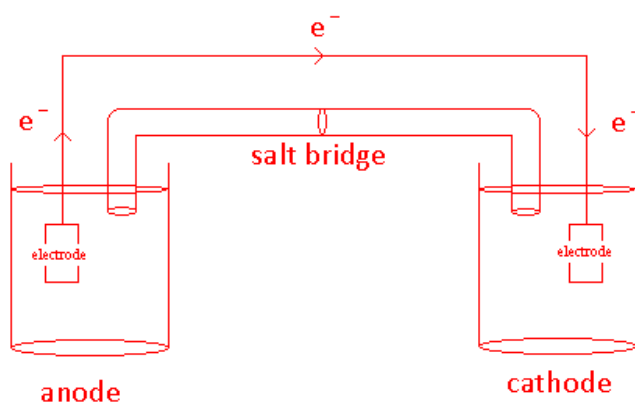## Galvanic Cells

1.   What is a galvanic cell?

Generically it is a battery. It utilizes the <u>spontaneous</u> electron transfer that occurs in a redox reaction to create electrical energy.

2.   Draw a galvanic cell and label all its components.

When dealing with galvanic cells always remember your ABC's to help with ordering

<u>A</u>node – <u>B</u>ridge – <u>C</u>athode

*On a side note, in most cases the anode is listed first. I have seen teachers/professors swap the order of anode and cathode on exams however. So, when on an exam, don't assume ABC order – verify it.

3.   Why is a salt bridge necessary to complete the circuit?

A salt bridge insures that there will not be a charge build up when the electrons transfer. Without the salt bridge the cathode would start to develop a negative charge and the anode would develop a positive charge due to the electron movement. This would prevent the cell from working

because the charge separation is not favorable – it is high energy.

Remember that a salt contains a cation and anion. The anion moves toward the anode compartment and the cation moves toward the cathode, maintaining the charge balance.
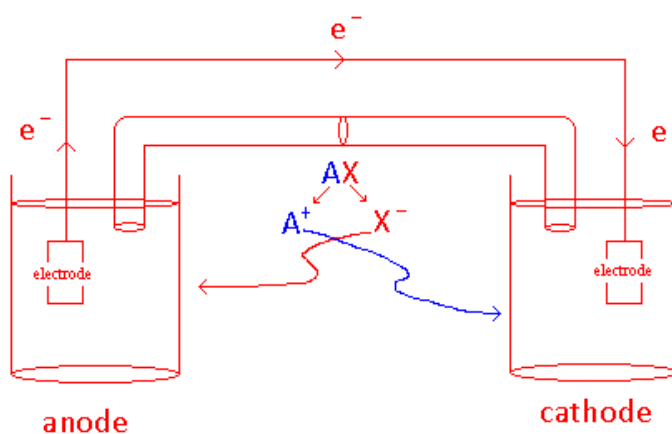
4.   What do the following acronyms mean?

     a. RED-CAT

   REDuction at CAThode

     b. OX-AN

       OXidation at ANode
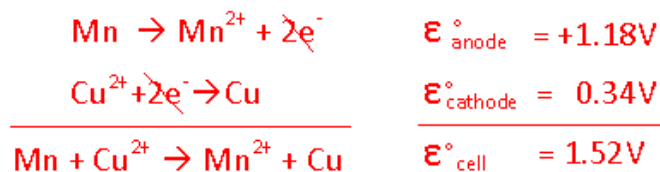
5.   What is the unit measure for cell potential?

$$\text{Volts (V)} = \frac{\text{Joule (J)}}{\text{Coulomb (C)}}$$

6. What are standard conditions?

    1M concentration and 1 atm pressure

7. You must break the redox reaction into half reactions in order to determine the anode and cathode.

8. For a galvanic cell the value of $\varepsilon°_{cell}$ must be positive as it indicates spontaneity.

9. What overall reaction would happen between based on the reduction potentials of each half reaction.?

    a. $Mn^{2+} + 2e^- \rightarrow Mn$ $\varepsilon° = -1.18V$
        $Cu^{2+} + e^- \rightarrow Cu$ $\varepsilon°=0.34V$
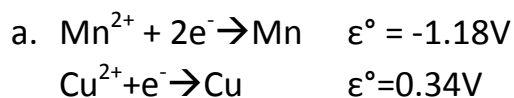
    Remember, these are both reduction reactions. You need to determine which one of the reaction must be flipped in order to create one reduction and one oxidation. Keep in mind that when you flip a reaction around, you will need to change the sign of the cell potential. Lastly, you will be able to determine which of the reaction needs to be flipped because you must obtain an overall positive $\varepsilon°_{cell}$.

