2}}{[\text{Cu}(\text{H}_2\text{O})_6]^{+2}}$$

Using the previously derived relationship above,

$$E^\circ = \frac{0.05916\text{V}}{2} \times \log(K_{eq}) = 1.005\text{ V}$$

which after rearrangement gives:

$$(K_{eq}) = \text{alog} \frac{1.005\text{ V} \times 2}{0.05916\text{ V}} = 9.455 \times 10^{33}$$

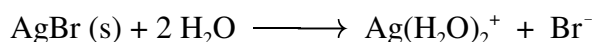


## Quantitative Redox Homework Problems



In order to do any of the following problems you will need to first balance each reaction using the half reaction method. Then, look up the correct  $E^\circ$  value for each half-reaction to produce the  $E^\circ_{\text{cell}}$ . Finally, any additional calculations of  $E$ ,  $K_{\text{eq}}$ , or  $\Delta G^\circ$  can be done using this  $E^\circ_{\text{cell}}$  value.

1. When silver nitrate solution and iron(II) sulfate solution are mixed, metallic silver and iron(III) ions are produced. Calculate  $E^\circ_{\text{cell}}$  for this reaction.
2. When metallic iron is added to  $1\text{M}$   $\text{Fe}(\text{NO}_3)_3$  the green ion,  $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ , is the only product formed. Calculate  $E^\circ_{\text{cell}}$  for this reaction.
3. Your car battery has a  $\text{Pb (s)}$  anode and a  $\text{PbO}_2 \text{ (s)}$  cathode. Sulfuric acid is the electrolyte inside the battery. During discharge both  $\text{Pb}$  and  $\text{PbO}_2$  are converted to  $\text{PbSO}_4 \text{ (s)}$ . Calculate  $E^\circ_{\text{cell}}$  for this reaction.
4. Silver metal dissolves in  $6\text{M}$   $\text{HNO}_3$  to give  $\text{Ag}(\text{H}_2\text{O})_2^+$  and  $\text{NO}$  as products. Calculate  $E^\circ_{\text{cell}}$  for this reaction and then calculate  $E_{\text{cell}}$  for this reaction in  $6\text{M}$   $\text{HNO}_3$ .
5. Show how the  $E^\circ$  for equation 15 in the redox table can be derived from the  $E^\circ$ 's for equations 11 and 13.
6. Aluminum metal dissolves in  $6\text{M}$   $\text{NaOH}$  to produce hydrogen gas and  $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$ . Calculate  $E_{\text{cell}}$  for this reaction under these conditions.
7. Consider the following cell in short hand notation:  $\text{Pt} / \text{H}_2 / \text{H}_3\text{O}^+ // \text{OH}^- / \text{H}_2 / \text{Pt}$ .
  - a) What is the reaction taking place at the anode? At the cathode? What is the cell reaction?
  - b) What is  $E^\circ_{\text{cell}}$  for this reaction?
  - c) Calculate  $\Delta G^\circ$  and  $K_{\text{eq}}$  for this reaction?
  - d) Go back to part a) and divide the two half-reactions and the overall reaction by 2. What is the "new" cell reaction? Does it look familiar?
  - e) As mentioned in class, multiplying a half-reaction by a number has NO effect on the  $E^\circ$  value. Therefore the reaction that you wrote in part d) has the **same**  $E^\circ_{\text{cell}}$  as the reaction in part a) but the reaction in part d) has **different**  $\Delta G^\circ$  and  $K_{\text{eq}}$ !! Calculate the  $\Delta G^\circ$  and  $K_{\text{eq}}$  values for the reaction in part d). Pretty cool, huh?!
8. Design a cell that has the following reaction as the cell reaction:



What is the  $E^\circ_{\text{cell}}$  for the reaction? What is the value of  $K_{\text{eq}}$  for this reaction? Does it match the book value for  $K_{\text{eq}}$ ?

