

Read Chapter 1, answer the following problems, and indicate with whom you worked: _____.

- (1) Do problems 19.8, 19.9, 19.10, 22.15, and 22.23 in Skoog and West, shown here, and using the CRC Standard Reduction Potentials table, or another resource when the values are not listed in the CRC. (See class website.)

***19-8.** Calculate the theoretical cell potential of the following cells. If the cell is short-circuited, indicate the direction of the spontaneous cell reaction.

(a) $\text{Zn}|\text{Zn}^{2+}(0.1000\text{ M})||\text{Co}^{2+}(5.87 \times 10^{-4}\text{ M})|\text{Co}$
 (b) $\text{Pt}|\text{Fe}^{3+}(0.1600\text{ M}), \text{Fe}^{2+}(0.0700\text{ M})||\text{Hg}_2^{2+}(0.0350\text{ M})|\text{Hg}$
 (c) $\text{Ag}|\text{Ag}^+(0.0575\text{ M})|\text{H}^+(0.0333\text{ M})|\text{O}_2(1.12\text{ atm}), \text{Pt}$
 (d) $\text{Cu}|\text{Cu}^{2+}(0.0420\text{ M})||\text{I}^-(0.1220\text{ M}), \text{AgI}(\text{sat'd})|\text{Ag}$
 (e) $\text{SHE}||\text{HCOOH}(0.1400\text{ M}), \text{HCOO}^-(0.0700\text{ M})|\text{H}_2(1.00\text{ atm}), \text{Pt}$
 (f) $\text{Pt}|\text{UO}_2^{2+}(8.00 \times 10^{-3}\text{ M}), \text{U}^{4+}(4.00 \times 10^{-2}\text{ M}), \text{H}^+(1.00 \times 10^{-3}\text{ M})||\text{Fe}^{3+}(0.003876\text{ M}), \text{Fe}^{2+}(0.1134\text{ M})|\text{Pt}$

19-9. Calculate the potential of the following two half-cells that are connected by a salt bridge:

* (a) a galvanic cell consisting of a lead electrode (right electrode) immersed in 0.0220 M Pb^{2+} and a zinc electrode in contact with 0.1200 M Zn^{2+} .
 (b) a galvanic cell with two platinum electrodes, the one on the left immersed in a solution that is 0.0445 M Fe^{3+} and 0.0890 M Fe^{2+} , the one on the right in a solution that is $0.00300\text{ M Fe}(\text{CN})_6^{4-}$ and $0.1564\text{ M Fe}(\text{CN})_6^{3-}$.
 *(c) a galvanic cell consisting of a standard hydrogen electrode on the left and a platinum electrode immersed in a solution that is $3.50 \times 10^{-3}\text{ M TiO}^{2+}$, 0.07000 M Ti^{3+} , and buffered to a pH of 3.00.

19-10. Use the shorthand notation (cell) to describe the cells in Problem 19-9. Each cell is supplied with a salt bridge to provide electrical contact between the solutions in the two cell compartments.

$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.811 - 0.792 = 0.019\text{ V}$
 Because E_{cell} is positive, the spontaneous reaction would be oxidation on the left and reduction on the right.

(c) $E_{\text{right}} = 1.229 - \frac{0.0592}{4} \log \left(\frac{1}{1.12(0.0333)^2} \right) = 1.142\text{ V}$
 $E_{\text{left}} = 0.799 - 0.0592 \log \left(\frac{1}{0.0575} \right) = 0.726\text{ V}$
 $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 1.142 - 0.726 = 0.416\text{ V}$
 The spontaneous reaction would be oxidation on the left, reduction on the right.

(d) $E_{\text{right}} = -0.151 - 0.0592 \log(0.1220) = -0.097\text{ V}$
 $E_{\text{left}} = 0.337 - \frac{0.0592}{2} \log \left(\frac{1}{0.0420} \right) = 0.296\text{ V}$
 $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.097 - 0.296 = -0.393\text{ V}$
 The spontaneous reaction would be reduction on the left, oxidation on the right, not the reaction in the direction considered.

(e) $\frac{[\text{H}_2\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.80 \times 10^{-4} = \frac{[\text{H}_2\text{O}^+](0.0700)}{0.1400}$
 $[\text{H}_2\text{O}^+] = \frac{(1.80 \times 10^{-4})(0.1400)}{0.0700} = 3.60 \times 10^{-4}$

$E_{\text{right}} = 0.000 - \frac{0.0592}{2} \log \left(\frac{1.00}{(3.60 \times 10^{-4})^2} \right) = -0.204\text{ V}$
 $E_{\text{left}} = 0.000\text{ V}$
 $E_{\text{cell}} = -0.204 - 0.000 = -0.204\text{ V}$
 Because E_{cell} is negative, the reaction would not proceed spontaneously in the direction considered (reduction on the left, oxidation on the right).

