PS7key

Thursday, April 20, 2017 11:13 AM

Problem Set 7 **(Due: April 24th 12:30 PM)**

1. For each of the following electrochemical reactions, calculate $\Delta G°$.
   a. $Cu (s) + Au^{3+} \rightarrow Cu^{2+} + Au (s)$
   b. $NO (g) + Cr_2O_7^{2-} \rightarrow Cr^{3+} + NO_3^-$
   c. $Mn^{2+} + Cl_2(g) \rightarrow MnO_4^{-1} + Cl^-$

2. For reaction 1a, determine ΔG if $[Au^{3+}]$ = 15 nM and $[Cu^{2+}]$ = 175 mM.
3. Which compounds in the attached table of standard reduction potentials can oxidize Co^{2+} to Co^{3+}?

4. Using fundamental chemical concepts (think Coulomb's law and electron configurations), clearly explain each of these observations:
   a. Cl_2 (g) is a stronger oxidizing agent than Br_2 (l)
   b. Al^{3+} is a better reducing agent than Al (s)
   c. Li (s) is the best reducing agent on the list.

5. Consider the following compounds. Rank them by increasing nitrogen oxidation state (most positive last). If any compounds are equal, explain why. **Note that NO has an unpaired electron**

   NO_3^- NH_4^+ NH_2OH CH_3NH_2 CH_2NH NO_2^- NO

6. Oxidation of glucose ($C_6H_{12}O_6$) to carbon dioxide and liquid H_2O by O_2 provides the foundation reaction for biological energy production. $\Delta G°$ for this reaction is -2870 kJ/mol. Answer the following question about this reaction:
   a. Write a balanced chemical equation for this electrochemical reaction.
   b. Determine ΔG if [glucose] = 1 μM, $[O_2]$ = 1 μM, and $[CO_2]$ = 1.5 M.
   c. If the concentration of CO_2 is 10 M and $[O_2]$ = 1 pM, what concentration of glucose is needed for the reaction to be at equilibrium?
   d. How many electrons can each oxygen molecule accept?
   e. Determine how many electrons are transferred from glucose to oxygen.
   f. Determine the standard reaction potential (E°).
   g. Determine the standard oxidation potential of glucose. Note that oxidation potentials describe the oxidation reaction.
   h. Which of these ions can be reduced to neutral atoms by glucose? Li^+, Mn^{2+}, Ca^{2+}, Au^{3+}, Zn^{2+}
   i. Choose one of the ions you identified in part e. Write a balanced electrochemical reaction with glucose and calculate $\Delta G°$ for the reaction.

7. In the intestinal epithelial cells that we discussed in class, Na^+ ions are transported from the stomach into the cell to ensure that glucose uptake is possible. As these ions are pumped into the cell, we would expect the cellular concentration of sodium to increase.
   a. How would this affect the membrane potential ($\Delta\Psi$)?
   b. Why would this be a bad thing for bringing glucose into the cell?
   c. In reality, the 12 mM Na^+ concentration is maintained by another sodium transporter on the other side of the cell. This one pumps Na^+ ions from the cell to the blood stream. A normal blood-sodium concentration is 140 mM. If the membrane potential is -70 mV (remember this means the inside of the cell is more negative), calculate ΔG for the cellular sodium export.
   d. The protein that facilitates this process is known as a Na^+/K^+ ATPase. This enzyme is able to pump ions against energy gradients by coupling ion transport with ATP hydrolysis. Hydrolysis of ATP produces -37 kJ/mol of energy. How many Na^+ ions can be pumped by a single ATP hydrolysis?

8. Cystic fibrosis is caused by a defect in a chloride ion transporter located in lung tissue. This protein, called CFTR, facilitates the transport of chloride ions which plays in important role in the clearance of mucous in the lung (improper clearance leads to serious problem).
   a. The membrane potential of the epithelial cells in lung tissue is +5 mV. Does this favor chloride transport into or out of the cell?
   b. If the extracellular [Cl-] = 28 mM and 86 mM inside the cell, which direction does chloride flow? Make sure to take into account both contributors to ΔG.

9. The function of neurons is absolutely dependent on the maintenance of ion gradients. As we discussed in class, these ion gradients are the fundamental basis of action potentials (which allow a neuron to very quickly communicate information long distances).
   a. Describe the role of ligand gated ion channels and voltage gated ion channels in this process.
   b. If a cation flows into the cell, what effect does this have on the membrane potential?
   c. In class, we discussed equilibrium potentials. What does this mean and why is it important in the function of a neuron?
   d. Calculate the equilibrium potential for chloride if the extracellular [Cl-] = 28 mM and 86 mM inside the cell.
   e. Once an action potential is completed, hyperpolarization occurs because the voltage gated K^+ channel is very slow to close.
      i. Why does this lead to the membrane potential becoming more negative?
      ii. Hyperpolarization stops when the membrane potential is -98.1 mV. Why?
      iii. At this point, the resting potential of the neuron (-60 mV) needs to be restored so that the neuron is ready for another action potential cycle. This involves moving Na^+ and K^+ ions against their concentration gradients; this process is facilitated by an ATPase, an ion transporter that couples the hydrolysis of ATP (ΔG = -37 kJ/mol) to Na^+ export and K^+ import. Does ATP hydrolysis provide enough energy to move a Na^+ out of the cell at -98.1 mV? Assume $[Na^+]_{in}$ = 14 mM and $[Na^+]_{out}$ = 143 mM.