# Some Half-reactions and Their E° Values (at 298.15 K)

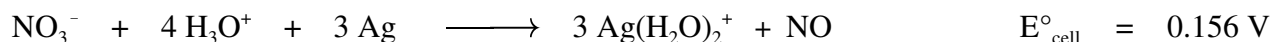
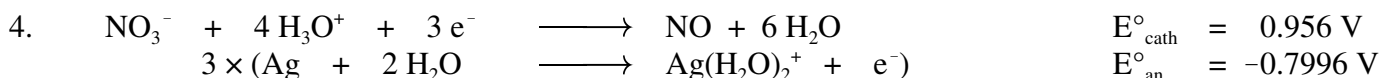
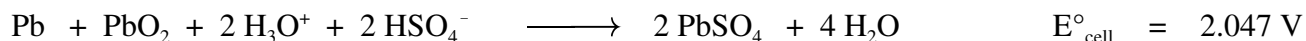
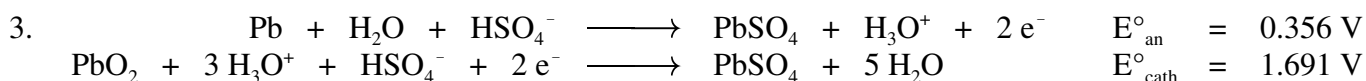
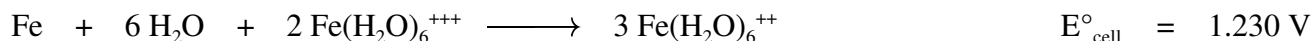
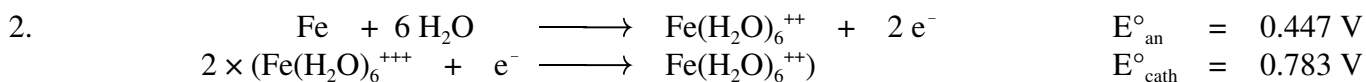
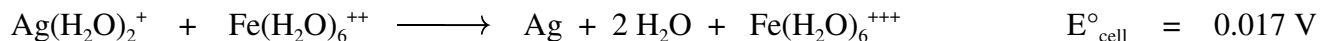
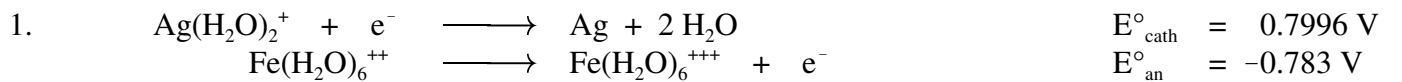
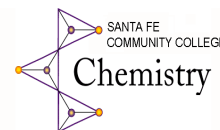
					E°
1.	$F_2$	$+ 2e^-$	$\longrightarrow$	$2 F^-$	2.866 Volts
2.	$MnO_4^- + 8 H_3O^+$	$+ 5e^-$	$\longrightarrow$	$Mn(H_2O)_6^{+2} + 6 H_2O$	1.507
3.	$PbO_2 + 3 H_3O^+ + HSO_4^-$	$+ 2e^-$	$\longrightarrow$	$PbSO_4 + 5 H_2O$	1.691
4.	$Cl_2$	$+ 2e^-$	$\longrightarrow$	$2 Cl^-$	1.35827
5.	$O_2 + 4 H_3O^+ \text{ (pH = 0)}$	$+ 4e^-$	$\longrightarrow$	$6 H_2O$	1.229
6.	$NO_3^- + 4 H_3O^+ \text{ (pH = 0)}$	$+ 3e^-$	$\longrightarrow$	$NO + 6 H_2O$	0.956
7.	$O_2 + 4 H_3O^+ \text{ (pH = 7)}$	$+ 4e^-$	$\longrightarrow$	$6 H_2O$	0.8277*
8.	$Ag(H_2O)_2^+$	$+ e^-$	$\longrightarrow$	$Ag + 2 H_2O$	0.7996
9.	$Fe(H_2O)_6^{+3}$	$+ e^-$	$\longrightarrow$	$Fe(H_2O)_6^{+2}$	0.783
10.	$MnO_4^- + 2 H_2O$	$+ 3e^-$	$\longrightarrow$	$MnO_2 + 4 OH^-$	0.595
11.	$Cu(H_2O)_2^+$	$+ e^-$	$\longrightarrow$	$Cu + 2 H_2O$	0.5072
12.	$O_2 + 2 H_2O \text{ (pH = 14)}$	$+ 4e^-$	$\longrightarrow$	$4 OH^-$	0.401
13.	$Cu(H_2O)_6^{+2}$	$+ 2e^-$	$\longrightarrow$	$Cu + 6 H_2O$	0.3377
14.	$AgCl$	$+ e^-$	$\longrightarrow$	$Ag + Cl^-$	0.22233
15.	$Cu(H_2O)_6^{+2}$	$+ e^-$	$\longrightarrow$	$Cu(H_2O)_2^+ + 4 H_2O$	0.1682
16.	$AgBr$	$+ e^-$	$\longrightarrow$	$Ag + Br^-$	0.07133
17.	$2 H_3O^+ \text{ (pH = 0)}$	$+ 2e^-$	$\longrightarrow$	$H_2 + 2 H_2O$	0.000000
18.	$Cu(NH_3)_4^{++} \text{ (aq)}$	$+ 2e^-$	$\longrightarrow$	$Cu + 4 NH_3 \text{ (aq)}$	-0.05
19.	$Pb(H_2O)_3^{+2}$	$+ 2e^-$	$\longrightarrow$	$Pb + 3 H_2O$	-0.1262
20.	$Sn(H_2O)_3^{+2}$	$+ 2e^-$	$\longrightarrow$	$Sn + 3 H_2O$	-0.1375
21.	$PbSO_4 + H_3O^+$	$+ 2e^-$	$\longrightarrow$	$Pb + HSO_4^- + H_2O$	-0.356
22.	$2 H_3O^+ \text{ (pH = 7)}$	$+ 2e^-$	$\longrightarrow$	$H_2 + 2 H_2O$	-0.4139 **
23.	$Fe(H_2O)_6^{+2}$	$+ 2e^-$	$\longrightarrow$	$Fe + 6 H_2O$	-0.447
24.	$Fe(H_2O)_3(OH)_3 + H_2O$	$+ e^-$	$\longrightarrow$	$Fe(H_2O)_4(OH)_2 + OH^-$	-0.56
25.	$CuS$	$+ 2e^-$	$\longrightarrow$	$Cu + S^{2-}$	-0.76
26.	$Zn(H_2O)_6^{+2}$	$+ 2e^-$	$\longrightarrow$	$Zn + 6 H_2O$	-0.7628
27.	$2 H_2O \text{ (pH = 14)}$	$+ 2e^-$	$\longrightarrow$	$H_2 + 2 OH^-$	-0.8277
28.	$Fe(H_2O)_4(OH)_2$	$+ 2e^-$	$\longrightarrow$	$Fe + 4 H_2O + 2 OH^-$	-0.88
29.	$PbS$	$+ 2e^-$	$\longrightarrow$	$Pb + S^{2-}$	-0.95
30.	$Zn(NH_3)_4^{2+} \text{ (aq)}$	$+ 2e^-$	$\longrightarrow$	$Zn + 4 NH_3 \text{ (aq)}$	-1.03
31.	$Al(H_2O)_6^{+3}$	$+ 3e^-$	$\longrightarrow$	$Al + 6 H_2O$	-1.676
32.	$Al(H_2O)_2(OH)_4^-$	$+ 3e^-$	$\longrightarrow$	$Al + 2 H_2O + 4 OH^-$	-2.310
33.	$Na^+$	$+ e^-$	$\longrightarrow$	$Na$	-2.713
34.	$Ca^{+2}$	$+ 2e^-$	$\longrightarrow$	$Ca$	-2.868
35.	$K^+$	$+ e^-$	$\longrightarrow$	$K$	-2.931

