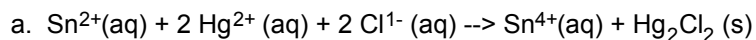


## Solutions to:

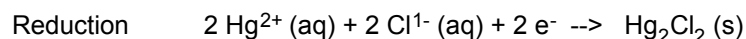
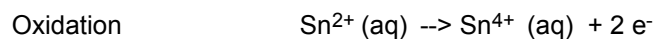
## Electrochemistry Homework Problem Set

S.E. Van Bramer 1/11/97

1. Balance the following chemical equations. Assume the reactions occur in acidic solutions (add  $H^{1+}$  and/or  $H_2O$  as necessary). For each reaction identify the oxidizing and reducing agent. Identify which reactant is oxidized and which is reduced. Write the appropriate half reactions. Determine  $\Delta G$  for the reaction and  $E^\circ$  for the reaction.

Oxidizing Agent  $Hg^{2+}$ Reducing Agent  $Sn^{2+}$ Oxidized  $Sn^{2+}$ Reduced  $Hg^{2+}$ 

Half Reactions



$$E_{\text{anode}} := 0.15 \cdot \text{volt}$$

$$F := 96485.309 \cdot \frac{\text{coul}}{\text{mole}}$$

$$E_{\text{cathode}} := 0.2682 \cdot \text{volt}$$

$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

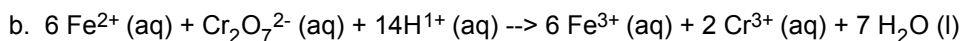
$$E_{\text{cell}} = 0.118 \text{ volt}$$

$$n := 2$$

$$\Delta G := -n \cdot F \cdot E_{\text{cell}}$$

$$\Delta G = -2.281 \times 10^4 \text{ mole}^{-1} \text{ joule}$$

Since the cell potentials are available for these half reactions, I will use them to calculate  $E_{\text{cell}}$ . Then Use  $E_{\text{cell}}$  to calculate  $\Delta G$ .



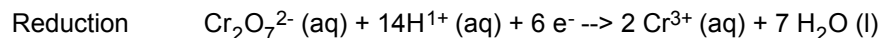
Oxidizing Agent  $\text{Cr}_2\text{O}_7^{2-}$

Reducing Agent  $\text{Fe}^{2+}$

Oxidized  $\text{Fe}^{2+}$

Reduced  $\text{Cr}_2\text{O}_7^{2-}$

Half Reactions



$$E_{\text{anode}} := 0.77 \cdot \text{volt}$$

$$E_{\text{cathode}} := 1.33 \cdot \text{volt}$$

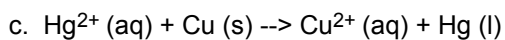
$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 0.56 \text{ volt}$$

$$n := 6$$

$$\Delta G := -n \cdot F \cdot E_{\text{cell}}$$

$$\Delta G = -3.242 \times 10^5 \text{ mole}^{-1} \text{ joule}$$



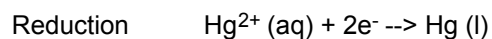
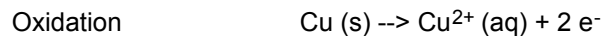
Oxidizing Agent  $\text{Hg}^{2+}$

Reducing Agent Cu

Oxidized Cu

Reduced  $\text{Hg}^{2+}$

Half Reactions



$$E_{\text{anode}} := 0.3402 \cdot \text{volt}$$

$$E_{\text{cathode}} := 0.7961 \cdot \text{volt}$$

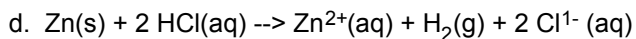
$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 0.456 \text{ volt}$$

$$n := 2$$

$$\Delta G := -n \cdot F \cdot E_{\text{cell}}$$

$$\Delta G = -8.798 \times 10^4 \text{ mole}^{-1} \text{ joule}$$



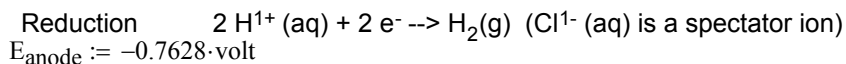
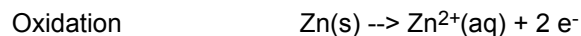
Oxidizing Agent  $\text{H}^{1+}$