    In this case:

    $$Mn \rightarrow Mn^{2+} + 2e^- \qquad \varepsilon°_{anode} = +1.18V$$
    $$Cu^{2+} + 2e^- \rightarrow Cu \qquad \varepsilon°_{cathode} = 0.34V$$
    $$\overline{Mn + Cu^{2+} \rightarrow Mn^{2+} + Cu \qquad \varepsilon°_{cell} = 1.52V}$$
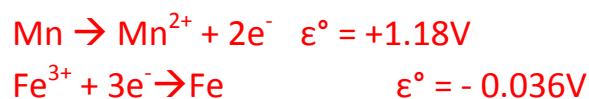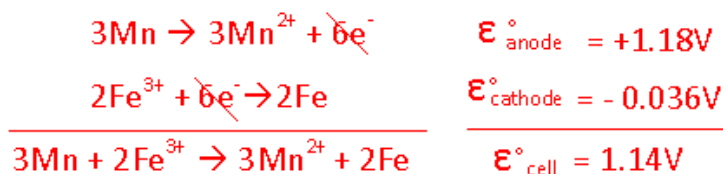
    A simple way to think about it is that you will always flip the reaction with the most negative reduction potential.

b. $Mn^{2+} + 2e^- \rightarrow Mn \qquad \varepsilon° = -1.18V$

$Fe^{3+} + 3e^- \rightarrow Fe \qquad \varepsilon° = -0.036V$
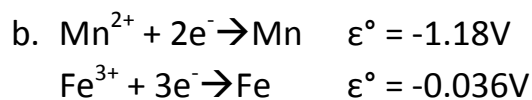
Lets try this problem using both methods described in the previous example.

$Mn \rightarrow Mn^{2+} + 2e^- \quad \varepsilon° = +1.18V$

$Fe^{3+} + 3e^- \rightarrow Fe \qquad\qquad \varepsilon° = -0.036V$

Remember that, for a redox reaction, we need to make sure that number of electrons being lost are equal to the number of electrons being gained.

$$3Mn \rightarrow 3Mn^{2+} + 6e^- \qquad \varepsilon°_{anode} = +1.18V$$
$$2Fe^{3+} + 6e^- \rightarrow 2Fe \qquad \varepsilon°_{cathode} = -0.036V$$
$$\overline{3Mn + 2Fe^{3+} \rightarrow 3Mn^{2+} + 2Fe \qquad \varepsilon°_{cell} = 1.14V}$$

Cell potential is an intensive property – that means that its value is not dependent on the amount of a substance present. That means that if we multiply a reaction through by a coefficient we do not have to the same to the value for the cell potential.
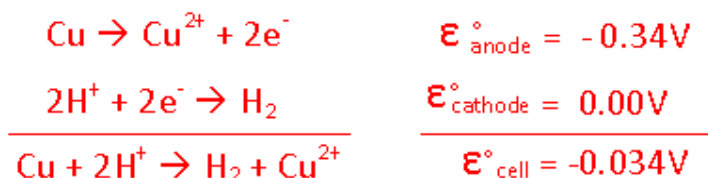
10. Answer the following using standard reduction potential values

a. Is $H^+_{(aq)}$ capable of dissolving $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$?

Keep in mind that the parameters are being set in this question. Meaning you are not manipulating the numbers to get a positive value – you are simply trying to determine if the cell they are describing would operate spontaneously or not. If you get a positive cell potential then yes. If negative, no.

Next we need to establish what it means to be "dissolved." In these types of questions – when a substance is being dissolved – that is that same as being oxidized.