\* The ingredients of this system are pure water with oxygen gas over the system at a partial pressure of 1 atm.

\*\*The ingredients of this system are pure water with hydrogen gas over the system at a partial pressure of 1 atm.



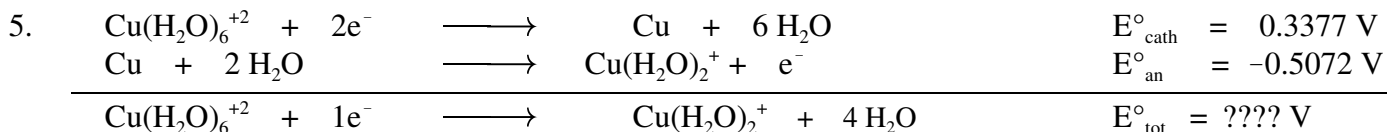
# Quantitative Redox Homework Answers



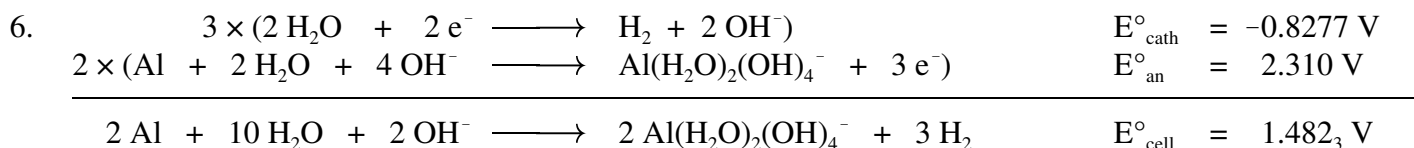
Using the Nernst Equation: 
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059160 \text{ V}}{n} \times \log Q$$

where Q (the reaction quotient) in the case is: 
$$Q = \frac{[\text{Ag(H}_2\text{O)}_2^+]^3 \cdot P_{\text{NO}}}{[\text{H}_3\text{O}^+]^4 \cdot [\text{NO}_3^-]}$$

the new  $E_{\text{cell}}$  is: 
$$E_{\text{cell}} = 0.156 \text{ V} - \frac{0.059160 \text{ V}}{3} \times \log \left( \frac{[1.000]^3 \cdot 1.000}{[6.0]^4 \cdot [6.0]} \right) = 0.233 \text{ V}$$



