Student name_____ TA name_____ Section_____

Things you should know when you leave Discussion today:

1. Reduction potential E°$_{red}$ at standard conditions use Chemistry: Human Activity, Chemical reactivity, Mahaffy et al., 2e Appendix F for information.
2. Cell potential $E_{cell}° = \frac{Joule}{charge}$ or Volt (V) is a measure of electrical potential difference.

$$E_{cell}° = E_{red(cathode)}° - E_{red(anode)}° = \frac{0.05912\ V}{n_e} \cdot \log K \quad (@25°C)$$

3. http://quantum.bu.edu/courses/ch102-spring-2016/notes/BalancingRedoxEquations.pdf
4. http://quantum.bu.edu/courses/ch102-spring-2016/notes/StandardRedcutionPotentials.pdf
5. Gibbs free energy and potential $\Delta G° = -n_e \cdot F \cdot E°$ where $F = 96485.3 \frac{charge}{mol\ (of\ electrons)}$
6. Magnitude of the cell potential is a measure of the available energy from the reaction.
7.

$$E = E° - \frac{0.05912\ V}{n_e} \cdot \log Q = -\frac{0.05912\ V}{n_e} \cdot \log \frac{Q}{K} \quad (@25°C)$$

   a. If Q = 1 then E = E° indicating we are at standard state conditions
   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. Choose all that must be true:
   a. Anode is an electrode where oxidation takes place
   b. Cathode is an electrode where reduction takes place
   c. Most positive reduction potential represents the strongest oxidizing agent (an oxidizing agent is an electron acceptor and is most likely to get reduced)
   d. Most negative reduction potential represents strongest reducing agent (most likely to get oxidized)
   e. E° is an intensive quantity as long as concentration does not change it does not depend on the size of the cell
   f. E° does not depend on the amount of charge transferred
   g. E° does not depend on stoichiometry (doubling the stoichiometry of all the species in the reaction has no effect on the E°)
   h. Sign of the cell potential tells the direction of electron flow
   i. Only reduction potentials are listed in the reference tables (oxidation potentials can be calculated from reduction potentials E°$_{ox}$ =−E°$_{red}$)

2. Write the balanced equation for the oxidation of $NO_{(g)}$ to $NO_3^-{}_{(aq)}$ by reduction of dichromate, $Cr_2O_7^{2-}{}_{(aq)}$ to $Cr^{3+}{}_{(aq)}$. Assign for each half-reaction if it is a cathodic half-reaction or an anodic half-reaction.
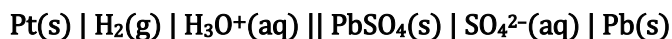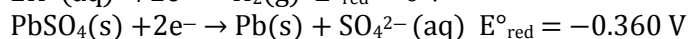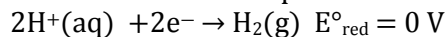
Oxidation half-reaction:

Reduction half-reaction:

Net reaction in acidic media:

Write the line notation for the galvanic cell corresponding to the redox reaction, using platinum electrodes, Pt$_{(s)}$, if needed.

3. You have an electrochemical reaction that takes place in acidic solution of lead sulfate. Coming out of solution is a lead electrode and a platinum electrode.

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E°_{red} = 0 \text{ V}$$
$$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq) \quad E°_{red} = -0.360 \text{ V}$$

$$\text{Pt(s) | H}_2\text{(g) | H}_3\text{O}^+\text{(aq) || PbSO}_4\text{(s) | SO}_4^{2-}\text{(aq) | Pb(s)}$$

Anode half-reaction:

Cathode half-reaction:

NET reaction:

Q =

E°$_{cell}$ =

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$_3$O$^+$] decreases			
2) Dissolving Na$_2$SO$_4$(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: $2H_2O + H_2(g) + PbSO_4(s) \leftrightarrows 2H_3O^+ (aq) + Pb(s) + SO_4^{2-} (aq)$ $n_e = 2$

$$E = E° - \frac{0.05912 \text{ V}}{n_e} \cdot \log Q \qquad\qquad Q = \frac{(H_3O^+)^2(SO_4^{2-})}{\left(H_{2(g)}\right)}$$

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 $E_{cell} = E°_{cell}$?

c. Calculate the equilibrium constant:

d. What pH is needed for $E_{cell} = 0$?

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?

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

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

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

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

6. Is the following expression $E = 0$

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

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

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

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

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

    a. Assuming the temperature is 25°C and $n_e = 2.00$ mol calculate the values of K_{eq} and Q to one significant figure.

3

9. For a reaction $A(aq) + B(aq) \rightleftharpoons 2C(aq)$ at 298K

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

$$Q = 1 \quad Q > 1 \quad Q < 1 \quad Q < K_{eq} \quad Q = K_{eq} \quad Q > K_{eq}$$

    b. If the concentration of C is doubled what is the $\frac{Q_{new}}{Q_{old}}$?

