

7.E: Electrochemistry (Exercises)

Q7.1

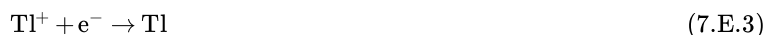
For an electrochemical cell driven by the reaction:



Determine the electromotive force of the cell under standard conditions. Standard reduction potentials for the half cells are given below



with $E^\circ = +1.36 \text{ V}$



with $E^\circ = -0.336 \text{ V}$

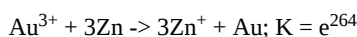
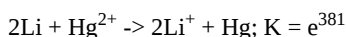
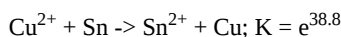
S7.1

The change in Gibbs free energy is an extrinsic quality that can be used to determine the EMF of the cell based on the SRPs of the half-cells. Because the number of electrons exchanged in each reaction are known, we can cancel out the Faraday constants in the equation to relate Gibbs' free energy directly to the EMF of the cell.

$$\Delta G_{\text{Tot}} = \Delta G_1 + \Delta G_2 \rightarrow E^\circ_{\text{tot}} n_{\text{tot}} F = E^\circ_1 n_1 F + E^\circ_2 n_2 F \rightarrow E^\circ_{\text{tot}} = (E^\circ_1 n_1 + E^\circ_2 n_2) / n_{\text{tot}} = (1.36 \text{ V} * (2) - 0.336 \text{ V} (1)) / 2 = 2.38 \text{ V}$$

Q7.8

For the following electrochemical cells, the value of K is given. Determine the change in Gibbs free energy for the reaction in the cell described, and determine the standard potential of the cell.



Q7.9

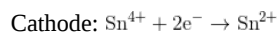
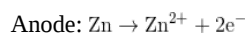
Refer to the reaction below for the following question.



Calculate the E° for the specified reaction at 298 K.

S7.9

First, identify the anode and the cathode:



With this information established, you can then calculate the E° using the half-reactions.

$$E^\circ = 0.151 \text{ V} - (-0.762 \text{ V}) = 0.913 \text{ V}$$

Q7.9



If the equilibrium constant is 8.66×10^{22} , what is the electric potential of the cell?

Q7.10a

In an experiment using standard conditions, you find the cell emf to be 0.0428 V for the following cell:



If the concentration of Ag^+ is 4.5 M at the cathode, calculate the concentration of Ag^+ at the anode.

S7.10a

Firstly, note the half reaction.



Then solve using the Nernst equation, noting that E° is 0 for concentration cells (same electrodes with different concentrations).

$$E = E^\circ - \frac{RT}{vF} \ln \frac{[Anode]}{[Cathode]} \quad (7.E.8)$$

$$0.0428 = 0 - \frac{(8.3145 \text{ J mol}^{-1})(298^\circ \text{ K})}{(1)(96,485 \text{ J})} \cdot \ln \frac{X}{4.5 \text{ M}} \quad (7.E.9)$$

$$0.0428 = -0.0257 \cdot \ln \frac{X}{4.5 \text{ M}} \quad (7.E.10)$$

$$-1.665 = \ln(x) - \ln(4.5) \quad (7.E.11)$$

$$\ln(4.5) + (-1.665) = \ln(x) \quad (7.E.12)$$

$$e^{-0.161} = e^{\ln(x)} \quad (7.E.13)$$

$$X = 0.85 \text{ M} \rightarrow [Ag^+] = 0.85 \text{ M} \quad (7.E.14)$$

Click [here](#) for more information on concentration cells.

Q7.10b

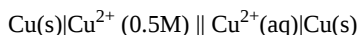
A concentration cell contains I and I_2 . What is the pressure of I if the cell emf is -0.05 V and the pressure of I_2 is 3.75 bar?

S7.10b



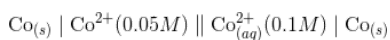
$$E = \frac{-0.0257 \text{ V}}{2} \ln \frac{3.75 \text{ bar}}{x} \rightarrow x = 13.0 \text{ bar} \quad (7.E.16)$$

Q7.14



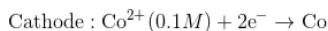
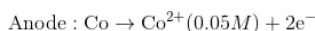
Calculate the electric potential difference for the above concentration cell

Q7.14

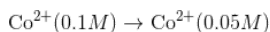


Using the above concentration cell, determine the emf. Assume the temperature is at 25°C.