(f) $E_{\text{right}} = 0.771 - 0.0592 \log \left(\frac{0.1134}{0.003876} \right) = 0.684\text{ V}$
 $E_{\text{left}} = 0.334 - \frac{0.0592}{2} \log \left(\frac{4.00 \times 10^{-2}}{(8.00 \times 10^{-3})(1.00 \times 10^{-3})^2} \right) = -0.042\text{ V}$
 $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.684 - (-0.042) = 0.726\text{ V}$
 The direction considered (oxidation on the left, reduction on the right) is the spontaneous direction.

19-9. (a) $E_{\text{right}} = -0.126 - \frac{0.0592}{2} \log \left(\frac{1}{0.0220} \right) = -0.175\text{ V}$
 $E_{\text{left}} = -0.763 - \frac{0.0592}{2} \log \left(\frac{1}{0.1200} \right) = -0.790\text{ V}$
 $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.175 - (-0.790) = 0.615\text{ V}$

(c) $E_{\text{right}} = 0.000\text{ V}$
 $E_{\text{left}} = 0.099 - 0.0592 \log \left(\frac{0.07000}{(3.50 \times 10^{-3})(10^{-1})^2} \right) = -0.333\text{ V}$
 $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.333 - 0.000 = -0.333\text{ V}$

Answers:

19-8. (a)

$$E_{\text{right}} = -0.277 - \frac{0.0592}{2} \log \left(\frac{1}{5.87 \times 10^{-4}} \right) = -0.373\text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2} \log \left(\frac{1}{0.100} \right) = -0.793\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.373 - (-0.793) = 0.420\text{ V}$$

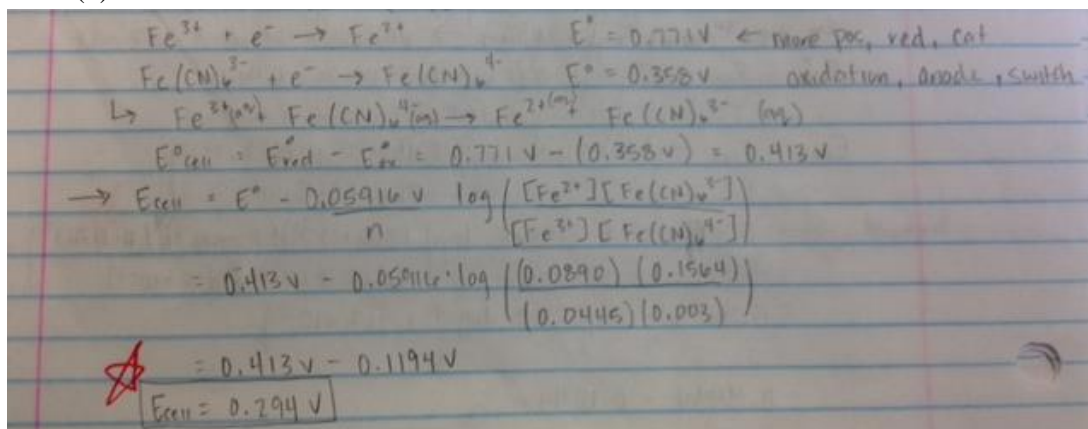
Because E_{cell} is positive, the reaction would proceed spontaneously in the direction considered (oxidation on the left, reduction on the right).

(b) $E_{\text{right}} = 0.854 - \frac{0.0592}{2} \log \left(\frac{1}{0.0350} \right) = 0.811\text{ V}$

$$E_{\text{left}} = 0.771 - \frac{0.0592}{1} \log \left(\frac{0.0700}{0.1600} \right) = 0.792\text{ V}$$

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19-9. (b)



19-10.