Standard Reduction Potentials at 298K, 1M, 1atm

HALF-REACTION	$E°$ (V)
$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$	+2.87
$O_{3(g)} + 2H^+_{(aq)} + 2e^- \rightarrow O_{2(g)} + H_2O_{(l)}$	+2.07
$Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$	+1.82
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	+1.77
$PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	+1.70
$Ce^{4+}_{(aq)} + e^- \rightarrow Ce^{3+}_{(aq)}$	+1.61
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.51
$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$	+1.50
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	+1.36
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
$MnO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.23
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	+1.23
$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$	+1.07
$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightarrow NO_{(g)} + 2H_2O_{(l)}$	+0.96
$2Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_2^{2+}{}_{(aq)}$	+0.92
$Hg_2^{2+} + 2e^- \rightarrow 2Hg_{(l)}$	+0.85
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)}\ 2e^- \rightarrow H_2O_{2(aq)}$	+0.68
$MnO_4^-{}_{(aq)} + 2H_2O_{(l)} + 3e^- \rightarrow MnO_{2(s)} + 4OH^-_{(aq)}$	+0.59
$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$	+0.53
$O_{2(g)} + 2H_2O + 4e^- \rightarrow 4OH^-_{(aq)}$	+0.40
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	+0.34
$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$	+0.22
$SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow SO_{2(g)} + 2H_2O_{(l)}$	+0.20
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	+0.15
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	+0.13
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0.00
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$	-0.13
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	-0.14
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.25
$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$	-0.28
$PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.31
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	-0.40
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.44
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.74
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.76
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$	-0.83
$Mn^{2+}_{(aq)} + 2e^- \rightarrow Mn_{(s)}$	-1.18
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$	-1.66
$Be^{2+}_{(aq)} + 2e^- \rightarrow Be_{(s)}$	-1.85
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	-2.37
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	-2.71
$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$	-2.87
$Sr^{2+}_{(aq)} + 2e^- \rightarrow Sr_{(s)}$	-2.89
$Ba^{2+}_{(aq)} + 2e^- \rightarrow Ba_{(s)}$	-2.90
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	-2.93
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	-3.05

1. $[Cu(s) \rightarrow Cu^{2+} + 2e^-]3 \quad E° = -0.34V$

$[3e^- + Au^{3+} \rightarrow Au(s)]2 \quad E° = 1.50V$

$3Cu(s) + 2Au^{3+} \rightarrow 3Cu^{2+} + 2Au(s) \quad E° = 1.16V$

$\Delta G° = -6(96485)(1.16) = \boxed{-671535.6\ J/mol}$

b. $2(NO(g) + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^-)2 \quad E° = -0.96V$

$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \quad E° = 1.33V$

$2NO(g) + 6H^+ + Cr_2O_7^{2-} \rightarrow 2NO_3^- + 3H_2O + 2Cr^{3+}$

$E° = 0.37V$

$\Delta G° = -6(96485)(0.37) = \boxed{-214,197\ J/mol}$

c. $2(Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-)2 \quad E° = -1.51$

c. $2(Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-)2$ $\mathcal{E}^\circ = -1.51V$

$(Cl_2 + 2e^- \rightarrow 2Cl^-)5$ $\mathcal{E}^\circ = 1.36V$

$2Mn^{2+} + 5Cl_2(g) + 8H_2O \rightarrow 2MnO_4^- + 10Cl^- + 16H^+$

$\Delta G^\circ = -10(96485)(-0.15V)$ $\mathcal{E}^\circ = -0.15V$

$\Delta G^\circ = 144727.5\ J/mol$

2. $\Delta G = -671535\frac{J}{mol} + 8.314\frac{J}{mol\cdot K}(298.15K)\ln\frac{0.175}{15\times10^{-9}} = -631{,}199\frac{J}{mol}$

3. The oxidation is highly unfavored ($E^\circ_{ox} = -1.82V$). Only a very good oxidizing agent can accomplish this... it must be $E^\circ_{red} > 1.82V$

