

Read Chapter 1 and answer the following problems.

- (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) $\text{Cu}|\text{Cu}^{2+}(0.0420\text{ M})||\text{I}^-(0.1220\text{ M}), \text{AgI}(\text{sar'd})|\text{Ag}$
 (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 in Fe^{3+} and 0.0890 M in Fe^{2+} , the one on the right in a solution that is 0.00300 M in $\text{Fe}(\text{CN})_6^{4-}$ and 0.1564 M in $\text{Fe}(\text{CN})_6^{3-}$.
 *(c) a galvanic cell consisting of a standard hydrogen electrode on the left and a platinum electrode immersed in a solution that is 3.50×10^{-3} M in TiO^{2+} , 0.07000 M in Ti^{3+} , and buffered to a pH of 3.00.

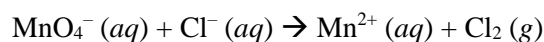
19-10. Use the shorthand notation (cell) to describe the cells in Problem 19-9. Each cell is supplied with a salt bridge to provide electrical contact between the solutions in the two cell compartments.

***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.

- (2) In Nikolaychuk, *Journal of Chemical Education*, 2014, 91, 763 (see class website), three-dimensional Pourbaix diagrams are described where the third dimension is another variable besides E and pH. Based on this, answer the following:
- Starting with equation (2), derive equation (3).
 - For Figure 1, assume the trends shown continue beyond the figure extrema, and answer the following.
 - 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.)
 - 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).
 - What is the trend (i.e. slope of the line) in more acidic conditions, and explain why this value makes sense?
 - What is the trend (i.e. slope of the line) in more alkaline conditions, and explain why this value makes sense?
 - What is the trend in the third dimension, and explain why this makes sense?

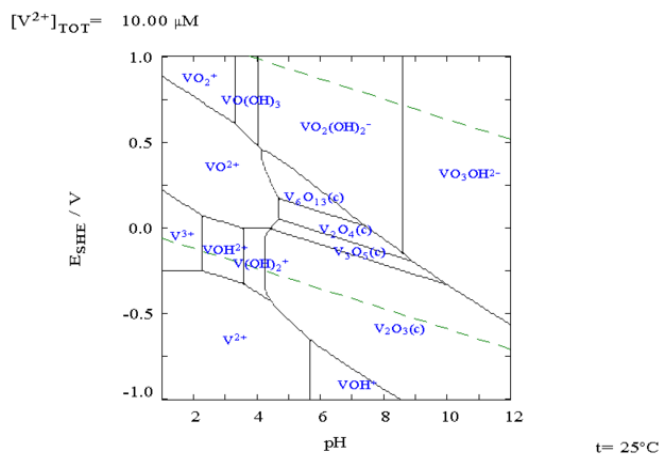
- (3) Balance the following redox reaction in acid, and then in base. For each condition, indicate if the reaction is spontaneous as written, and calculate the standard change in Gibbs free energy and the equilibrium constant. Lastly, for each, circle the reducing agent and underline the oxidizing agent.



- (4) In Ardo & Meyer, *Chemical Society Reviews*, 2009, 38, 115 (see class website), a Latimer-type diagram for iodine is shown in Scheme 1, which is partially incorrect; “I₂⁻” should have read “I₂⁻ + I⁻” because there should be two products of the half-reaction with I₃⁻. Based on this, answer the following:

- What is the standard potential for disproportionation of di-iodide (I₂⁻)? And, is this process thermodynamically favorable?
 - Determine the standard potential for reduction of tri-iodide (I₃⁻) to iodide (I⁻).
 - 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 I₃⁻ reduction be favorable when the two electrodes are connected using an ammeter?
 - 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.
 - 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?
 - Draw the Latimer diagram for chromium, based on its non-alkaline reduction potentials listed in the CRC Standard Reduction Potentials table. (See class website.)
- (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:

- In order to maximize the standard potential from the battery, which two half-reactions and one pH should be used?
- What is the largest standard potential one can expect from this battery?
- Which half-reaction occurs at the positive electrode?
- A Nafion proton-exchange membrane separates the two compartments of this cell. What is one of the purposes of the Nafion membrane?



http://www.cs.mcgill.ca/~rwest/link-suggestion/wpcd_2008-09_augmented/wp/v/Vanadium.htm