S7.14



The overall reaction is:

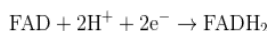


The emf of the cell is dependent upon the concentrations of Co^{2+} at the anode and at the cathode.

$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{0.05}{0.1} = 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.05}{0.1} = 0.009 \text{ V}$$

Q7.16

Referring to the reaction:



and taking into account that at 298 K, the E° is -0.219 V. Use this information to determine the E' at pH = 3. Note: Both FAD and $FADH_2$ have equal moles of concentration.

S7.16

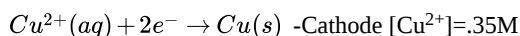
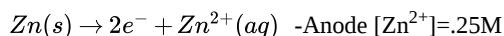
$$\begin{aligned}
 E' = E^{\circ'} &= -0.219V - \frac{0.0257V}{\nu} \ln \frac{[\text{FADH}_2]}{[\text{FAD}][\text{H}^+]/10^{-7}} \\
 &= -0.219V - \frac{0.0257V}{2} \ln \frac{3}{(3)(0.3/10^{-7})^2} \\
 &= 0.164V
 \end{aligned}$$

Q7.15

Calculate E for the following reaction:



S7.15



$$E^{\circ} = E_{\text{cathode}} - E_{\text{anode}} = .342V - (-.762V) = 1.104V \quad (7.E.17)$$

$$E = E^{\circ} - \frac{.0257V}{2} \ln \frac{\text{Cu}^{2+}}{\text{Zn}^{2+}} = 1.10V - \frac{0.0257V}{2} \ln \frac{.35M}{.25M} = 1.08V \quad (7.E.18)$$

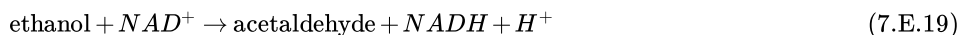
Q7.14



Calculate the emf for the above concentration cell.

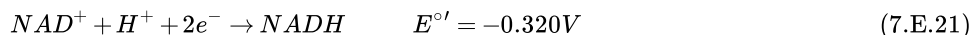
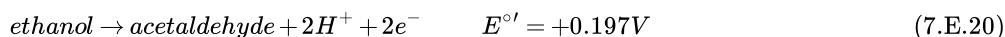
Q7.21

To breakdown consumed alcohol, our body converted ethanol into an acetaldehyde by forming a redox reaction with NAD^+ .



Determine $\Delta_r G^{\circ'}$ of reaction at 298 K and pH = 7 (Hint: Set up half reactions and find $E^{\circ'}$ of the whole reaction.)

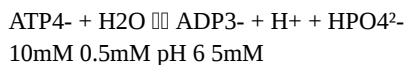
S7.21



$$\Delta_r G^{\circ'} = -\nu F \Delta E^{\circ'} = -(2)(96500 \frac{C}{mol})(-0.123V) = 23739J = \mathbf{23.7kJ/mol} \quad (7.E.23)$$

Q7.21

The hydrolysis of ATP with the following concentrations:



Calculate the change in biochemical standard Gibbs energy of reaction.

Q7.22

Calculate the equilibrium constant and $\Delta_r G^{\circ'}$ for hydrolysis of ATP at 25.0°C:



- $[\text{Glucose}]_{\text{initial}} = 0.05M$
- $[\text{Glucose}]_{\text{equilibrium}} = 0.01M$

S7.22

$$K_C = (0.04\text{M}/1\text{M})/(0.01\text{M}/1\text{M})=4.0$$

$$\Delta_r G^\circ = -8.3145\text{J/Kmol} \cdot (25+273.15)\text{K} \cdot \ln 4.0 = -3.44 \cdot 10^3\text{kJ/mol}$$

Q7.23

Calculate the $\Delta_r G^\circ$ of a certain biochemical reaction that involves the exchange of 2 electrons and where $E^\circ = 3.25\text{ V}$

S7.23

$$\Delta_r G^\circ = -vFE^\circ \quad (7.E.25)$$

$$\Delta_r G^\circ = -(2)(96500\text{C mol}^{-1})(3.25\text{V}) \quad (7.E.26)$$

$$\Delta_r G^\circ = -627\text{kJ mol}^{-1} \quad (7.E.27)$$

Q7.25

In intestinal epithelial cells, transport of lactose across a membrane is coupled with the transport of 2 H^+ ions from a high to low concentration.

$$\Delta_r G^\circ = 16.2\text{kJ} \quad \psi = -0.15\text{V} \quad (7.E.28)$$

How much will the pH change across the membrane at 298 K and 1 atm be if one lactose molecule is transported?