(a) $\text{Zn}(s) | \text{Zn}^{2+}(0.1200 \text{ M}, aq) || \text{Pb}^{2+}(0.0220 \text{ M}, aq) | \text{Pb}(s)$ (b) $\text{Pt}(s) | \text{Fe}^{2+}(0.0890 \text{ M}, aq), \text{Fe}^{3+}(0.0445 \text{ M}, aq) || \text{Fe}(\text{CN})_6^{3-}(0.1564 \text{ M}, aq), \text{Fe}(\text{CN})_6^{4-}(0.00300 \text{ M}, aq) | \text{Pt}(s)$ (c) $\text{Pt} | \text{H}_2(\text{activity} = 1 \approx 1 \text{ bar}, g) | \text{H}_3\text{O}^+(\text{activity of } 1 \approx 1 \text{ M}, aq) || \text{TiO}^{2+}(3.50 \times 10^{-3} \text{ M}, aq), \text{Ti}^{3+}(0.07000 \text{ M}, aq), \text{H}_3\text{O}^+(0.001 \text{ M}) | \text{Pt}$

*22-15. Calculate the initial potential needed for a current of 0.065 A in the cell
 $\text{Co} | \text{Co}^{2+}(5.90 \times 10^{-3} \text{ M}) || \text{Zn}^{2+}(2.95 \times 10^{-3} \text{ M}) | \text{Zn}$
 if this cell has a resistance of 4.50 Ω .

22-23. Calculate the time needed for a constant current of 0.8510 A to deposit 0.250 g of Co(II) as
 (a) elemental cobalt on the surface of a cathode.
 (b) Co_3O_4 on an anode.
 Assume 100% current efficiency for both cases.

Answers:

22-15.

$$E_{\text{right}} = -0.763 - \frac{0.0592}{2} \log \left(\frac{1}{2.95 \times 10^{-3}} \right) = -0.838 \text{ V}$$

$$E_{\text{left}} = -0.277 - \frac{0.0592}{2} \log \left(\frac{1}{5.90 \times 10^{-3}} \right) = -0.343 \text{ V}$$

$$E_{\text{cell}} = -0.838 - (-0.343) - 0.065 \times 4.50 = -0.788 \text{ V}$$

22-23. (a)

$$0.250 \text{ g Co} \times \frac{1 \text{ mol Co}}{58.93 \text{ g}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Co}} \times \frac{1 \text{ F}}{96,485 \text{ C}} = 8.186 \times 10^2 \text{ C}$$

$$8.186 \times 10^2 \text{ C} \times \frac{1 \text{ A} \times \text{s}}{\text{C}} \times \frac{1}{0.851 \text{ A}} \times \frac{1 \text{ min}}{60 \text{ s}} = 16.0 \text{ min}$$

(b) $3\text{Co}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Co}_3\text{O}_4(s) + 8\text{H}^+ + 2e^- \quad \left(\frac{3}{2}\right) \text{ mol Co}^{2+} = 1 \text{ mol } e^-$

$$0.250 \text{ g Co} \times \frac{1 \text{ mol Co}}{58.93 \text{ g}} \times \frac{2 \text{ mol } e^-}{3 \text{ mol Co}} \times \frac{1 \text{ F}}{96,485 \text{ C}} = 2.727 \times 10^2 \text{ C}$$

$$2.727 \times 10^2 \text{ C} \times \frac{1 \text{ A} \times \text{s}}{\text{C}} \times \frac{1}{0.851 \text{ A}} \times \frac{1 \text{ min}}{60 \text{ s}} = 5.34 \text{ min}$$

(2) In Nikolaychuk, *Journal of Chemical Education*, 2014, 91, 763, three-dimensional Pourbaix diagrams are described where the third dimension is another variable besides E and pH. Based on this, answer the following:

a. Starting with equation (2), derive equation (3).

Answer: Starting with equation (2),

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b \cdot a_{H^+}^m}, \text{ the change-of-}$$

base formula states that $\ln X = \frac{\log X}{\log e}$,

$$\text{and so } E = E^0 - \frac{RT}{nF \cdot \log e} \log \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b \cdot a_{H^+}^m},$$

and now using a logarithm law, which

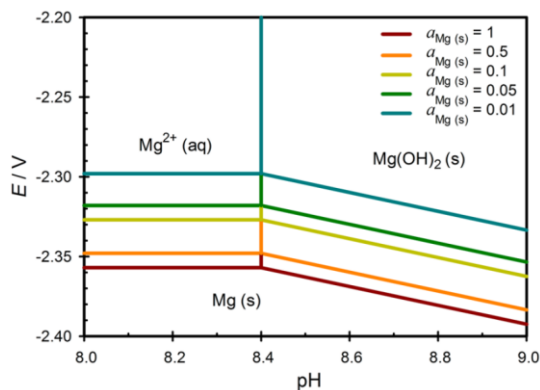
$$\text{state that } \log\left(\frac{a}{X^y}\right) = \log(a) -$$

