Chemistry 102 2018 Discussion #10, Chapter 16

Student name___________________ TA name________________ Section_______________

Things you should know when you leave Discussion today:

1. Potential $E°_{cell}$ at standard conditions.(all concentrations are at 1M)
2. Cell potential $E°$ [J/C] is a measure of electrical potential difference.
   a. $E°_{cell} = E°_{red}$**(cathode)** – $E°_{red}$**(anode)**
   b. $E° = \frac{0.05912V}{n_e} \log K$ (at 25°C);
3. Magnitude of the cell potential is a measure of the available energy from the reaction.

$$E = E° - \frac{0.05912V}{n_e} \log Q = -\frac{0.05912V}{n_e} \log \frac{Q}{K} \quad \text{at 25°C only}$$

   a. If $Q=1$ then $E = E°$ indicating we are at standard state conditions. (All concentrations are 1M and all pressures are 1atm)
   b. If $Q=K$ then $E = 0$ indicating we are at equilibrium
      i. $E>0$ forward reaction proceeds
      ii. $E<0$ reverse reaction proceeds
      iii. $E=0$ no electron flow (battery is dead)

1. Is the following expression at at 25°C $E = E° - \frac{0.05912V}{n_e} \log Q$

   Always true never true only true when Q=1 only true when Q=K

2. Is the following expression at 25°C $E° = \frac{0.05912V}{n_e} \log K$

   Always true never true only true when Q=1 only true when Q=K

3. Is the following expression $E=0$

   Always true never true only true when Q=1 only true when Q=K

4. Is the following expression $E = E°$

   Always true never true only true when Q=1 only true when Q=K

5. If $E = -2.00$ V and $E° = 1.00$ V circle everything that must be true: (Hint: remember what does it mean for Q to be equal to1?)

   Q=*1* ***Q>1*** ***Q<1*** ***$Q<K_{eq}$*** ***$Q=K_{eq}$*** ***$Q>K_{eq}$***

   a. **(at home)** Assuming the temperature is 25ºC and n_e= 2.00 mol calculate the values of K_{eq} and Q to 1 sig. fig. (Answers: $2 \cdot 10^{33}$, $1 \cdot 10^{100}$)

6. For a reaction **A(aq) + B(aq) <==> 2C(aq)** at 298K

a. ***E*** = 2.00 V and ***E*°** = – 1.00V and n_e= 2.00mol circle everything that must be true:

Q=1 ***Q>1*** ***Q<1*** ***$Q<K_{eq}$*** ***$Q=K_{eq}$*** ***$Q>K_{eq}$***

b. If the concentration of C is doubled what is the ***Q_{new}/Q_{old}***?

c. If the concentration of C is doubled what is the new value of *E*°.

d. If concentration of the C is tripled how will the magnitude of **E** increase or decrease?

e. *(*At home calculate the new value of *E)(Answer:1.97)*

7. You have an electrochemical cell consisting of two separate solutions. Coming out of the first solution is a lead electrode and a platinum electrode is coming out of the second solution.

From last week handout: **$Pt(s) \mid H_2(g) \mid H_3O^+(aq) \parallel PbSO_4(s) \mid SO_4^{2-}(aq) \mid Pb(s)$**

Anode (oxidation takes place): $H_2(g) \Leftrightarrow 2H^+(aq) + 2e^-$ $E°_{red} = 0V$

Cathode (reduction takes place): $PbSO_4(s) + 2e^- \Leftrightarrow Pb(s) + SO_4^{2-}(aq)$ $E°_{red} = -0.36V$

$$E°_{cell} = E°_{red}(\text{cathode}) - E°_{red}(\text{anode}) = -0.360V - 0V = -0.360V$$

Net reaction: $2H_2O + H_2(g) + PbSO_4(s) \Leftrightarrow 2H_3O^+(aq) + Pb(s) + SO_4^{2-}(aq)$ $n_e = 2$

$$E = E° - \frac{0.05912V}{n_e} \log Q \qquad Q = \frac{(H_3O^+)^2 (SO_4^{2-})}{(H_2(g))}$$

Check-off one of the following:

Change in the cell	*Increase in E*	*Decrease in E*	*No effect on E*
1) increase in pH of the solution $[H_3O^+]$ decreases			
2) dissolving $Na_2SO_4(s)$ in the solution K_{sp} >>1			
3) increase in size of the Pb(s) electrode			
4) decrease in H_2 gas pressure			
5) increase H_2 gas pressure			
6) increase in the amount of $PbSO_4(s)$ K_{sp}<<1			
7) adding HCl in the solution			
8) addition of water to the solution (hint: how does concentration vary with volume?)			