Hint: What is the change in [Gibbs Free Energy](#) for the movement of 2H^+ across this membrane? Write this as an expression as a function of change in pH.

S7.25

When we consider the chemical potential of a single H^+

$$\mu_{\text{H}^+} = \mu_{\text{H}^+}^\circ + RT \ln[\text{H}^+] + Fz\psi \quad (7.E.29)$$

- z = the ion charge
- F = Faraday constant
- ψ = electrical potential

$$pH = -\log[\text{H}^+] \quad (7.E.30)$$

$$\ln[\text{H}^+] = -2.3 \log[\text{H}^+] = -2.3pH \quad (7.E.31)$$

$$\mu_{\text{H}^+} = \mu_{\text{H}^+}^\circ - 2.3RTpH + F\psi \quad (7.E.32)$$

Change in Gibbs free energy is defined as the initial and final chemical potentials, or:

$$\Delta_r G = \mu_{\text{H}^+}(\text{low}) - \mu_{\text{H}^+}(\text{high}) \quad (7.E.33)$$

$$= -2.3RT\Delta pH + F\Delta\psi \quad (7.E.34)$$

As a function of change in pH, the equation can be written as

$$\Delta pH = \frac{\Delta_r G - F\Delta\psi}{-2.3RT} \quad (7.E.35)$$

Since this equation describes chemical potential across a membrane for a H^+ ions, the sign for change in Gibbs's free energy should be opposite that of the transport lactose, or -16.2 KJ. Setting change in electric potential as -0.15 V and converting 12.7 KJ to J

$$\Delta pH = \frac{-16200\text{J} - (96500\frac{\text{C}}{\text{mol}})(-0.15\text{V})}{(298\text{K})(-2.3)(8.3145\frac{\text{J}}{\text{K}\cdot\text{mol}})} \quad (7.E.36)$$

$$= 0.30 \quad (7.E.37)$$

Q7.28

You are studying muscle cells. You notice inside the muscle there is 255 mM of Li^+ and 16 mM of Rb^+ and there is 58 mM of Li^+ and 249 mM of Rb^+ outside the cell. From this information, decide if the membrane is more permeable to Li^+ or Rb^+ .

S7.28

$$\Delta E_{Rb^+} = 0.0257V \ln \frac{[Rb^+]_{ex}}{[Rb^+]_{in}}$$

$$= 0.0275(1) \ln \frac{16}{249}$$

$$= -0.075$$

$$\Delta E_{Li^+} = 0.0257V \ln \frac{[Li^+]_{ex}}{[Li^+]_{in}}$$

$$= 0.0275(1) \ln \frac{255}{58}$$

$$= 0.0407$$

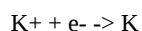
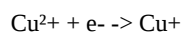
So Rb^+ has a greater magnitude so the membrane is more permeable to it

Q7.29

Calculate the membrane potential of a cell that has $[K^+]_{out} = 8$ and $[K^+]_{in} = 200$. Assume standard temperature of 298 K.

Q7.30

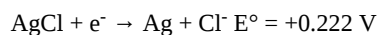
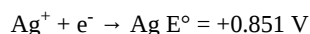
Find E° for:



How can E° be used to find K_{sp} ?

Q7.30a

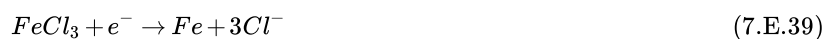
Given the values of E° for the following reactions:



Determine the solubility product (K_{sp}) of AgCl at 23.5°C.

Q7.30b

Given the half-reduction reaction:



Calculate the K_{sp} of $FeCl_3$ at 298 K

Q7.31

Given the following reaction at pH 7.0:



a. Write down the reaction that produces H^+ ion in term of E°

b. Calculate the concentration of $CH_3COCOOH$ at 25°C. Given the emf of the cell is -0.70 V.