O_3 + F_2 are the only things

4. $Cl_2 \rightarrow 2Cl^-$ vs. $Br_2 \rightarrow 2Br^-$

Chlorine is more electronegative... it attracts electrons better than Br

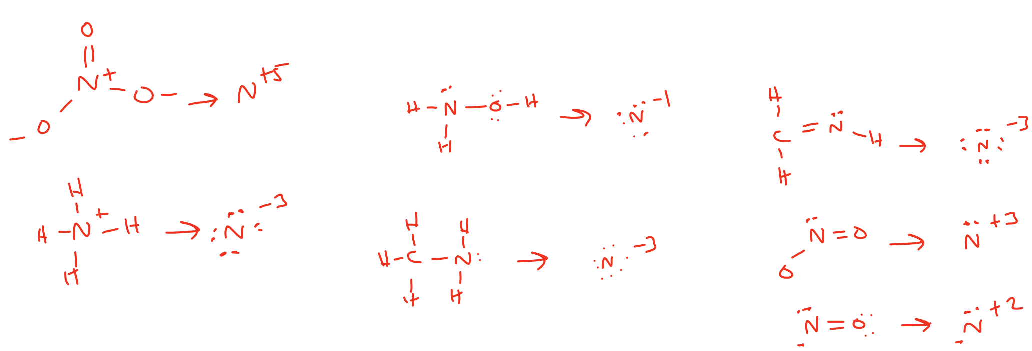
Al^{3+} vs. $Al(s)$

Al(s) getting reduced would make $Al^- \rightarrow$ metals are NEVER anions!

Li(s) Really wants to get oxidized! $Li(s) \rightarrow Li^+ + e^-$

This process creates a full $1s^2$ config. All e^- are really close to the nucleus & very stable!

5.



$NH_4^+ = CH_3NH_2 = CH_2NH < NH_2OH < NO < NO_2^- < NO_3^-$

Nitrogen is bonded to less electronegative atoms only.

6. a. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

b. $\Delta G = -2870{,}000 \frac{J}{mol} + 8.314\,(298.15) \ln \frac{(1.5)^6}{(1E-6)^6 (1E-6)} =$

$\Delta G = -2629271\ J/mol$

c. Can't solve because calculator limitations

d. $O_2 \rightarrow$ H–O–H or O=C=O

ox. state = 0 ; ox. state = −2 ; −2

each oxygen atom can accept $2e^-$ (or 4 per O_2)

e. $6O_2 \left(\frac{4e^-}{O_2}\right) = 24e^-$

f. $\Delta G^\circ = -nF\mathcal{E}^\circ$

$-2870000 = -24\,(96485)\,\mathcal{E}^\circ$

$E^\circ = 1.239\ V$

g. $6H_2O + C_6H_{12}O_6 \rightarrow 6CO_2 + 24H^+ + 24e^-$ $E^\circ =$?

$(4e^- + 4H^+ + O_2 \rightarrow 2H_2O)\,6$ $E^\circ = 1.23\ V$

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $E^\circ = 1.239\ V$

$E^\circ_{ox} = 1.239 - 1.23 = 0.009\ V$

h. glucose oxidation is $+0.009V$. so any $E^\circ_{red} > -0.009V$

$Li^+ \rightarrow$ NO! $Mn^{2+} \rightarrow$ NO $Ca^{2+} \rightarrow$ NO

$Au^{3+} \rightarrow$ yes $Zn^+ \rightarrow$ NO

7. a. If Na^+ comes into the cell, this would make the inside more (+)
$\Delta\psi$ would become more positive

b. The $\Delta\psi < 0$ provides a thermodynamic driving force ($\Delta G = ZF\Delta\psi$). without this, Na^+ transport cannot fuel glucose transport

c. $Na^+_{out} \rightleftharpoons Na^+_{in}$ $\Delta G_c = 8.314\,(310.15) \ln \frac{140}{12} = 6334.9\ J/mol$

$\Delta G_{MP} = +1\,(96485)\,(-0.07) = -6753.95\ J/mol$

$\Delta G = \Delta G_c + \Delta G_{MP} = -419.04\ J/mol$

ΔG for export $= 419.04 \frac{J}{mol}$ for out → in

d. $\frac{37{,}000\ J}{mol} \left| \frac{1\ mol\ Na^+}{419\ J} \right. =$ **88 Na^+ ions for 1 ATP**

8. a. Into the cell. $\Delta\Psi > 0$ means the inside is positive. Cl^- is attracted to the (+) inside the cell.

b. $\Delta G = 8.314(310.15) \ln \frac{86}{28} + (-1)(96485)(0.005)$

$\Delta G = 2411.1\ J/mol$

$Cl^-_{out} \rightleftarrows Cl^-_{in}$ reactants are favored!

← export

9. a. Ligand gated responds to neurotransmitter and allows all ions to pass. voltage gated responds to $\Delta\Delta\Psi$ and are specific to one type of ion

b. increase it

c. it is $\Delta\Psi$ at which ion transport is at equilibrium. Any deviation from this value allows you to easily predict the direction of ion flow

d. $\Delta G_c = 8.314(310.15) \ln \frac{86}{28} = 2893.5$

$-2893.5 = (-1)(96485)\Delta\Psi$ $\Delta\Psi = 0.025$

25 mV

e. i because cations (K^+) are leaving the cell

ii. This is the equilibrium potential for K^+.

iii. $\Delta G = (8.314)(310.15) \ln \frac{14}{143} + (1)(96485)(-0.0981)$

$\Delta G = -15{,}457\ J/mol$

↳ this is the energy released when Na^+ comes INTO the cell.

it takes $15{,}457 \frac{J}{mol}$ of energy to move Na^+ OUT

ATP hydrolysis provides $-37{,}000$, so yes, there is enough energy!