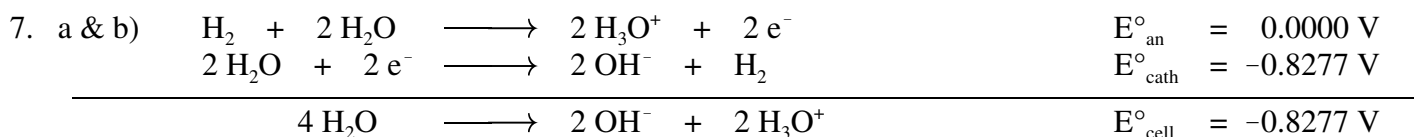
$$E^\circ_{\text{tot}} = \frac{(E^\circ_{\text{an}} \times n_{\text{an}}) + (E^\circ_{\text{cath}} \times n_{\text{cath}})}{n_{\text{tot}}} = \frac{(-0.5072 \text{ V} \times 1) + (0.3377 \text{ V} \times 2)}{1} = 0.1682 \text{ V}$$



Using the Nernst Equation:  $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059160 \text{ V}}{n} \times \log Q$

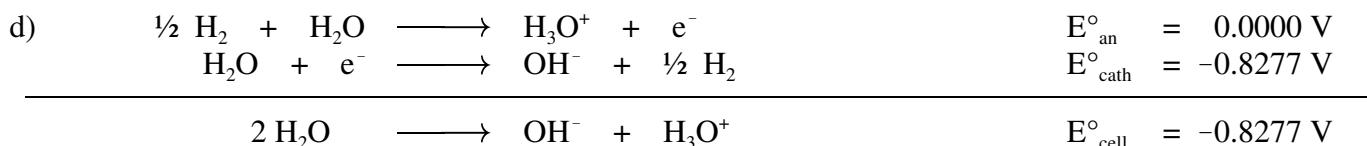
where Q (the reaction quotient) in the case is:  $Q = \frac{[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-]^2 \cdot (P_{\text{H}_2})^3}{[\text{OH}^-]^2}$

the new  $E_{\text{cell}}$  is:  $E_{\text{cell}} = 1.482_3 \text{ V} - \frac{0.059160 \text{ V}}{6} \times \log \left( \frac{[1.000]^2 \cdot 1.000^3}{[6.0]^2} \right) = 1.497_6 \text{ V}$



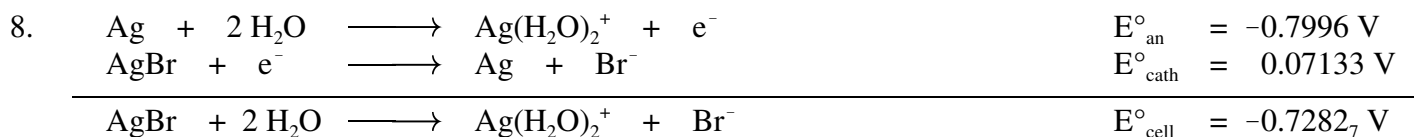
c)  $\Delta G^\circ = -nFE^\circ = (-2 \text{ mol})(96485.3 \text{ C/mol})(-0.8277 \text{ V}) = 1.597 \times 10^5 \text{ J}$

$$E^\circ = \frac{0.059160 \text{ V}}{n} \times \log K_{\text{eq}} \text{ or } K_{\text{eq}} = 10^{\frac{n \cdot E^\circ}{0.059160 \text{ V}}} = 10^{\frac{2(-0.8277 \text{ V})}{0.059160 \text{ V}}} = 1.0 \times 10^{-28}$$



e)  $\Delta G^\circ = -nFE^\circ = (-1 \text{ mol})(96485.3 \text{ C/mol})(-0.8277 \text{ V}) = 7.986 \times 10^4 \text{ J/mol}$

$$\text{and } E^\circ = \frac{0.059160 \text{ V}}{n} \times \log K_{\text{eq}} \text{ or } K_w = 10^{\frac{n \cdot E^\circ}{0.059160 \text{ V}}} = 10^{\frac{1(-0.8277 \text{ V})}{0.059160 \text{ V}}} = 1.0 \times 10^{-14}$$



$$E^\circ = \frac{0.059160 \text{ V}}{n} \times \log K_{\text{eq}} \text{ or } K_{\text{SP}} = 10^{\frac{n \cdot E^\circ}{0.059160 \text{ V}}} = 10^{\frac{1(-0.7282_7 \text{ V})}{0.059160 \text{ V}}} = 4.9 \times 10^{-13}$$