Q7.31

A certain reaction in solution has provides H^+ ions and has an E° of .48V. If a calomel electrode is placed in solution (as part of a pH meter) and has an E_{ref} of .11 V. Find the pH of the solution.

S7.31

$$pH = \frac{E - E_{ref}}{0.0591V} \quad (7.E.41)$$

$$pH = \frac{.37V}{0.0591V} \quad (7.E.42)$$

$$pH = 6.26 \quad (7.E.43)$$

Q7.32a

If a zinc and iron block were to be exposed for an extended period of time, which would rust first?

S7.32a

Zinc is a more electropositive metal with a reduction potential of -0.762 V while iron has a reduction potential of -0.447 V. Since Zinc is more electropositive, it will be more likely to be oxidized so it will rust first.

Q7.32b

Aluminum is used widely to be a better protective metal than lead because it forms a corrosion resistance layer in most of environments. Explain this using Standard Reduction Potentials values?

Q7.34

The ΔrS° of the Daniell cell is found to be $-26.8 JK^{-1} mol^{-1}$. Given this value at $95^\circ C$ calculate the emf of the cell and the temperature coefficient.

S7.34

Step 1: (Hint: ΔrS° is directly related to temperature coefficient.)

$$\Delta rS^\circ = vF \left(\frac{\partial E^\circ}{\partial T} \right)_P \quad (7.E.44)$$

$$\Delta rS^\circ = vF \left(\frac{\partial E^\circ}{\partial T} \right)_P = \frac{\Delta rS^\circ}{vF} = \frac{-26.8 JK^{-1} mol^{-1}}{2(96500 C mol^{-1})} = -1.38860 \times 10^{-4} V K^{-1} \quad (7.E.45)$$

Step 2:

$$\left(\frac{\partial E^\circ}{\partial T} \right)_P = \frac{E^\circ_{369.15K} - E^\circ_{298.15K}}{369.15 - 298.15K} = \frac{E^\circ_{368.15K} - 1.104V}{70K} = 1.39 \times 10^{-4} V K^{-1} \quad (7.E.46)$$

$$E^\circ_{268.15K} = 1.094V \quad (7.E.47)$$

Q7.36

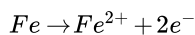
Calculate the equilibrium constant for the following reaction:



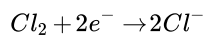
(Hint: look up the reduction potential for the half reactions)

S7.36

Half reactions are



$$\varepsilon^\circ = 0.44V (\text{this is oxidation})$$

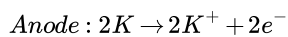


$$\varepsilon^\circ = 1.36V (\text{this is reduction})$$

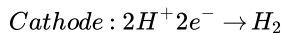
$$\varepsilon^\circ = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode} = 1.36V - 0.44V = 0.92V$$

$$K = e^{\frac{vF\varepsilon^\circ}{RT}} = e^{\frac{(96500 C/mol)(0.92V)}{(8.314 J/K \cdot mol)(298.15K)}} = 3.58 \times 10^{15}$$

S7.36



$$\varepsilon^{\circ} = 5.84V$$



$$\varepsilon^{\circ} = 0V$$

$$\varepsilon^{\circ} = \varepsilon^{\circ}_{\text{cathode}} - \varepsilon^{\circ}_{\text{anode}} = -5.84V$$

$$\Delta_r \tilde{G}^{\circ} = -vF\varepsilon^{\circ} = 2\Delta_f \tilde{G}^{\circ}[K^{+}] + \Delta_f \tilde{G}^{\circ}[H_2] - 2\Delta_f \tilde{G}^{\circ}[K] - 2\Delta_f \tilde{G}^{\circ}[H^{+}]$$

$$\begin{aligned} \Delta_f \tilde{G}^{\circ}[K^{+}] &= -\frac{1}{2}vF\varepsilon^{\circ} - \frac{1}{2}\Delta_f \tilde{G}^{\circ}[H_2] + \Delta_f \tilde{G}^{\circ}[K] + \Delta_f \tilde{G}^{\circ}[H^{+}] \\ &= -\frac{1}{2}(2)(96500C/mol)(-5.84V) - \frac{1}{2}(0kJ/mol) + (0kJ/mol) + (0kJ/mol) = 5.6 * 10^5 J/mol \end{aligned}$$

Q7.36

Do you expect a high K_w value at 276 K or 373 K? Explain.