Reducing Agent Zn

Oxidized Zn

Reduced  $\text{H}^{1+}$

Half Reactions



$$E_{\text{anode}} := -0.7628 \cdot \text{volt}$$

$$E_{\text{cathode}} := 0 \cdot \text{volt}$$

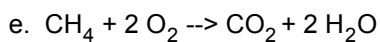
$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 0.763 \text{ volt}$$

$$n := 2$$

$$\Delta G := -n \cdot F \cdot E_{\text{cell}}$$

$$\Delta G = -1.472 \times 10^5 \text{ mole}^{-1} \text{ joule}$$



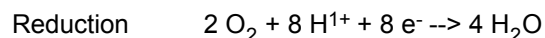
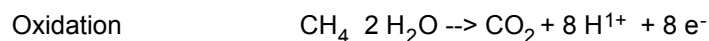
Oxidizing Agent  $\text{O}_2$

Reducing Agent  $\text{CH}_4$

Oxidized  $\text{CH}_4$

Reduced  $\text{O}_2$

Half Reactions



$$\text{kJ} := 10^3 \cdot \text{joule}$$

$$\Delta G := [(-394.359 + (2 \cdot -228.572))] - (-50.72 + 2 \cdot 0) \cdot \text{kJ}$$

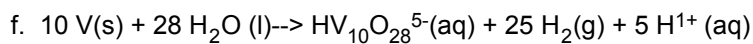
$$\Delta G = -8.008 \times 10^5 \text{ joule}$$

$$n := 8$$

$$E := \frac{-\Delta G}{n \cdot F}$$

$$E = 1.037 \text{ mole volt}$$

Since the reduction potentials are not available (readily) for these half reactions, I will use  $\Delta G_f$  to calculate  $\Delta G_{\text{rxn}}$  and then use this to calculate  $E_{\text{cell}}$ .



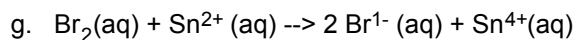
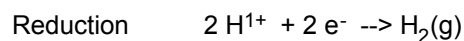
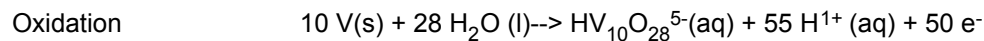
Oxidizing Agent  $\text{H}_2\text{O}$

Reducing Agent  $\text{V}$

Oxidized  $\text{V}$

Reduced  $\text{H}_2\text{O}$

Half Reactions



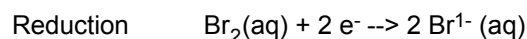
Oxidizing Agent  $\text{Br}_2$

Reducing Agent  $\text{Sn}^{2+}$

Oxidized  $\text{Sn}^{2+}$

Reduced  $\text{Br}_2$

Half Reactions



$$E_{\text{anode}} := 0.15 \cdot \text{volt}$$

$$E_{\text{cathode}} := 1.066 \cdot \text{volt}$$

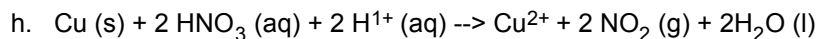
$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 0.916 \text{ volt}$$

$$n := 2$$

$$\Delta G := -n \cdot F \cdot E_{\text{cell}}$$

$$\Delta G = -1.768 \times 10^5 \text{ mole}^{-1} \text{ joule}$$



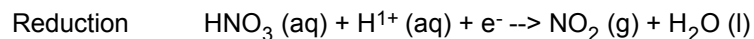
Oxidizing Agent  $\text{HNO}_3$

Reducing Agent  $\text{Cu}$

Oxidized  $\text{Cu}$

Reduced  $\text{HNO}_3$

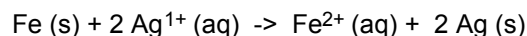
Half Reactions



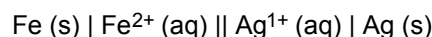
2. Write a figure showing an electrochemical cell that will generate electricity based upon the oxidation of iron to iron (II), and the reduction of silver (I) to silver metal.