If H^+ is doing the oxidizing, then it has been reduced. You will want to look up the reduction half-reaction/cell potentials.

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad \varepsilon^\circ_{anode} = -0.34V$$
$$\underline{2H^+ + 2e^- \rightarrow H_2} \qquad \underline{\varepsilon^\circ_{cathode} = 0.00V}$$
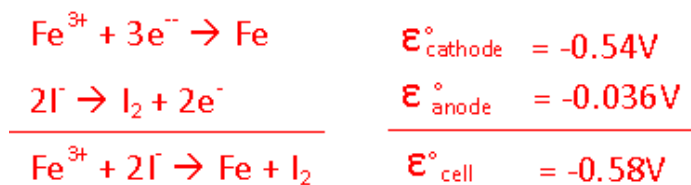$$Cu + 2H^+ \rightarrow H_2 + Cu^{2+} \qquad \varepsilon^\circ_{cell} = -0.034V$$

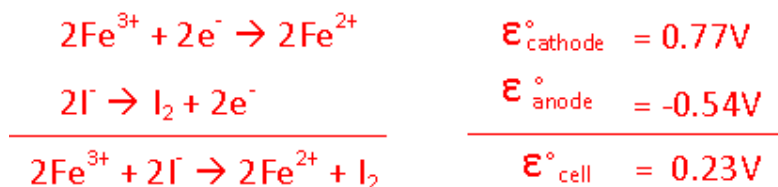Because this results in a negative value for the cell potential, this is NOT a reaction that would readily happen.

b. Is $Fe^{3+}_{(aq)}$ capable of oxidizing $I^-_{(aq)}$?

In this case the Fe^{3+} would be reduced in the process of oxidizing I^-. This one is a little bit tricky because there are 2 possibilities for the reduction of Fe^{3+} - you will need to figure out if one , both or none of them would work.

First we'll look at:

$$Fe^{3+} + 3e^- \rightarrow Fe \qquad \varepsilon^\circ_{cathode} = -0.54V$$
$$\underline{2I^- \rightarrow I_2 + 2e^-} \qquad \underline{\varepsilon^\circ_{anode} = -0.036V}$$
$$Fe^{3+} + 2I^- \rightarrow Fe + I_2 \qquad \varepsilon^\circ_{cell} = -0.58V$$

This one does not work as it results in a negative cell potential. Let's look at the second reduction of Fe^{3+}:

$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$$

$$2I^- \rightarrow I_2 + 2e^-$$

$$\overline{2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2}$$

$$\mathcal{E}^\circ_{cathode} = 0.77V$$

$$\mathcal{E}^\circ_{anode} = -0.54V$$
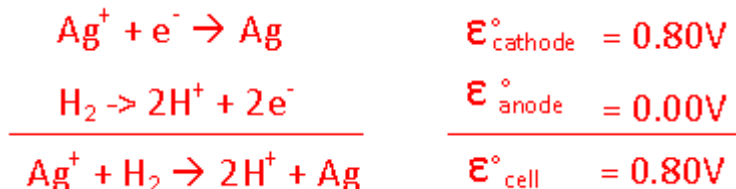
$$\overline{\mathcal{E}^\circ_{cell} = 0.23V}$$

Because this results in a positive cell potential, we know that this would be a spontaneous reaction.

So we know that when I^- is oxidized by Fe^{3+}, Fe^{2+} would be the resulting reduction product and Fe would not.

c. Is $H_{2(g)}$ capable of reducing $Ag^+_{(aq)}$?

In this case H_2 would be oxidized in the process of reducing Ag^+.

$$Ag^+ + e^- \rightarrow Ag$$

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$\overline{Ag^+ + H_2 \rightarrow 2H^+ + Ag}$$

$$\mathcal{E}^\circ_{cathode} = 0.80V$$

$$\mathcal{E}^\circ_{anode} = 0.00V$$

$$\overline{\mathcal{E}^\circ_{cell} = 0.80V}$$

Because this results in a positive cell potential, we know that this would be a spontaneous reaction.

d. Is $Fe^{2+}_{(aq)}$ capable of reducing $Cr^{3+}_{(aq)}$ to $Cr^{2+}_{(aq)}$?