S7.36

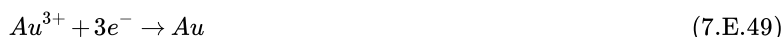
We expect a higher K_w value for 373 K.

Q7.38a

What is the the reaction for a solution with $Au^{3+} + 3e^{-} \rightarrow Au$ and $Ag^{+} + e^{-} \rightarrow Ag$

S7.38a

The first thing we do is look at the standard reduction potentials table. We see that the reduction potential is higher for Au^{3+} so that will be the one that gets reduced. This means we reverse the reaction for Ag^{+} .



$3x(Ag \rightarrow Ag^{+} + e^{-})$ we need the charges to add up to zero so we multiply it by 3 so there will be 3 electrons here as well

We end up with:



Q7.38b

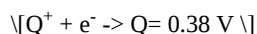
The magnitudes of the standard electrode potentials of two metals, A and B, are



Where the $| |$ notation denotes that only the magnitude (but not the sign) of the E° value is shown. When the half-cells of A and B are connected, electrons flow from A to B. When A is connected to a SHE, electrons flow from A to SHE. (a) What are the signs for each of the E° ? (b) What is the standard emf of a cell made up of A and B?

Q7.38c

The electrochemical properties of a pair of newly discovered metals, Q and G, are being studied in a lab. Their associated reduction reactions are shown below. A lab technician collecting the data makes a mistake, and does not record the sign of the standard potential for the half-cells in their notes. However, he remembers that when he connected the cell containing Q to the standard hydrogen electrode, the Q electrode was oxidized, and when he connected G to the standard hydrogen electrode, it was reduced. What are the signs of the standard potentials for the half-cells? When the two half-cells are connected, what is the electromotive force of the complete Q/G cell?



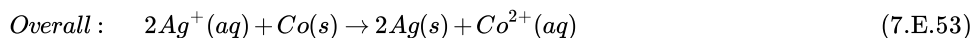
Q7.39

Consider a galvanic (voltaic) cell with silver wire suspended in $0.5M \text{ Ag}^{+}$ solution and a cobalt wire in $1.0M \text{ Co}^{2+}$ solution. Write out the half cell reactions and overall reaction to find the cell's equilibrium constant and observed emf.

Hint: Look at examples of setting up [half reactions](#)

S7.39

Half cell reactions:



$$E^\circ = 0.800 \text{ V} - (-.277 \text{ V}) = +1.077 \text{ V} \quad (7.E.54)$$

$$E^\circ = \frac{RT}{vF} \ln K \quad (7.E.55)$$

$$+1.077 \text{ V} = \frac{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} (298 \text{ K})}{(2)(26485) \frac{\text{C}}{\text{mol}}} \ln K \quad (7.E.56)$$

$$K = 2.51 \times 10^{36} \quad (7.E.57)$$

$$E = E^\circ - \frac{RT}{v} \ln \frac{[\text{Co}^{2+}]}{[\text{Ag}^+]} = +1.077 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1.0 \text{ M}}{0.5 \text{ M}} \quad (7.E.58)$$

$$E = +1.068 \text{ V} \quad (7.E.59)$$

Q7.40a

Answer the following questions about aluminum:

- Given that the standard electrical potential of Al^{3+} is -1.662, why does aluminum tarnish in air?
- Would the the following reaction be spontaneous?



- Predict the reaction between aluminum and chloride gas.

Hint: look up values for E° and appropriate half reactions.

S7.40a

- Silver tarnishes in air because the reduction potential for oxygen is high enough that it oxidizes aluminum.