See Figure 21.3 on page 959 of Kotz for a figure of a voltaic cell.

a. Write a balanced chemical equation



b. Write the cell notation for this system



c. Write the half reactions for each cell



d. Label the anode and the cathode

The Anode is the piece of Fe

The cathode is the piece of Ag

e. Show the direction of electron motion through the external circuit

Electrons flow from the anode to the cathode

f. Show the motion of ions in the solution

At the anode an excess of cations (positive ions) are produced, at the cathode cations are consumed. To balance the charge in the half cells anions (negative ions) must move from the cathode side (where they are no longer needed to balance the charge) to the anode side (where more are needed to balance the additional charge)

g. Show the transfer of ions at the electrode surface

Anode:  $\text{Fe}^{2+}$  ions are produced so ions go from the electrode surface into solution.

Cathode:  $\text{Ag}^{1+}$  ions are consumed so ions go from the solution to the electrode surface.

h. Calculate the standard cell potential

$$E_{\text{anode}} := -0.44 \text{ volt}$$

$$E_{\text{cathode}} := 0.7994 \text{ volt}$$

$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 1.239 \text{ volt}$$

i. Is this cell spontaneous?

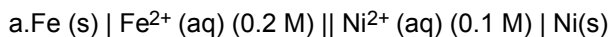
Yes,  $E_{\text{cell}}$  is positive

j. Calculate the standard cell potential for the reverse reaction.

$$E_{\text{reverse}} := -E_{\text{cell}}$$

$$E_{\text{reverse}} = -1.239 \text{ volt}$$

3. Identify the anode, the cathode, the reduced species and the oxidized species for the following electrochemical cells. Write the half reactions for the anode and cathode, the overall reaction. Calculate the standard cell potential and the cell potential.



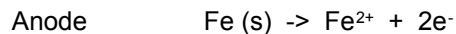
Anode Fe (s)

Cathode Ni (s)

Reduced  $\text{Ni}^{2+}$

Oxidized Fe (s)

Half Reactions



Standard Reduction Potentials for each half reaction:

$$E_{\text{anode}} := -0.409 \cdot \text{volt}$$

$$E_{\text{cathode}} := -0.23 \cdot \text{volt}$$

Standard Cell potential:

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 0.179 \text{ volt}$$

Some Constants:

$$M := \text{mole} \cdot \text{liter}^{-1}$$

$$R := 8.314 \cdot \text{joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$F = 9.649 \times 10^4 \text{ coul} \cdot \text{mole}^{-1}$$

$$T := (273.15 + 25) \cdot \text{K}$$

Cell Potential:

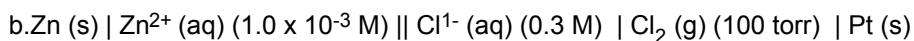
$$C_{\text{Fe}} := 0.2 \cdot M$$

$$C_{\text{Ni}} := 0.1 \cdot M$$

$$n := 2$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Fe}}}{C_{\text{Ni}}} \right)$$

$$E_{\text{cell}} = 0.17 \text{ volt}$$



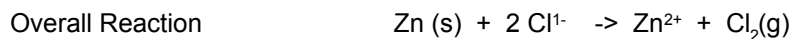
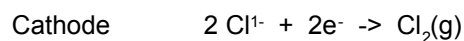
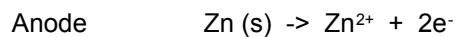
Anode Zn (s)

Cathode Pt (s)

Reduced Cl<sub>2</sub>

Oxidized Zn (s)

Half Reactions



Standard Reduction Potentials for each half reaction:

$$E_{\text{anode}} := -0.7628 \cdot \text{volt}$$

$$E_{\text{cathode}} := 1.3583 \cdot \text{volt}$$

Standard Cell potential:

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 2.121 \text{ volt}$$

Cell potential

$$C_{\text{Zn}} := 1.0 \cdot 10^{-3}$$

$$C_{\text{Cl}} := 0.3$$

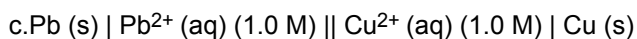
$$C_{\text{Cl}_2} := \frac{100}{760}$$

$$n := 2$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Zn}} \cdot C_{\text{Cl}_2}}{C_{\text{Cl}}^2} \right)$$

$$E_{\text{cell}} = 2.205 \text{ volt}$$

NOTE: For these equilibrium calculations, all concentrations must be relative to the standard state. Concentrations are in molarity, gas pressure in atmosphere.