$$\log(X^y) = \log(a) - y \log(X), E =$$

$$E^0 - \frac{RT}{nF \cdot \log e} \left(\log \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} - m \log a_{H^+} \right) = E^0 - \frac{RT}{nF \cdot \log e} \left(\log \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} - m \cdot pH \right) = E^0 -$$

$$\frac{RT}{nF \cdot \log e} \log \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} - \frac{RT \cdot m}{nF \cdot \log e} pH. \text{ Lastly, one must realize that } \log e = \log_{10} e = \frac{\ln e}{\ln 10} =$$

$$\frac{1}{\ln 10}, \text{ and so } E = E^0 - \frac{RT \cdot \ln 10}{nF} \log \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} - \frac{RT \cdot m \cdot \ln 10}{nF} pH, \text{ which is equation (3).}$$



- b. For Figure 1, assume the trends shown continue beyond the figure extrema, and answer the following.

- i. Write the Nernst equation for the redox reaction at (1) pH 8 and (2) pH 9, and plug in values from the CRC Standard Reduction Potentials table. (See our website.)

Answer: For (1) pH 8, the redox reaction is $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ and so using Equation (3) from the paper one gets,

$$E = E^0 - \frac{0.05916 \text{ V}}{2} \log \frac{a_{Mg}^1}{a_{Mg^{2+}}^1} - \frac{0.05916 \text{ V} \cdot 0}{2} pH, \text{ and using the standard state value}$$

from the CRC table ($E^0 = -2.372$) and simplifying, one obtains,

$$E = -2.372 \text{ V} - 0.02958 \text{ V} \cdot \log \frac{a_{Mg}}{a_{Mg^{2+}}}, \text{ which suffices as an answer. (One}$$

would have obtained the same answer using the typical Equation (2).) Typically solid species (i.e. Mg) are assumed to have unity activities but not here, and thus a_{Mg} must remain in the reaction quotient.

For (2) pH 9, the redox reaction in acid would be $2H^+ + Mg(OH)_2(s) + 2e^- \rightarrow Mg(s) + 2H_2O$ and so in base (what we are looking for) it would be $Mg(OH)_2(s) + 2e^- \rightarrow Mg(s) + 2OH^-(aq)$. Because we are in base we have to use the typical Nernst equation (i.e. Equation (2)),

$$E = E^0 - \frac{0.05916 \text{ V}}{2} \log \frac{a_{Mg}^1 \cdot a_{OH^-}^2}{a_{Mg(OH)_2}^1}, \text{ and again using the standard state value from}$$

the CRC table ($E^0 = -2.690$),

$$E = -2.690 - 0.02958 \text{ V} \cdot \log \frac{a_{Mg} \cdot a_{OH^-}^2}{a_{Mg(OH)_2}}. \text{ THIS SUFFICES AS AN}$$

ANSWER. However, if one wanted to write this in terms of pH, one should use log laws to pull out the a_{OH^-} term as,

$$E = -2.690 - 0.02958 \text{ V} \cdot \log \frac{a_{Mg}}{a_{Mg(OH)_2}} - 0.05916 \text{ V} \cdot \log a_{OH^-}, \text{ and then using}$$

$$K_w = a_{OH^-} a_{H^+} = 10^{-14} \text{ one gets,}$$

$$E = -2.690 - 0.02958 \text{ V} \cdot \log \frac{a_{Mg}}{a_{Mg(OH)_2}} - 0.05916 \text{ V} \cdot \log \frac{10^{-14}}{a_{H^+}}, \text{ and so,}$$

$$E = -2.690 - 0.02958 \text{ V} \cdot \log \frac{a_{Mg}}{a_{Mg(OH)_2}} + 0.82824 + 0.05916 \text{ V} \cdot \log a_{H^+},$$

which simplifies to,

$$E = -1.86176 - 0.02958 \text{ V} \cdot \log \frac{a_{Mg}}{a_{Mg(OH)_2}} + 0.05916 \text{ V} \cdot \log a_{H^+}, \text{ and thus,}$$

$$E = -1.86176 - 0.02958 \text{ V} \cdot \log \frac{a_{Mg}}{a_{Mg(OH)_2}} - 0.05916 \text{ V} \cdot \text{pH. One would}$$

have arrived at the same answer by first converting to an equation containing pOH which equals “ $-\log(a_{OH^-})$ ” and then using the fact that $\text{pOH} = 14 - \text{pH}$.

- ii. Compare the reduction potentials for $a_{Mg} = 1$ at (1) pH 8 and (2) pH 9 with those calculated using the equations from part (i).