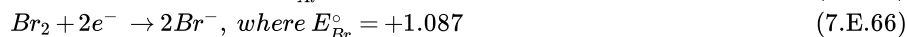
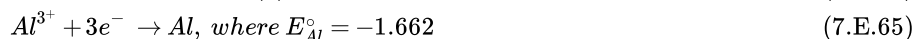
$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \quad (7.E.61)$$

$$E_{\text{cell}}^\circ = E_{\text{oxygen}}^\circ - E_{\text{aluminum}}^\circ \quad (7.E.62)$$

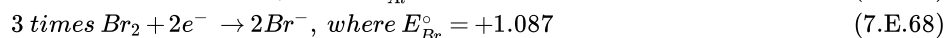
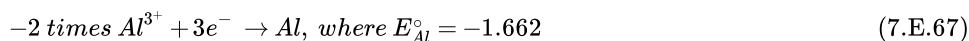
$$E_{\text{cell}}^\circ = 1.23 \text{ V} - (-1.662 \text{ V}) > 0 \quad (7.E.63)$$

Since $E^\circ > 0$, then $\Delta_r G$ is less than zero (since $\Delta_r G = -vFE$). Thus the reaction is spontaneous and aluminum will be oxidized (tarnish) in contact with air.

- Find the appropriate half reactions to fulfill the equation.



Multiply both sides by the appropriate integer to fulfill equation (1).



Switching around the half reactions you should achieve the following, which matches up to the equation (1).



Use the equation to find the E° . Keep in mind cathodes are reduced in the half reaction (you want the electrons to be on the left hand side of the half reaction after balancing) and anodes are oxidized in the half reaction (electrons on the right). Also note how standard reduction potential is an intrinsic property so there is no need to multiply by molar coefficients represented in the balanced equation.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \quad (7.E.70)$$

$$E_{\text{cell}}^{\circ} = E_{\text{bromide}}^{\circ} - E_{\text{aluminum}}^{\circ} \quad (7.E.71)$$

$$E_{\text{cell}}^{\circ} = (1.087 \text{ V}) - (-1.662 \text{ V}) > 0 \quad (7.E.72)$$

$$E_{\text{cell}}^{\circ} = 2.749 \text{ V} \quad (7.E.73)$$

Since $E^{\circ} > 0$, then $\Delta_r G$ is less than zero (since $\Delta_r G = -vFE$). Thus the reaction is spontaneous.

(c) $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$ since Al^{3+} is aluminum's most stable form and Cl^- . Then it's a matter of balancing the equation.

Check [here](#) for additional information on Redox Chemistry.

Q7.40b

Using the electrochemical principle to explain how the reduction potential for oxygen is not adequate to oxidize the gold metal.

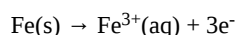
Q7.40c

Answer the following questions for the half-reaction below and $E^{\circ}[\text{Pt}|\text{O}_2, \text{H}_2\text{O}] = 1.229 \text{ V}$.



(a) Predict whether or not iron will rust in air.

(b) Will the following half-reaction have a positive E° ? ($E^{\circ}[\text{Pt}|\text{Fe}^{3+}, \text{Fe}^{2+}] = 0.771 \text{ V}$)



(c) Predict the reaction between iron and bromine gas ($E^{\circ}[\text{Br}_2] = 1.087 \text{ V}$)

Q7.40d

The [standard reduction potential](#) for Platinum, Pt, is as follows:

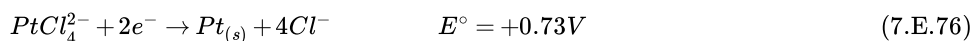


a. Platinum is often used as a metal in fine jewelry because it does not tarnish noticeably. Why is this the case?

b. Based on the above standard reduction potential, will the following reaction be spontaneous,



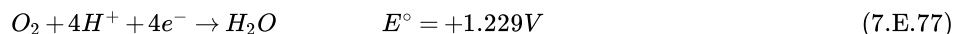
given that



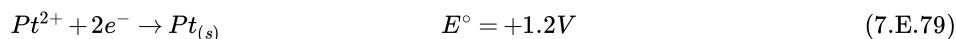
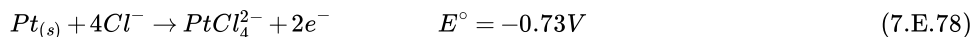
c.) Gold is also used as a metal in fine jewelry. Based on your answer to part (a.) and the standard reduction potential for gold Au^{3+} , $E^{\circ} = 1.69$, does gold tarnish?