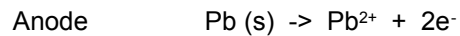
Anode Pb (s)

Cathode Cu (s)

Reduced  $\text{Cu}^{2+}$ 

Oxidized Pb (s)

Half Reactions



Standard Reduction Potentials for each half reaction:

$$E_{\text{anode}} := -0.1263 \cdot \text{volt}$$

$$E_{\text{cathode}} := 0.3402 \cdot \text{volt}$$

Standard Cell potential:

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 0.467 \text{ volt}$$

Some Constants:

$$M := \text{mole} \cdot \text{liter}^{-1}$$

$$R := 8.314 \cdot \text{joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$F = 9.649 \times 10^4 \text{ coul mole}^{-1}$$

$$T := (273.15 + 25) \cdot \text{K}$$

Cell Potential:

$$C_{\text{Pb}} := 1 \cdot M$$

$$C_{\text{Cu}} := 1 \cdot M$$

$$n := 2$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Pb}}}{C_{\text{Cu}}} \right)$$

$$E_{\text{cell}} = 0.467 \text{ volt}$$

d.  $\text{Pb (s)} \mid \text{Pb}^{2+} \text{ (aq)} (1.0 \times 10^{-5} \text{ M}) \parallel \text{Cu}^{2+} \text{ (aq)} (1.0 \times 10^{-2} \text{ M}) \mid \text{Cu (s)}$

Anode  $\text{Pb (s)}$

Cathode  $\text{Cu (s)}$

Reduced  $\text{Cu}^{2+}$

Oxidized  $\text{Pb (s)}$

Half Reactions

Anode  $\text{Pb (s)} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$

Cathode  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu (s)}$

Overall Reaction  $\text{Pb (s)} + \text{Cu}^{2+} \rightarrow \text{Pb}^{2+} + \text{Cu (s)}$

Standard Reduction Potentials for each half reaction:

$$E_{\text{anode}} := -0.1263 \cdot \text{volt}$$

$$E_{\text{cathode}} := 0.3402 \cdot \text{volt}$$

Standard Cell potential:

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 0.467 \text{ volt}$$

Some Constants:

$$M := \text{mole} \cdot \text{liter}^{-1}$$

$$R := 8.314 \cdot \text{joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$F = 9.649 \times 10^4 \text{ coul} \cdot \text{mole}^{-1}$$

$$T := (273.15 + 25) \cdot \text{K}$$

Cell Potential:

$$C_{\text{Pb}} := 1.0 \cdot 10^{-5} \cdot \text{M}$$

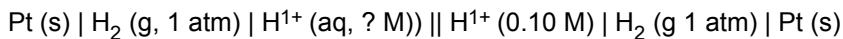
$$C_{\text{Cu}} := 1.0 \cdot 10^{-2} \cdot \text{M}$$

$$n := 2$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Pb}}}{C_{\text{Cu}}} \right)$$

$$E_{\text{cell}} = 0.555 \text{ volt}$$

4. The following cell has a potential of 0.100 V. Calculate the pH at the anode:



The two half reactions (written as reductions are)			E <sub>o</sub>
Anode (unknown H <sup>+</sup> )	Oxidation	H <sup>+</sup> + 2e <sup>-</sup> <-> H <sub>2</sub>	0.000
Cathode (0.1M H <sup>+</sup> )	Reduction	H <sup>+</sup> + 2e <sup>-</sup> <-> H <sub>2</sub>	0.000