For (1) pH 8, at $a_{Mg} = 1$, this paper has $E(\text{Mg}^{2+}/\text{Mg}) \approx -2.36$ while using the Nernst equation above, in part (i), one gets -2.372 and so they are close. *For the species in the figure whose activities are not specifically defined, one must assume unity activity.* Note that at $a_{Mg} = 0.1$, both values will shift by 0.029258 V and this trend continues for all a_{Mg} values.

For (2) pH 9, at $a_{Mg} = 1$, this paper has $E(\text{Mg}(\text{OH})_2/\text{Mg}) \approx -2.39$ while using the Nernst equation above, in part (i), one gets $E = -1.86176 - 0.02958 \text{ V} \cdot \log\left(\frac{1}{1}\right) - 0.05916 \text{ V} \cdot 9$, which simplifies to -2.3942 and so they are VERY close. Note that, again, as a_{Mg} changes both values change in the same manner.

- iii. What is the trend (i.e. slope of the line) in more acidic conditions, and explain why this value makes sense?

Answer: **In more acidic conditions (i.e. pH 8), the slope is zero.** This makes sense, because as the pH changes (i.e. proton activity changes), the potential for the redox reaction does not change; that is, the Nernst equation in part (i) is not dependent on a_{H^+} .

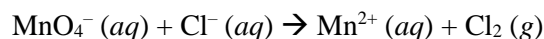
- iv. What is the trend (i.e. slope of the line) in more alkaline conditions, and explain why this value makes sense?

Answer: **In more alkaline conditions (i.e. pH 9), the slope is 59.16 mV based on the Nernst equation, which is ~60 based on looking at the figure.** This makes sense, because as the pH changes, the potential for the redox reaction also changes; that is, the Nernst equation in part (i) is dependent on a_{H^+} and has a constant of -0.05916 V in front of the pH.

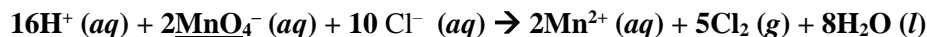
- v. What is the trend in the third dimension, and explain why this makes sense?

Answer: In the third dimension (i.e. “ $-\log a_{Mg} = \text{pMg}$ ”), the slope is **0.029258 V** based on the Nernst equations, which is **~30** based on looking at the figure. This makes sense, because as the pMg changes, the potential for the redox reaction also changes; that is, the Nernst equations in part (i) is dependent on a_{Mg} and would have a constant of -0.02958 V in front of the pMg , if you calculated the pMg .

- (3) Balance the following redox reaction in acid, and then in base. For each condition, indicate if the reaction is spontaneous as written, and calculate the standard change in Gibbs free energy and the equilibrium constant, using the CRC Standard Reduction Potentials table as necessary. Lastly, for each, circle the reducing agent and underline the oxidizing agent.



Answer: Use the process described in Slides 42 – 45 of Lecture #1 and solve the half-reactions to get, $8 \text{H}^+ (aq) + \text{Mn}^{\text{VII}}\text{O}_4^- (aq) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (aq) + 4 \text{H}_2\text{O} (l)$ and $2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2\text{e}^-$. Multiply the first by 2 and the second by 5 and add them (cancel 10e^-) to get:



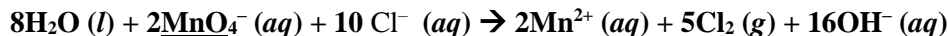
From the CRC, $E^0(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.507 \text{ V}$ vs. SHE, and $E^0(\text{Cl}_2/\text{Cl}^-) = +1.35827 \text{ V}$ vs. SHE

Thus, $E^0_{\text{cell}} = E^0_{\text{red}} - E^0_{\text{ox}} = (+1.507 \text{ V}) - (+1.35827 \text{ V}) = +0.14873 \text{ V}$

Because $\Delta G^0 = -nFE^0$, $\Delta G^0 = -(10)(96485 \text{ C/mol})(+0.14873 \text{ J/C}) = -143,502.1405 \text{ J/mol}$

Because $\Delta G^0 = -RT \ln K$, $K = e^{-\frac{\Delta G^0}{RT}} = e^{-\frac{-143,502.1405 \text{ J/mol}}{(8.314 \text{ J/K})(298.15 \text{ K})}} = e^{57.89} = 7.213 \times 10^{26}$. This illustrates that small potentials ($\sim 150 \text{ mV}$) can result in large changes in free energy, due to the number of electrons being transferred, and thus huge equilibrium constants.