Net reaction: $2H_2O + H_2(g) + PbSO_4(s) \Leftrightarrow \mathbf{2H_3O^+}(aq) + Pb(s) + SO_4^{2-}(aq)$ $n_e = 2$

$$\boldsymbol{E = E° - \frac{0.05912V}{n_e} logQ} \qquad \mathbf{Q} = \frac{(H_3O^+)^2(SO_4^{2-})}{(H_2(g))}$$

a. At Q=1 was the reaction a spontaneous proces?

For the following questions [SO_4^{2-}(aq)] and p(H_2(g)) are kept at standard states. You can only change concentration of [H_3O^+].

b. What pH is needed for $E_{cell} = E°_{cell}$?
(Answer:0)

c. Calculate equilibrium constant:
(Answer: $6.6 \cdot 10^{-13}$)

d. What pH is needed for $E_{\text{cell}} = 0$?
(Answer: 6.1)

e. Give an example of the pH that will make this reaction spontaneous. (Explain why):

f. If the cell pH=10, what is E_{cell} ? Was this process spontaneous at pH=10?
(Answer: 0.23)

8. Answer the questions for the following redox reaction at 25 ºC. (Answers: *1.56,0.01, 1.62)*
($E°_{\text{red}}(Zn^{2+} | Zn) = -0.76$ V; $E°_{\text{red}}(Ag^+ | Ag) = 0.80$ V)

$$Zn(s) \mid Zn^{2+}(aq, 0.01M) \parallel Ag^+(aq, 1M) \mid Ag(s)$$

a. Cathodic RXN:

b. Anodic RXN:

c. Net RXN:

d. E^o_{cell} =

e. Q=

f. E_{cell} =

9. Answer the questions for the following redox reaction(Answers: 0, 0.09) :

$Cu(s) \mid Cu^{2+}(aq, 0.001M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$ $E^{o}_{red}(Cu^{2+} \mid Cu) = 0.34V$

a. Cathode RXN:

b. Anode RXN:

c. Net RXN:

d. E^{o}_{cell} =

e. Q=

f. E_{cell} =

10. Answer the questions for the following redox reaction at 25 ºC. (Answer: 0, 0.18)

$Ag(s) \mid Ag^{+}(aq, 0.0010M) \parallel Ag^{+}(aq, 1.0M) \mid Ag(s)$

a. Cathodic RXN:

b. Anodic RXN:

c. Net RXN:

d. E^{o}_{cell} =

e. Q=

f. $\boldsymbol{E_{cell}}$ **=**

11. Calculate the voltage (E) of a concentration cell constructed with the Cl^{-} concentration difference between sea water and river water at 25 ºC. Assume that the Cl^{-} concentration (due to dissolved NaCl) of sea water is 35 g/L and then that of river water is 1.0 mg/L. (Answers: 0, 0.27)

a. Cathode RXN:

b. Anode RXN:

c. E^{o}_{cell} =

d. Q=

e. E_{cell} =

12. The standard cell potential for the process of **A(aq) + B(aq) <==> 2C(aq)** at 25 °C in which three moles of electrons are transferred is $\boldsymbol{E^o_{cell}}$ = **3.00 V**. An electrochemical cell for this process is constructed and the measured voltage is $\boldsymbol{E_{cell}}$ **= 5.00 V.** Circle all the correct statements. (Answers: 10^{152}, 3.00, 9, 4.98, 4.99)

    a. $Q<1$ $Q = 1$ $Q > 1$ $Q = K$ $Q > K$ $Q < K$

    b. If concentration of the C is tripled will the new $\boldsymbol{E^o_{cell}}$

    Increase **Decrease** **Stay the same**

    c. If concentration of the C is tripled how will the magnitude of ***E*** change?