Calculate the standard cell potential:

$$E_{\text{anode}} := 0.000 \cdot \text{volt}$$

$$E_{\text{cathode}} := 0.000 \cdot \text{volt}$$

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}} \quad E_{\text{std\_cell}} = 0 \text{ volt}$$

$$n := 2$$

Then from the Nernst equation

$$E_{\text{cell}} := 0.1 \cdot \text{volt}$$

$$E_{\text{cell}} = E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$E_{\text{cell}} = \frac{-R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$Q := \exp \left[ -E_{\text{cell}} \cdot n \cdot \frac{F}{(R \cdot T)} \right]$$

$$Q = 4.16 \times 10^{-4}$$

From the balanced equation:

$$C_{\text{anode}} = X \quad C_{\text{cathode}} := 0.1 \cdot \text{M}$$

$$P_{\text{anode}} := 1 \cdot \text{atm} \quad P_{\text{cathode}} := 1 \cdot \text{atm}$$

$$Q = \frac{C_{\text{anode}}^2 \cdot P_{\text{cathode}}}{C_{\text{cathode}}^2 \cdot P_{\text{anode}}}$$

$$C_{\text{anode}} := \sqrt{\frac{Q \cdot C_{\text{cathode}}^2 \cdot P_{\text{anode}}}{P_{\text{cathode}}}}$$

$$C_{\text{anode}} = 2.04 \times 10^{-3} \text{ M}$$

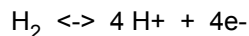
$$\text{pH} := -\log(C_{\text{anode}} \cdot \text{M}^{-1})$$

$$\text{pH} = 2.69$$

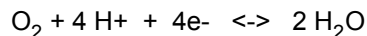
5. On space craft, a  $\text{H}_2/\text{O}_2$  fuel cell is used to produce electricity.

a. The reactions

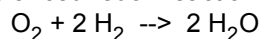
i. What is the reaction at the anode?



ii. What is the reaction at the cathode?



iii. What is the balanced redox reaction?



iv. What is  $E_{\text{cell}}$  assuming  $P_{\text{O}_2} = 2 \cdot \text{atm}$ , and  $P_{\text{H}_2} = 2 \cdot \text{atm}$ .

What is  $E_{\text{cell}}$  when:

$$P_{\text{O}_2} := 2 \cdot \text{atm}$$

$$P_{\text{H}_2} := 2 \cdot \text{atm}$$

$$T := 293.15 \cdot \text{K}$$

First Calculate  $E_{\text{cell}}^\circ$ :

$$E_{\text{anode}} := 0.000 \cdot \text{volt}$$

$$E_{\text{cathode}} := 1.229 \cdot \text{volt}$$

$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 1.229 \text{ volt}$$

Then calculate  $E_{\text{cell}}$  under these conditions

$$Q := \frac{1 \cdot \text{atm}^3}{P_{\text{O}_2} \cdot P_{\text{H}_2}^2}$$

The  $\text{atm}^3$  is just to cancel the units for pressure. The concentration of water is not included in the expression (as with  $K_a$  for acids).

Nernst Equation:

$$E_{\text{cell}} := E_{\text{std\_cell}} - \left( \frac{R \cdot T}{n \cdot F} \right) \cdot \ln(Q)$$

$$E_{\text{cell}} = 1.255 \text{ volt}$$

b. If two cylinders of  $H_2$  and 1 cylinder of  $O_2$  (cylinder: volume=200 liter, pressure = 3000 psi) are used.

i. How many moles of electrons can be produced?

$$V_{\text{cylinder}} := 200 \cdot \text{liter} \quad P_{\text{cylinder}} := 3000 \cdot \text{psi}$$

Use the ideal gas law to find moles of gas in a cylinder

$$R = 8.314 \text{ joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1} \quad T = 293.15 \text{ K}$$

$$\text{mole}_{\text{cylinder}} := \frac{P_{\text{cylinder}} \cdot V_{\text{cylinder}}}{R \cdot T}$$

$$\text{mole}_{\text{cylinder}} = 1.697 \times 10^3 \text{ mole}$$

Moles of each gas

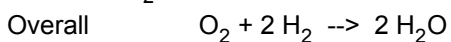
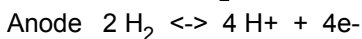
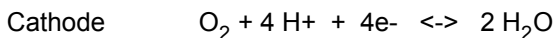
$$O_{2\text{mole}} := \text{mole}_{\text{cylinder}}$$

$$O_{2\text{mole}} = 1.697 \times 10^3 \text{ mole}$$

$$H_{2\text{mole}} := 2 \cdot \text{mole}_{\text{cylinder}}$$

$$H_{2\text{mole}} = 3.395 \times 10^3 \text{ mole}$$

Next from the balanced half reactions:



Each mole of  $O_2$  that reacts, uses 4 moles of electrons so that

$$O_{2\text{mole}} = 0.5 H_{2\text{mole}}$$

Moles of  $O_2$  and Moles  $H_2$  are in correct stoichiometry so no limiting reagent.

$$\text{mole}_{\text{electron}} := 4 \cdot O_{2\text{mole}}$$

$$\text{mole}_{\text{electron}} = 6.789 \times 10^3 \text{ mole}$$

ii. How much energy (joules) is this?