    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. What is new new value of E?

10. Answer the questions for the following redox reaction at 25°C. $E°_{red}(Zn^{2+} | Zn) = -0.76$ V; $E°_{red}(Ag^+ | Ag) = 0.80$ V

$$Zn(s) | Zn^{2+}(aq, 0.01M) || Ag^+(aq, 1M) | Ag(s)$$
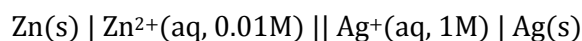
    a. Cathodic reaction:

    b. Anodic reaction:

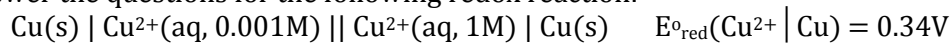   c. Net reaction:

    d. $E°_{cell} =$

    e. Q=

    f. $E_{cell} =$

11. Answer the questions for the following redox reaction:
    $Cu(s) | Cu^{2+}(aq, 0.001M) || Cu^{2+}(aq, 1M) | Cu(s)$ $E°_{red}(Cu^{2+} | Cu) = 0.34$V
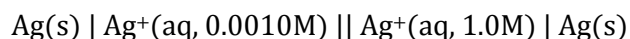
    a. Cathode reaction:

    b. Anode reaction:

    c. Net reaction:

    d. $E°_{cell} =$

    e. Q=

    f. $E_{cell} =$

12. Answer the questions for the following redox reaction at 25°C.

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

    a. Cathodic reaction:

    b. Anodic reaction:

    c. Net reaction:

    d. $E^o_{cell} =$

    e. $Q =$

    f. $E_{cell} =$

13. Calculate the voltage (E) of a concentration cell constructed with the Cl- concentration difference between sea water and river water at 25°C. 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.

    a. Cathode reaction:

    b. Anode reaction:

    c. $E^o_{cell} =$

    d. $Q=$

    e. $E_{cell} =$

14. The standard cell potential for the process of $A_{(aq)} + B_{(aq)} \rightleftarrows 2C_{(aq)}$ at 25°C in which three moles of electrons are transferred is $E^o_{cell} = 3.00$ V. An electrochemical cell for this process is constructed and the measured voltage is $E_{cell} = 5.00$ V. Circle all the correct statements.

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

    b. If concentration of the C is tripled, will the new E^o_{cell} will:

                      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 $Q_{new}/Q_{old} =$

    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:

15. 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 $\dfrac{[H_3O^+{}_{outside}]}{[H_3O^+{}_{inside}]}$ that accounts for this electrochemical potential.

Assume $E = -\dfrac{0.05912\ V}{n_e} \cdot \log\dfrac{Q}{K}$

16. The voltage of an electrochemical cell for the reaction $2\ C_{(s)} + D^{2+}{}_{(aq)} \rightarrow 2\ C^+{}_{(aq)} + D_{(s)}$ is $E = 0.80$ volts when $Q = 0.10$ at 25°C. Calculate the voltage at 25°C after the solution in the cathode is diluted so that the ion concentrations in the cathode are reduced to exactly half their starting concentrations.

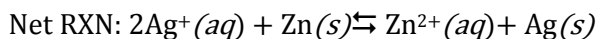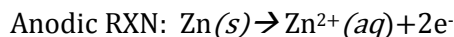17. Below is a plot of the measured voltage at 298 K of an electrochemical cell at different values of log(Q).
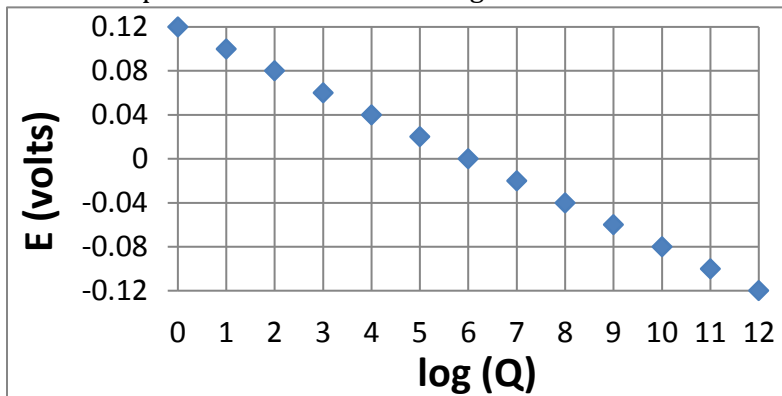
a) Determine $E°_{cell}$ from the plot.