    Increase **Decrease** **Stay the same**

    d. If concentration of the C is tripled what is the new $\mathbf{Q_{new}/Q_{old}}$ =

    e. What is a new value of *E*?

    f. If the concentration of C is doubled (assuming the temperature is 298K), calculate the new value of ***E.***

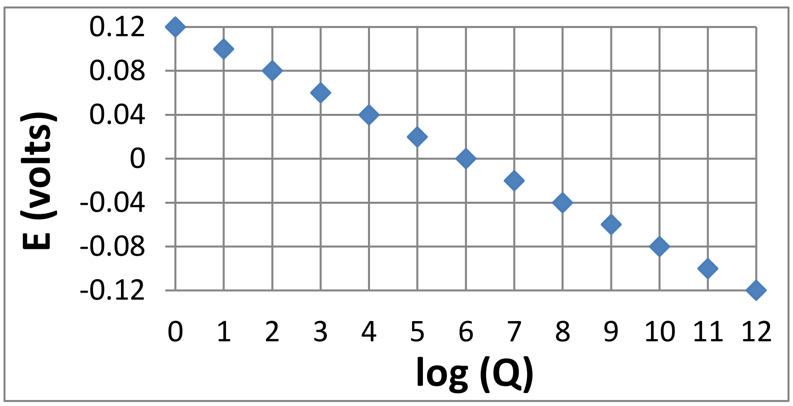
    g. Calculate K:

13. ADP is converted to ATP in mitochondria of human cells. The energy required for this process is provided in part by the concentration of H_3O^+ being high outside than inside the inner membrane of the mitochondria. The concentration difference results in an electrochemical potential $E = 0.150$ V across the membrane. Calculate the ratio $[H_3O^+(\text{outside})]/[H_3O^+(\text{inside})]$ that accounts for this electrochemical potential. Assume $E = -\frac{0.06V}{n_e} log \frac{Q}{K}$ (Answer: $3 \cdot 10^2$)

$[H_3O^+(\text{outside})]/[H_3O^+(\text{inside})]$ = ______

14. The voltage of an electrochemical cell for the reaction 2 C(*s*) + D^{2+}(*aq*) → 2 C^{+}(*aq*) + D(*s*) is *E* = 0.80 volts when *Q* = 0.10 at 25 ºC. Calculate the voltage at 25 ºC after the solution in the cathode is diluted so that the ion concentrations in the cathode are reduced to exactly half their starting concentrations.(Answer:0.79)

15. Below is a plot of the measured voltage at 298 K of an electrochemical cell at different values of log(Q). (Answers: 0.12, 3)



a) Determine E^{o}_{cell} from the plot.

b) How many moles of electrons are transferred per mole of reaction?

In preparation for next week and information for take home quiz 9.

1. http://quantum.bu.edu/courses/ch102-spring-2016/notes/SecondLaw.pdf

2. Calculating arrangements due to distribution of molecules:
   $W_{pos}(a,b,c,\ldots.) = \frac{(a+b+c+...)!}{a!b!c!....}$; Where a, b, c, ...— number of different particles
3. Calculating arrangements due to distribution of quanta (q) of energy among particles (m) or with (p) partitions(where p=m-1):
   $$W(m,q) = \frac{(q+p)!}{q!\,p!} = \frac{(q+(m-1))!}{q!(m-1)!};$$
4. Entropy S : S= k_B lnW ; $k_B = 1.381 \times 10^{-23}$ J/K is a Boltzmann constant)

   i. $S_{total} = S_1+S_2 = R \ln W_{object1} + R \ln W_{object2} = R \ln(W_1 * W_2)$

   $$W_{total} = W_{object1} * W_{object2}$$

   ii. $\Delta S = S_{final} - S_{initial} = R \ln W_{final} - R \ln W_{initial} = R \ln(\frac{W_{final}}{W_{initial}})$

   $\Delta S > 0$ process is *spontaneous*: $\ln(\frac{W_{final}}{W_{initial}}) > 0$; $\frac{W_{final}}{W_{initial}} > 1$; $W_f > W_{in}$

   $\Delta S < 0$ process is *not spontaneous*: $\ln(\frac{W_{final}}{W_{initial}}) < 0$; $\frac{W_{final}}{W_{initial}} < 1$; $W_f < W_{in}$

Look up the following concepts in Human Activity, Chemical reactivity, Mahaffy et al., 2e, pages 671-684

1. State the Second Law of Thermodynamics:

2. Define $\Delta S_{universe}(\Delta S_{net})$

3. What is the relationship between ΔS_{system} and $\Delta S_{reaction}$?

4. What equation relates ΔS_{system} and ΔH_{system} when the system is at equilibrium?

5. What is the relationship between $\Delta S_{surrounding}$ and $\Delta S_{reaction}$?

6. What equation relates $\Delta S_{surrounding}$ and $\Delta H_{surroundings}$?

7. What equation relates $\Delta S_{surrounding}$ and ΔH_{system}?