Then in base, add hydroxides to neutralize protons and cross out waters on both sides to get:



From the CRC, $E^0(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.507 \text{ V}$ vs. SHE (in acid); thus, the relation with the standard potential in base is,

$$E = E^0_{\text{base}} - \frac{0.05916 \text{ V}}{n} \log \left(\frac{[\text{Mn}^{2+}]^2 [\text{OH}^-]^{16}}{[\text{MnO}_4^-]^2 [\text{H}_2\text{O}]^8} \right) = E^0_{\text{base}} - \frac{0.05916 \text{ V}}{10} \log \left(\frac{(1)^2 (10^{-14})^{16}}{(1)^2} \right) = E^0_{\text{base}} + 0.05916 \text{ V}(22.4), \text{ and then } E_{\text{acid}} = E^0_{\text{base}} + 1.325184 \text{ V} = +1.507 \text{ V}, \text{ and so } E^0_{\text{base}} = 0.181816 \text{ V}$$

Luckily, $E^0(\text{Cl}_2/\text{Cl}^-) = +1.35827 \text{ V}$ vs. SHE still

Thus, $E^0_{\text{cell}} = E^0_{\text{red}} - E^0_{\text{ox}} = (+0.181816 \text{ V}) - (+1.35827 \text{ V}) = -1.176454 \text{ V}$

Because $\Delta G^0 = -nFE^0$, $\Delta G^0 = -(10)(96485 \text{ C/mol})(-1.176454 \text{ J/C}) = 1,135,101.9229 \text{ J/mol}$

Because $\Delta G^0 = -RT \ln K$, $K = e^{-\frac{\Delta G^0}{RT}} = e^{-\frac{1,135,101.9229 \text{ J/mol}}{(8.314 \text{ J/K})(298.15 \text{ K})}} = e^{-457.92} \approx 0$. This illustrates that large potentials (~ 1 V) will result in large changes in free energy, and due to the number of electrons being transferred can result in ridiculously huge equilibrium constants.

(4) In Ardo & Meyer, *Chemical Society Reviews*, 2009, 38, 115, a Latimer-type diagram for iodine is shown in Scheme 1, which is partially incorrect; “ I_2^- ” should have read “ $\text{I}_2^- + \text{I}^-$ ” because there should be two products of the half-reaction with I_3^- . Based on this, answer the following:

- a. What is the standard potential for disproportionation of di-iodide (I_2^-)? And, is this process thermodynamically favorable?

Answer: A better scheme would have looked like this to the right:

Anyway, $E = E_{\text{red}} - E_{\text{ox}} = (+1.03 \text{ V}) - (+0.04 \text{ V}) = \mathbf{0.99 \text{ V}}$, which is thermodynamically favorable.

- b. Determine the standard potential for reduction of tri-iodide (I_3^-) to iodide (I^-).

Answer: Convert all potentials to free energies using $\Delta G = -nFE$, and then use the conservation of energy to equate two paths between I_3^- and I^- . Thus,

$$\Delta G_{\text{I}_3^- \rightarrow \text{I}_2^-} = -1 \cdot F \cdot (+0.04 \text{ V})$$

$$\Delta G_{\text{I}_2^- \rightarrow \text{I}^-} = -1 \cdot F \cdot (+1.03 \text{ V}), \text{ and}$$

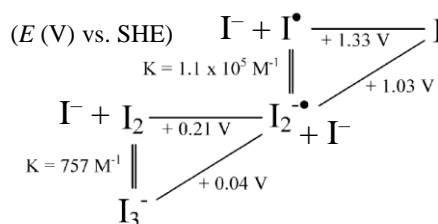
$$\Delta G_{\text{I}_3^- \rightarrow \text{I}^-} = -2 \cdot F \cdot (x); \text{ because } \Delta G_{\text{I}_3^- \rightarrow \text{I}^-} = \Delta G_{\text{I}_3^- \rightarrow \text{I}_2^-} + \Delta G_{\text{I}_2^- \rightarrow \text{I}^-},$$

$$-2 \cdot F \cdot (x) = -1 \cdot F \cdot (+0.04 \text{ V}) + -1 \cdot F \cdot (+1.03 \text{ V})$$

$$-2x = -0.04 \text{ V} - 1.03 \text{ V}, \text{ and so}$$

$$x = \mathbf{0.535 \text{ V}} \text{ vs. SHE, which is the average of the original two,}$$

but typically the answer is not simply the average



Scheme 1

- c. If you made an electrochemical cell consisting of an SCE and a Pt wire that drove the reaction in part (b), for what activities of species would I_3^- reduction be favorable when the two electrodes are connected using an ammeter?