In this case Fe^{2+} is being oxidized in the process of reducing Cr^{-3+} to Cr^{2+}.

$$Fe^{2+} \rightarrow Fe^{3=} + e^-$$

$$Cr^{3+} + e^- \rightarrow Cr^{2+}$$

$$\overline{Fe^{2+} + Cr^{3+} \rightarrow Fe^{3+} + Cr^{2+}}$$

$$\mathcal{E}^\circ_{anode} = -0.77V$$

$$\mathcal{E}^\circ_{cathode} = -0.50V$$

$$\overline{\mathcal{E}^\circ_{cell} = -1.27V}$$
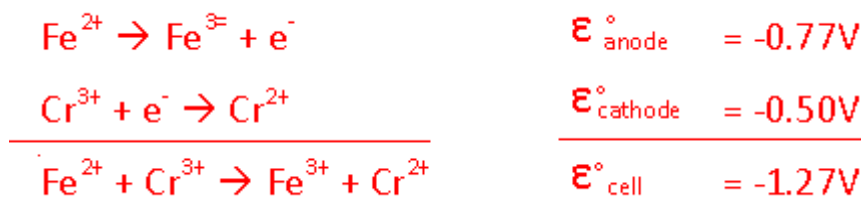
As this reaction results in a negative cell potential, it will not be a

viable reaction.

11.   Using the standard reduction potential and considering

Na^+, Cl^-, Ag^+, Ag, Zn^{2+}, Zn and Pb

answer the following

a. Which is the strongest oxidizing agent?

The strongest oxidizing agent would be the most readily reduced substance.
There are two things that you will want to keep mind when dealing with these kinds of problems.

First, determine what on the list is actually capable of being reduced – meaning what would want to gain electrons.

Secondly, remember that the more positive the standard reduction potential, the better at being reduced.

Step 1 – What would be most favorably reduced (i.e. happiest to gain e⁻)?

Na^+, Ag^{-+}, Zn^{2+}.

All of the other substances would result in an unfavorable negative charge.

Step 2 – Compare the standard reduction potentials for each – find most positive value.

$$Na^+ + e^- \rightarrow Na \qquad \varepsilon° = -2.71V$$
$$Ag^+ + e^- \rightarrow Ag \qquad \varepsilon° = 0.80V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad \varepsilon° = -0.76V$$

In this case the reduction of Ag^+ has the most positive, therefore most favorable, reduction value so it would be the best oxidizing agent.

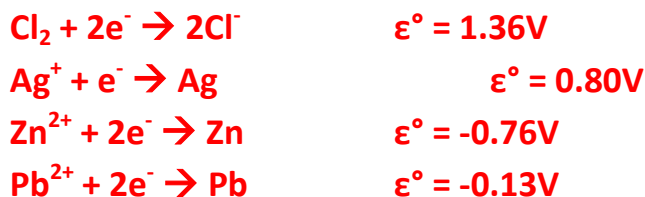b. Which is the strongest reducing agent?

The strongest reducing would be the substance that is the most readily oxidized.

Step 1 – What would be most favorably oxidized (i.e. happiest to lose e^-)?

Cl^-, Ag, Zn, Pb

All of the other species would result in an unfavorable positive charge.

Step 2 - Compare the standard reduction potentials for each – find most negative value.

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad \varepsilon° = 1.36V$$
$$Ag^+ + e^- \rightarrow Ag \qquad \varepsilon° = 0.80V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad \varepsilon° = -0.76V$$
$$Pb^{2+} + 2e^- \rightarrow Pb \qquad \varepsilon° = -0.13V$$

These number show that Zn would be the best reducing agent as it has the most negative reduction potential. Remember the reduction potential tells us how easy it is to add electrons to a substance. If that value is negative, it means that it is not at all favorable and the substance would rather lose electrons (or be oxidized) – the more negative the number the greater the preference for oxidation.

c. Which species can be oxidized by $SO_4^{2-}_{(aq)}$ in acid?