From the moles of electrons and Faraday's constant, the amount of electricity is:

$$F = 9.649 \times 10^4 \text{ coul} \cdot \text{mole}^{-1}$$

$$\text{charge} := \text{mole}_{\text{electron}} \cdot F$$

$$\text{charge} = 6.551 \times 10^8 \text{ coul}$$

How much energy (joules) is this:

$$\text{Energy} := \text{charge} \cdot E_{\text{cell}}$$

$$\text{Energy} = 8.223 \times 10^8 \text{ joule}$$

iii. If this energy has to last for 1 week, what is the average power (watts) available?

Average Power (watts) for 1 week:

$$\text{time} := 7 \cdot \text{day} \quad \text{time} = 6.048 \times 10^5 \text{ sec}$$

$$\text{Power} := \frac{\text{Energy}}{\text{time}} \quad \text{Power} = 1.36 \times 10^3 \text{ watt}$$

$$\text{light} := 75 \cdot \text{watt} \quad \text{Power} = 18.128 \text{ light}$$

This reaction provides enough energy to power 18, 75 watt light bulbs for 1 week.

c. Compare the amount of energy produced by this fuel cell to the energy produced by the combustion of the same amount of H<sub>2</sub> and O<sub>2</sub> using  $\Delta G_{\text{rxn}}$ .

Energy from combustion:

$$\Delta G_{\text{rxn\_std}} := -237.129 \cdot 10^3 \cdot \text{joule} \cdot \text{mole}^{-1}$$

$$\Delta G_{\text{rxn}} := \Delta G_{\text{rxn\_std}} + R \cdot T \cdot \ln \left[ \frac{1}{\left( \frac{P_{\text{H}_2}}{1 \cdot \text{atm}} \right)^2 \cdot \left( \frac{P_{\text{O}_2}}{1 \cdot \text{atm}} \right)} \right]$$

$$\text{Combustion} := \Delta G_{\text{rxn}} \cdot \text{H}_2 \text{mole}$$

$$\text{Combustion} = -8.222 \times 10^8 \text{ joule}$$

This is essentially identical to the value calculated from the cell potential. The different signs are the result of different conventions.  $\Delta G$  is the energy of the reactants (since they lose energy to the surroundings it is negative). The cell potential calculates the energy released by the reaction (so it is positive).

6. Electrochemical Analysis techniques are capable of detecting very small amounts of certain metals. In one type of analysis  $\text{Cd}^{2+}$  undergoes electrolysis. In this experiment it is possible to detect a signal from 1 pA of current, lasting only 1 ms.

a. How many moles of  $\text{Cd}^{2+}$  does this correspond to?

$$\text{current} := 1 \cdot 10^{-12} \cdot \text{amp} \quad \text{time} := 1 \cdot 10^{-3} \cdot \text{sec}$$

Find the electrical charge

$$\text{charge} := \text{current} \cdot \text{time}$$

$$\text{charge} = 1 \times 10^{-15} \text{ coul}$$

Find the moles of electrons from the charge and Faraday's constant:

$$\text{electron}_{\text{mole}} := \frac{\text{charge}}{F}$$

$$\text{electron}_{\text{mole}} = 1.036 \times 10^{-20} \text{ mole}$$

From the balanced half reaction  $\text{Cd}^{2+} + 2\text{e}^- \leftrightarrow \text{Cd}$

$$\text{Cd} := \frac{1}{2} \cdot \text{electron}_{\text{mole}}$$

$$\text{Cd} = 5.182 \times 10^{-21} \text{ mole}$$

b. How many atoms is this?

$$\text{atom} := \frac{1 \cdot \text{mole}}{6.02 \cdot 10^{23}}$$

$$\text{Cd} = 3.12 \times 10^3 \text{ atom}$$