Because we want E_{cell} which is E^0 versus SCE, $E_{\text{red}}^0 = +0.535 \text{ V}$ (vs. SHE) and $E_{\text{ox}}^0 = +0.2412 \text{ V}$ (vs. SHE) and so

$$E_{\text{cell}}^0 = (+0.535 \text{ V}) - (+0.2412 \text{ V}) = +0.2938 \text{ V}$$

Thus, when an ammeter is present it is a low-resistance path between the electrodes and so E_{cell} is favorable (i.e. $E_{\text{cell}} < 0$) when $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.05916 \text{ V}}{n} \log Q > 0$.

Because $\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$, $E_{\text{cell}} = +0.2938 \text{ V} - \frac{0.05916 \text{ V}}{2} \log \left(\frac{a_{\text{I}^-}^3}{a_{\text{I}_3^-}} \right) > 0$, and so,

$$-0.2958 \text{ V} \cdot \log\left(\frac{a_{\text{I}^-}^3}{a_{\text{I}_3^-}}\right) > -0.2938 \text{ V}, \text{ and so,}$$

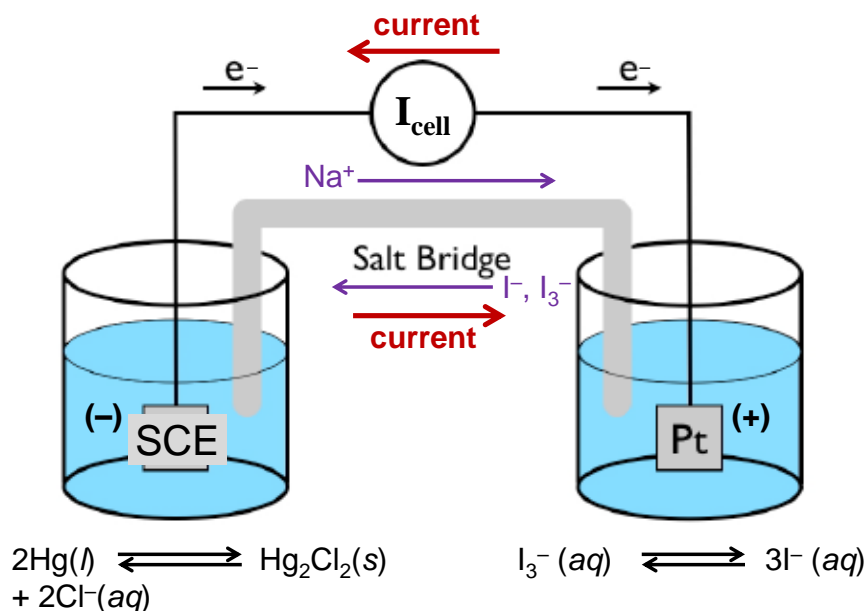
$$\log\left(\frac{a_{\text{I}^-}^3}{a_{\text{I}_3^-}}\right) > 0.9932, \text{ or } \frac{a_{\text{I}^-}^3}{a_{\text{I}_3^-}} > 9.8455. \text{ The answer is,}$$

$$\text{when } a_{\text{I}^-} > \sqrt[3]{9.8455 a_{\text{I}_3^-}} \text{ and/or when } a_{\text{I}_3^-} < 0.10157 a_{\text{I}^-}^3.$$

- d. Draw a picture of the cell in part (c) (assuming aqueous conditions on both sides and that all species have unity activity) and indicate which net direction the current flows, the electrons move, and each ion moves (remember all spectator ions), and the positive and negative electrodes.

Answer: Note that Cl^- will not be driven from the SCE side to the iodide side because only cations will have net movement in that direction. Also, the spectator cation could have been any cation, and balancing each half-reaction and writing the line notation for the cell, were both not required for this problem.

- e. If a low-impedance ammeter is used to complete the circuit, what will happen to the



potential over time and at what applied potential bias will the initial net current equal zero?

Answer: Over time, the potential will approach (tend toward) zero and the initial net current will equal zero when the applied potential opposes E_{cell}^0 ; thus, when $E_{\text{app}} = -0.2938 \text{ V}$.

- f. Draw the Latimer diagram for chromium, based on its non-alkaline reduction potentials listed in the CRC Standard Reduction Potentials table. (See class website.)