Fist we need to figure out what the reduction reaction involving the SO_4^{2-} is (you would do this by looking it up in a standard reduction potential table – you are looking for a reaction that incorporates SO_4^{2-} in acid or H^+). The reaction that fits this requirement is:

$$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O \qquad \varepsilon° = 0.20V$$

The most straightforward way to solve this problem is to consider the formula

$$\varepsilon°_{cell} = \varepsilon°_{cathode} - \varepsilon°_{anode}$$

You know that in order for this reaction to occur (i.e. be spontaneous) the value of $\varepsilon°_{cell}$ must be greater than zero. Additionally you know that because the reaction involving SO_4^{2-} occurs at the cathode, as it is being reduced. Plugging our knowns into the expression we get:

$$0 < 0.20V - \varepsilon°_{anode}$$

$$\boxed{\varepsilon°_{anode} < 0.20V}$$

This means that any substance with a standard reduction potential less than 0.20V would be capable of being oxidized by SO_4^{2-}.

d. Which species can be reduced by $Al_{(s)}$?

In this case the Al is being oxidized – so we will first need to determine the reaction and cell potential associated with this.

$$Al^{3+} + 3e^- \rightarrow Al \qquad \varepsilon° = -1.66V$$

This reaction, as it is Al is being oxidized, would occur at the anode.

Additionally we know that for this reaction to occur, the overall cell potential must be greater than zero.

Plugging this information into $\varepsilon°_{cell} = \varepsilon°_{cathose} - \varepsilon°_{anode}$ we get

$$0 < \varepsilon°_{cathode} - (-1.66V)$$

$$\boxed{\varepsilon°_{cathode} > -1.66V}$$

This means that any substance with a standard reduction potential greater than -1.66V would be capable of oxidizing Al.

12. What equation relates $\varepsilon°$ and $\Delta G°$?

$$\Delta G° = - n F \varepsilon°$$

This relationship also stands under non-standard conditions:

$$\Delta G = - n F \varepsilon$$

a. What is F?

$$\text{Faraday's Constant (F)} = 96,485 \ \frac{C}{mol \ e^-}$$

b. What is n?

Total moles of electrons transferred.

13. Just as the value of ΔG is dependent upon the concentrations of reactants/products – ε is as well. Leading to the following equations:
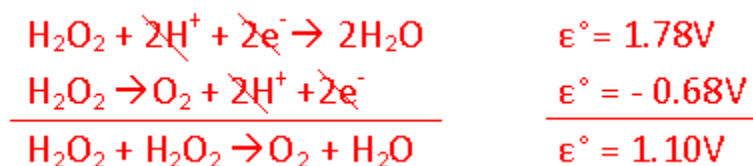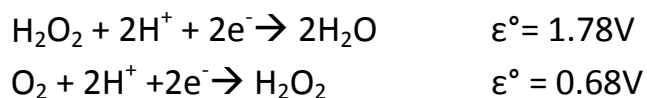
a. For non-standard cells:

$$\varepsilon = \varepsilon° - \frac{RT}{nF} \ln Q$$

b. At equilibrium:

$$\varepsilon° = \frac{RT}{nF} \ln K$$

14. Calculate the values of $\Delta G°$ and K for the following cell

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $\varepsilon° = 1.78V$
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $\varepsilon° = 0.68V$

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $\varepsilon° = 1.78V$
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ $\varepsilon° = -0.68V$
$\overline{H_2O_2 + H_2O_2 \rightarrow O_2 + H_2O}$ $\varepsilon° = 1.10V$

From the equations above we are able to establish that there are 2 moles of electrons transferred. We have also determined the standard cell potential for this reaction – we are, therefore, able to now plug in and solve for $\Delta G°$.

$$\Delta G° = -(2 \text{ mol } e^-)(96485\frac{C}{\text{mol } e^-})(1.10\frac{J}{C}) = \boxed{-212000J}$$

Next we will solve for K using either

$$\varepsilon° = \frac{RT}{nF} \ln K$$
or at 25°C
$$\varepsilon° = \frac{0.0591}{n} \log K$$