S7.40d

a.) Platinum does not tarnish, or oxidize, very quickly in air since its reduction potential is only slightly lower than that of oxygen. Thus, any oxidation which does occur does so very slowly.



b.) If the reaction has a positive standard reduction potential, then it is spontaneous. The reaction can be broken up into two half reactions whose values are provided.



so the standard reduction potential is:

$$E^{\circ} = -0.73 \text{ V} + 1.2 \text{ V} = +0.47 \text{ V} \quad (7.E.81)$$

Thus, the reaction is spontaneous.

c.) No. Since the standard reduction potential of gold is greater than that of oxygen, oxygen cannot spontaneously react with gold and oxidize it.

Q7.41

In figure 7.1 we observe a voltaic cell. Here the anode is oxidized (loss of electrons) and the cathode is reduced (gains electrons). The Zinc metal loses electron and Zn (s) becomes Zn^{2+} ions. Explain how the Cu^{2+} ions become solid Copper.

Q7.42a

In the following reaction at 298K,



Calculate the pressure of H_2 in bar to maintain equilibrium. The concentration of $[Ca^{2+}] = 0.026M$ and the pH of the solution is buffered at 1.60 pH.

S7.42a

Step1:



$$E^o = 0V - (-0.34) = 0.34 \quad (7.E.85)$$

Step 2: EMF calculation

$$E = E^o - \frac{0.0257V}{v} \ln \frac{[Ca^{+2}]P_{H_2}}{[H^+]^2} \quad (7.E.86)$$

$$From\ the\ pH, [H^+] = 10^{-1.60} = 2.51 \times 10^{-2} M$$

At E=0,

$$0 = 0.34 - \frac{0.0257V}{2} \ln \frac{(0.026)P_{H_2}}{(2.51 \times 10^{-2})^2} \quad (7.E.87)$$

$$P_{H_2} = 7.5 \times 10^9 bar \quad (7.E.88)$$

Q7.42b

For the reaction at 300K:



Given pressure following the reaction is 296.07 atm, and molarity of acid used is 0.025M. Compute the molarity of the Mg^{2+} .

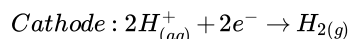
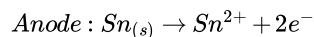
Q7.44a

For the ion Sn^{2+} , use the electric potential table to determine the value of $\Delta_f \bar{G}^o$.

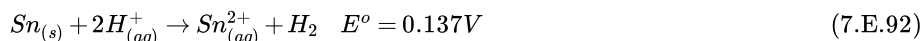
S7.44a



$$E^o = -0.137 \quad (7.E.91)$$



Overall Equation,



$$\Delta_r G^o = -vFE^o = \Delta_f \bar{G}^o [Sn_{(aq)}^{2+}] + \Delta_f \bar{G}^o [H_{2(g)}] - \Delta_f \bar{G}^o [Sn_{(s)}] - 2\Delta_f \bar{G}^o [H_{(aq)}^+] \quad (7.E.93)$$

$$-(2)(96500 C \text{ mol}^{-1})(0.137 V) = \Delta_f \bar{G}^\circ [Sn_{(aq)}^{2+}] + 0 kJ \text{ mol}^{-1} - 0 kJ \text{ mol}^{-1} - 2(0 kJ \text{ mol}^{-1}) \quad (7.E.94)$$

$$\Delta_f \bar{G}^\circ [Sn_{(aq)}^{2+}] = -2.6 \times 10^4 J \text{ mol}^{-1} \quad (7.E.95)$$

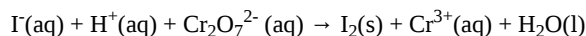
Q7.44b

Calculate the $\Delta_f \bar{G}^\circ$ for K^+ in the following reaction:



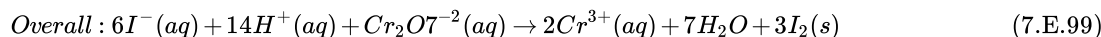
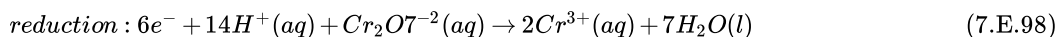
Q7.46a

Determine the standard emf E° for the following reaction (at 298 K and pH 0)



Hint: Use standard change in free energy of formation and use the relationship between G° and E°