Answer: Use entries 1 – 4 and 6 – 8 in the table to get the following:

	$\text{Cr}^{2+} + 2 e \rightleftharpoons \text{Cr}$	-0.913
	$\text{Cr}^{3+} + e \rightleftharpoons \text{Cr}^{2+}$	-0.407
	$\text{Cr}^{3+} + 3 e \rightleftharpoons \text{Cr}$	-0.744
	$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 e \rightleftharpoons 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	1.36
	$\text{CrO}_2 + 2 \text{H}_2\text{O} + 3 e \rightleftharpoons \text{Cr} + 4 \text{OH}^-$	-1.2
	$\text{HCrO}_4^- + 7 \text{H}^+ + 3 e \rightleftharpoons \text{Cr}^{3+} + 4 \text{H}_2\text{O}$	1.350
	$\text{CrO}_2 + 4 \text{H}^+ + e \rightleftharpoons \text{Cr}^{3+} + 2\text{H}_2\text{O}$	1.48
	$\text{Cr(V)} + e \rightleftharpoons \text{Cr(IV)}$	1.34
	$\text{CrO}_4^{2-} + 4 \text{H}_2\text{O} + 3 e \rightleftharpoons \text{Cr(OH)}_3 + 5 \text{OH}^-$	-0.13
	$\text{Cr(OH)}_3 + 3 e \rightleftharpoons \text{Cr} + 3 \text{OH}^-$	-1.48

Cr^{V}	+1.34 V	Cr^{IV}
----->		----->
	+1.48 V	Cr^{III}
	----->	----->
	-0.407 V	Cr^{II}
	----->	----->
	-0.913 V	Cr^{0}
$\text{Cr}^{\text{VI}}\text{O}_7^{2-}$	+1.36 V	----->
----->		----->
$\text{HCr}^{\text{VI}}\text{O}_4^-$	+1.350 V	----->
----->		----->

- (5) A battery technology that is projected to be useful for large, grid-scale storage of electricity is called a redox flow battery. Historically, one of the most promising redox flow batteries is based on vanadium redox chemistry in strong sulfuric acid electrolyte. Based on this battery and the Pourbaix diagram below, answer the following:

- a. In order to maximize the standard potential from the battery, which two half-reactions and one pH should be used?

Answer: To obtain the largest potential from the galvanic cell, the two half-reactions should be **$\text{V}^{2+} \rightarrow \text{V}^{3+} + e^-$ and, $2\text{H}^+ + \text{V}^{\text{V}}\text{O}_2^+ + e^- \rightarrow \text{V}^{\text{IV}}\text{O}^{2+} + \text{H}_2\text{O}$ at pH 1.**

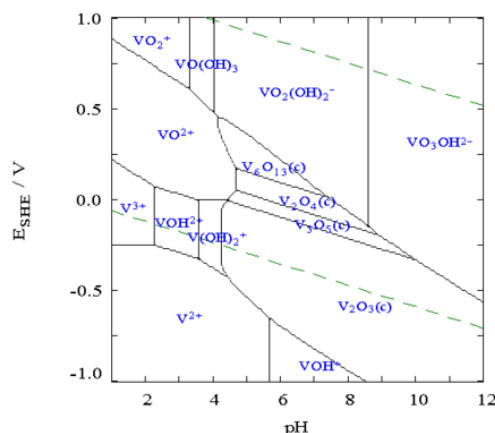
- b. What is the largest standard potential one can expect from this battery?

Answer: At pH 1, $E_{\text{cell}}^0 = E_{\text{red}} - E_{\text{ox}} = (+0.875 \text{ V}) - (-0.25 \text{ V}) = +1.125 \text{ V}$

- c. Which half-reaction occurs at the positive electrode?

The battery starts charged and so initially the positive electrode (for a galvanic cell) is the cathode. Thus, **$2\text{H}^+ + \text{V}^{\text{V}}\text{O}_2^+ + e^- \rightarrow \text{V}^{\text{IV}}\text{O}^{2+} + \text{H}_2\text{O}$** occurs at this electrode.

$[\text{V}^{2+}]_{\text{TOT}} = 10.00 \mu\text{M}$



$t = 25^\circ\text{C}$

http://www.cs.mcgill.ca/~rwest/link-suggestion/wpcc_2008-09_augmented/wp/v/Vanadium.htm

- d. A Nafion proton-exchange membrane separates the two compartments of this cell. What is one of the purposes of the Nafion membrane?

Nafion serves two main purposes but one will suffice for a complete answer. **Nafion acts as a salt bridge between the compartments to allow for rapid ion transport, while also slowly transporting vanadium species so that the high-energy (large potential) species on one side cannot react in solution with the low-energy (small potential) species on the other side;** this would waste the potential between the species and liberate this stored electrochemical potential as heat.