I'll use the second formula. Keep in mind that I know the temperature = 25°C because I am using the standard cell potential values which are evaluated at 25°C.
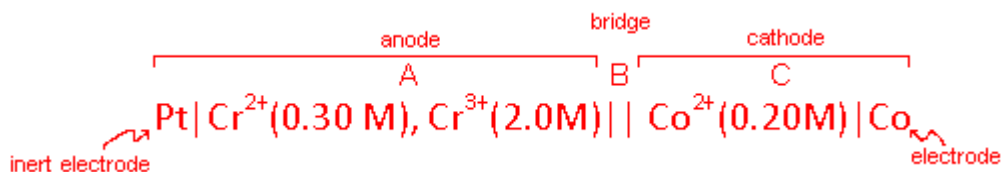
$$1.10V = \frac{0.0591}{2 \text{ mol } e^-} \log K$$

$$K = 10^{\frac{1.10V (2 \text{ mol } e\text{-})}{0.0591}} = 10^{37.22} = \boxed{1.62 \times 10^{37}}$$

15. Consider the following galvanic cell at 25°C:

$Pt|Cr^{2+}(0.30 \text{ M}), Cr^{3+}(2.0M) || Co^{2+}(0.20M)|Co$ $K = 2.79 \times 10^7$
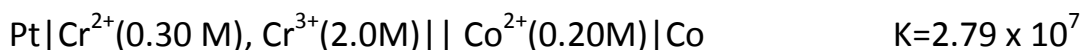
Calculate the cell potential and ΔG for this galvanic cell.

In order to obtain the reactions for this problem you just need to remember ABC:

An "inert electrode" is one that does not participate in the reaction. It is only there to facilitate the movement of electrons from the anode to the cathode. So it will not be incorporated into the overall cell reaction.
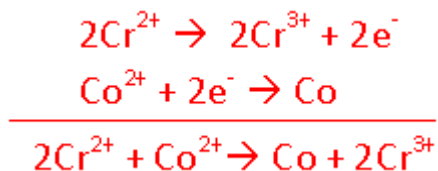
Based on the information the reaction occurring in the anode is:

$$Cr^{2+} \rightarrow Cr^{3+} + e^-$$

Based on the information the reaction occurring in the cathode is:

$$Co^{2+} + 2e^- \rightarrow Co$$

Adding them together we get

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$$
$$\underline{Co^{2+} + 2e^- \rightarrow Co}$$
$$2Cr^{2+} + Co^{2+} \rightarrow Co + 2Cr^{3+}$$

It is REALLY important to notice that we are NOT solving for the standard cell potential or standard free energy. You know this because the concentrations in the cell are not 1.0M, and they all have to be 1.0M to be a standard cell.

To solve for the non-standard cell potential at 25°C we will use

$$\varepsilon = \varepsilon° - \frac{0.0591}{n} \log Q$$

There is only one complication to completing this problem and that is if you look in your book you will not find a standard reduction potential for the cathode reaction, so we are going to have to find the $\varepsilon°_{cell}$ another way.

If you take a look at the information provided to you in the problem you may notice that are given the equilibrium constant, K. You may also note that there is an equation that relates $\varepsilon°_{cell}$ to K:

$$\varepsilon° = \frac{0.0591}{n} \log K$$

Plug in the provided information and you are able to solve for the value of $\varepsilon°_{cell}$.

$$\varepsilon°_{cell} = \frac{0.0591}{2 \text{ mol } e^-} \log (2.79 \times 10^7) = 0.22V$$

Before plugging in to solve for the non standard cell potential, remember that for the reaction

$$aA + bB \rightarrow \leftarrow cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

the only states of matter that you include
in this expression are
aqueous and gaseous.