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

Handout Answers:

1.
2.
3. E = -0.360 V
    a. No
    b. 0
    c. K=6.6·10⁻¹³
    d. pH = 6.1
    e. pH>6
    f. 0.24, Yes
4. Always true
5. Always true

6. Only true when Q=K
7. Only true when Q=1
8.
    a. Q>1, Q>K_{eq}
    b. 7·10³³; 10¹⁰⁰
9.
    a. Q<1, Q< K_{eq}
    b. 4
    c. -1 V
    d. 1.97

10. Cathodic RXN: $2Ag^+ (aq) + 2e^- \rightarrow Ag(s)$

   Anodic RXN: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

   Net RXN: $2Ag^+ (aq) + Zn(s) \leftrightarrows Zn^{2+}(aq) + Ag(s)$

   $E°_{cell} = 0.80V + 0.76V = 1.56V$ $E_{cell} = 1.56V - \dfrac{0.05912V}{n_e} \log\dfrac{0.01}{1^2} = 1.62V$

11.
    a. Cathode RXN $Cu^{2+}(aq,\ 1M) + 2e^- \rightarrow Cu(s)$
    b. Anode RXN: $Cu(s) \rightarrow Cu^{2+}(aq,\ 0.001M) + 2e^-$
    c. Net RXN: $Cu\ (aq,\ 1M) \leftrightarrows Cu^{2+}(aq,\ 0.001M)$
    d. $E°_{cell} = 0V$
    e. $Q = \dfrac{[Cu2+(aq,0.001M)]}{[Cu2+(aq,1M)]} = 0.001$
    f. $E_{cell} = 0 - \dfrac{0.05912V}{n_e} \log 0.001 = 0.09V$; $n_e = 2$

12. Cathodic RXN: $Ag^+ (aq,\ 1M) + e^- \rightarrow Ag(s)$

6

Anodic RXN: $Ag(s) \rightarrow Ag^+ (aq, 0.001M) + e^-$

Net RXN: $Ag(aq, 1M) \leftrightarrows Ag^+ (aq, 0.001M)$

$E^o_{cell} = 0V$ $\boldsymbol{E_{cell}} = 0 - \dfrac{0.05912V}{n_e} \log 0.001 = 0.18V;$ $n_e = 1$

13. Cathodic RXN : $2Cl^-(aq) \rightarrow Cl_{2(g)} + 2e^-$ (sea water)
    Anodic RXN: $Cl_2(g) + 2e^- \rightarrow 2Cl^-$ (aq) (river water)

$$E_{cell} = 0 - \dfrac{0.05912V}{n_e} \cdot \log \dfrac{\left(\dfrac{1\,mg}{L} \cdot \dfrac{g}{1000\,mg} \cdot \dfrac{35.5\,g}{mol}\right)^2}{\left(\dfrac{1\,mol}{L}\right)^2} = 0.27V;$$ $n_e = 2$

14.
   a. $Q < 1, Q < K$
   b. Stay the same
   c. Decrease
   d. 9
   e. *4.981*
   f. 4.988
   g. 10^{152}

15. $3 \cdot 10^2$
16. 0.79
17.
   a. 0.12
   b. 3

In preparation for next week and information for take home, quiz 8:

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

2. Calculating arrangements due to distribution of molecules:
$$W_{pos}(a,b,c,....) = \dfrac{(a+b+c+...)!}{a! \cdot b! \cdot c! ...};$$ 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):
$$W_{(m,q)} = \dfrac{(q+p)!}{q! \cdot p!} = \dfrac{(q+(m-1))!}{q! \cdot (m-1)!}$$

4. Entropy S: $S = k_B \cdot \ln W$; (where $k_B = 1.381 \times 10^{-23}$ J/K Boltzmann constant)

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

    ii. $\Delta S = S_{final} - S_{initial} = R \cdot \ln W_{final} - R \cdot \ln W_{initial} = R \cdot \ln \dfrac{W_{final}}{W_{initial}}$

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

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

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}?

<div align="center">Exam 2 Answers:</div>

1. 0.124 if $(K_1{}^2 \cdot K_2$ 2 points)
2.
    a. $NO_2(g)$ decrease
    b. K increase; $N_2O_3(g)$ decrease
    c. $NO_2(g)$ decrease
3.
    a. 0.93bar
    b. 0.57
4. $1.5 \cdot 10^{-10}$
5.
    a. Basic
    b. Basic
6.
    a. $1.36 \cdot 10^{-2}\%$
    b. $2.83 \cdot 10^{-13}M$
7. $2.04 \cdot 10^{-33}$ or $3.80 \cdot 10^{-30}$
8. $1.6 \cdot 10^{-6}$
9. $1 \cdot 10^{-5}$
10. $4.5 \cdot 10^{-13}$
11.
    a. 2.00 M
    b. -0.301
    c. $6.7 \cdot 10^{-}M$
12. HA is a weak acid; A^- is a weak base; $K_a > K_w$; $[H_3O^+] > [OH^-]$; $[A^-] < [HA]$