S7.46a



$$\Delta_r G^\circ = 2\Delta_f G^\circ(Cr^{3+}) + 3\Delta_f G^\circ(I_2) + 7\Delta_f G^\circ(H_2O) - 6\Delta_f G^\circ(I^-) - 14\Delta_f G^\circ(H^+) - \Delta_f G^\circ(Cr_2O_7^{2-}) \quad (7.E.100)$$

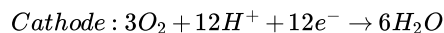
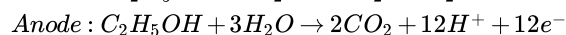
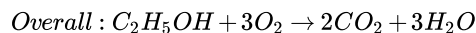
$$\Delta_r G^\circ = [2(-214.2) + 3(0) + 7(-237.2) - 6(51.57) - 14(0) - (-1301.1)] \frac{kJ}{mol} = -1097.12 \frac{kJ}{mol} \quad (7.E.101)$$

$$E^\circ = -\frac{\Delta_r G^\circ}{vF} = -\frac{-1097.12 \frac{kJ}{mol} \times \frac{1000J}{1kJ}}{(6)(96500 \frac{C}{mol})} = +1.89V \quad (7.E.102)$$

Q7.46b

Calculate the ε° for the combustion of ethanol given that $\Delta_f \bar{G}^\circ_{ethanol} = -174.8 kJ/mol$.

S7.46b



$$\begin{aligned} \Delta_r G^\circ &= 2\Delta_f \bar{G}^\circ[CO_2] + 3\Delta_f \bar{G}^\circ[H_2O] - \Delta_f \bar{G}^\circ[C_2H_5OH] - 3\Delta_f \bar{G}^\circ[O_2] \\ &= 2(-394.4 kJ/mol) + 3(-237.14 kJ/mol) - (-174.8 kJ/mol) - 3(0 kJ/mol) \\ &= -1325.42 kJ/mol \end{aligned}$$

$$\varepsilon^\circ = -\frac{\Delta_r G^\circ}{vF} = -\frac{-1325.42 \times 10^3 J/mol}{(12)(96500 C/mol)} = 1.145V$$

Q7.47a

Explain the biological significance of cytochromes by comparing the following half reaction in cytochrome c, a, or f vs. an electrode:



S7.47a

For cytochrome c, $E^\circ = +0.254$

For $Pt|Fe^{3+}, Fe^{2+}$, $E^\circ = +0.771$

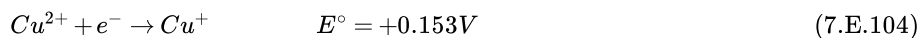
Since cytochrome c has a smaller reduction potential, it makes it easier for Iron to exist in both the oxidized form Fe^{3+} or the reduced form Fe^{2+} . This allows cytochromes to transfer electrons easily between other cytochromes in the electron transport chain. keep in mind that different cytochromes have slightly different reduction potentials.

See [here](#) more details about Electron Transfer Proteins.

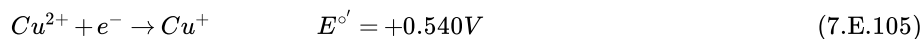
Q7.47b

Practice

The standard reduction potential for the reduction of copper in aqueous solution is as follows:



In hemocyanin, the primary oxygen carrier in invertebrate blood, however, the standard reduction potential is:



Why do these reduction potentials differ?

S7.47b

The [standard reduction potential](#) is used to measure the readiness with which an atom may be reduced at standard conditions (25 °C, 1 atm, reactants at 1M). In biological half-reactions, standard reduction potentials differ because the process cannot occur at standard concentrations. $E^{\circ'}$ occurs at pH 7, as opposed to pH 0, the reference point for electrode half reactions. To obtain a more intuitive understanding, we may use the [Nernst equation](#):

$$E^{\circ'} = E^{\circ} - \frac{RT}{\gamma F} \ln \frac{[\text{Cu}^{+}]}{[\text{Cu}^{2+}]} \quad (7.E.106)$$

At a higher pH, more electrons are found in solution, due to the formation of Hydrogen ions. By [le chatelier's principle](#), this pushes the above half reaction forward so that the concentration of Cu^{2+} is greater than that of Cu^{+} . This makes the value produced by the natural log negative. Thus, $E^{\circ'}$ is greater than E° at higher pH.

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