So for the following reaction

$$2Cr^{2+}_{(aq)} + Co^{2+}_{(aq)} \rightarrow Co_{(s)} + 2Cr^{3+}_{(aq)}$$

We know that ions are always aqueous (in the context of this chapter) and
the neutral metal is always a solid (in the context of this chapter).

$$Q = \frac{[Cr^{3+}]^2}{[Cr^{2+}]^2 [Co^{2+}]}$$

Now we have the necessary information to plug in and solve for ε.

$$\varepsilon_{cell} = 0.22V - \frac{0.0591}{2 \text{ mol } e^-} \log \frac{(2.0M)^2}{(0.20M)(0.30M)^2} = \boxed{0.15V}$$

Now we will turn our attention to solving for free energy using:

$$\Delta G = - n F \varepsilon$$

Plugging in we get

$$\Delta G = -(2 \text{ mol } e^-)(96485 \frac{C}{\text{mol } e^-})(0.15 \frac{J}{C}) = \boxed{-29000J}$$

16. Consider the cell described below

$Al|Al^{3+}(1.00M)||Pb^{2+}(1.00M)|Pb$

Calculate the cell potential after the reaction has operated long enough for the $[Al^{3+}]$ to have changed by 0.60 mol/L. (assume T=25°C)
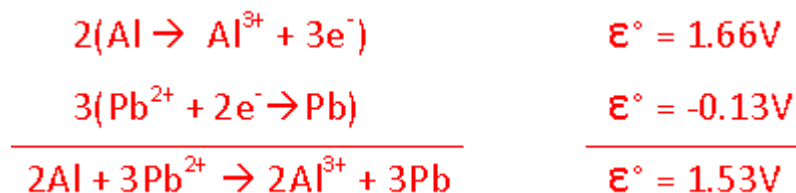
First, Identify whether this cell is standard or non-standard. Noticing that all aqueous compounds have a concentration of 1.0M, we can see that it did start out under standard conditions.

The question, however, is not asking for the cell potential of the cell as given. It is asking for the cell potential after $[^{Al3+}]$ has changed by 0.60M. Thus, they want the cell potential for a point at which it would no longer be standard. That means we will need to use the following equation to solve:

$$\varepsilon = \varepsilon° - \frac{0.0591}{n} \log Q$$

We can determine the value of $\varepsilon°_{cell}$ by looking up the values for standard reduction potential.

Based on the information given, we can determine the 2 half reactions are:

$2(Al \rightarrow Al^{3+} + 3e^-)$	$\varepsilon° = 1.66V$
$3(Pb^{2+} + 2e^- \rightarrow Pb)$	$\varepsilon° = -0.13V$
$2Al + 3Pb^{2+} \rightarrow 2Al^{3+} + 3Pb$	$\varepsilon° = 1.53V$

Remember that I need to multiply each half-reaction by a factor that will

make the number of electrons gained in the reduction equal to the number of electrons lost in the oxidation. And because cell potential is an intensive property, I do not need to multiply the cell potential by those factors.

Next, based on the overall balanced equation, let's determine the expression for Q.

$$Q = \frac{[Al^{3+}]^2}{[Pb^{2+}]^3}$$

Before we can plug in and solve for the value of the cell potential, we need to now figure out the concentrations of the Al^{3+} and Pb^{2+} that we would plug into the expression for Q. All we are told is that we want the cell potential once the Al^{3+} has changed by 0.6M.

A common error here is that people assume that means you *used* 0.6M Al^{3+}. This is not the case because Al^{3+} is on the product side, thus we have *formed* that amount of Al^{3+}.

The second misleading assumption people make is that the Pb^{2+} changed by the same amount. This cannot be the case as there is not a 1:1 mole ratio between the two substances. Using mole ratios you would discover:

$$\frac{0.6 mol\ Al^{3+}}{L} \quad \frac{3\ mol\ Pb^{2+}}{2\ mol\ Al^{3+}} \quad = \quad \frac{0.9\ mol\ Pb^{2+}}{L}$$

Let's organize what we know in a pseudo-ICE chart.

	2Al $_{(aq)}$ +	3Pb^{2+}	$\rightleftharpoons$	2Al^{3+}	+	3Pb
I	——	1.00M		1.00M		——
C	——	-0.9M		+0.6M		——
F	——	0.10M		1.60M		——

From the chart we can see that final values that we will plug into the expression for Q.

Now we can plug in and solve for $\varepsilon°_{cell}$.

$$\varepsilon°_{cell} = 1.53V - \frac{0.0591}{6 \ mol \ e^-} \ log \ \frac{(1.6M)^2}{(0.1M)^3} = \boxed{1.50V}$$