CH102 Spring 2019	9	
Discussion #9		
Chapter 15,16		
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1. At 20°C, an ionic solid,  $A_2X_{3(s)}$ , has a  $K_{sp} = 5.0 \times 10^{-14}$ . A 0.50L solution of 1.00 M  $A^{3+}_{(aq)}$  and a 0.50 L solution of 1.0 M  $X^{2-}_{(aq)}$  are combined, and  $A_2X_{3(s)}$  precipitates. Calculate the molarity of  $X^{2-}_{(aq)}$  after the combined solution has come to equilibrium.

2. The number of moles of a solid that dissolves in 1 liter of water is called the molar solubility. For  $Mn_3(PO_4)_2$ , the molar solubility is  $4.0 \times 10^{-5}$  M. What is the K<sub>sp</sub> for this compound?

3. The  $K_{sp}$  of Mg(OH)<sub>2</sub> is 5.6 x10<sup>-12</sup>. You have saturated solution of Mg(OH)<sub>2</sub>. What is the final concentration of OH<sup>-</sup> in the presence of 0.10 M MgCl<sub>2</sub> after equilibrium is reestablished.

### Useful information Chapter 16:

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

$$\mathbf{E}_{cell}^{\circ} = \mathbf{E}_{red(cathode)}^{\circ} - \mathbf{E}_{red(anode)}^{\circ} = \frac{0.05912 \text{ V}}{n_e} \cdot \log \mathbf{K} \qquad (@25^{\circ}\text{C})$$

- <u>http://quantum.bu.edu/courses/ch102-spring-2016/notes/BalancingRedoxEquations.pdf</u>
- Gibbs free energy and potential  $\Delta G^{\circ} = -n_e \cdot F \cdot E^{\circ}$  where F = 96485.3  $\frac{charge}{mol \ (of \ electrons)}$
- 4. 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.  $E^{\circ}$  does not depend on stoichiometry (doubling the stoichiometry of all the species in the reaction has no effect on the  $E^{\circ}$ )
  - 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  $E^{\circ}_{ox} = -E^{\circ}_{red}$ )
- 5. Write the balanced equation for the reduction of  $Fe^{2+}_{(aq)}$  to  $Fe_{(s)}$  using  $H_{2(g)}$ . Assign for each half-reaction if it is a cathodic half-reaction or an anodic half-reaction.

Oxidation half-reaction:

Reduction half-reaction

Net redox reaction in acidic media:

Draw the galvanic cell corresponding to the redox reaction:

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

 $E^{o}_{cell} =$ 

6. 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.

7. When zinc metal is burned in air, ZnO<sub>(s)</sub> is formed. Assuming the same chemical reaction, formation of zinc oxide from zinc metal, takes place instead in galvanic cell write the balanced reactions.

Oxidation half-reaction:

Reduction half-reaction:

Net reaction:

8. Answer the questions for the following redox reaction:  $Cu_{(s)} | Cu^{2+}_{(aq)} | | Ag^{+}_{(aq)} | Ag_{(s)}$ 

 $E_{red}^{o}(Cu^{2+} | Cu) = 0.34V$   $E_{red}^{o}(Ag^{+} | Ag) = 0.80 V$ 

- a. Cathode half-reaction:
- b. Anode half-reaction:
- c. Net reaction:
- d.  $E^{o}_{cell} =$
- 9. Write the balanced net reaction for aluminum solid reacting with lead (II) to yield lead solid and aluminum ion.
  - i. Give the line notation for the corresponding electrochemical cell.
  - ii. Given  $E^{\circ}_{red} (Pb^{2+} | Pb) = -0.13 V$  and  $E^{\circ}_{red} (Al^{3+} | Al) = -1.66 V$ , calculate the standard cell potential.

10. Answer the questions below using the list of standard reduction potentials.

	<u>E°<sub>red</sub> (V)</u>		<u>E°<sub>red</sub> (V)</u>
Pb <sup>4+</sup>   Pb <sup>2+</sup>	+1.67	In+   In	-0.14
Ce <sup>3+</sup>   Ce	+1.61	V3+   V2+	-0.26
Mn <sup>3+</sup>   Mn <sup>2+</sup>	+1.51	Cr <sup>3+</sup>   Cr <sup>2+</sup>	-0.41
$0_3   0_2$	+1.24	Fe <sup>2+</sup>   Fe	-0.44
Br <sub>2</sub>   Br-	+1.09	Zn <sup>2+</sup>   Zn	-0.76
Ag+   Ag	+0.80	Al <sup>3+</sup>   Al	-1.66

- a. Which one is the best oxidizing agent?
- b. Which one is the best reducing agent?
- c. Circle the species that will reduce  $Br_2$  but not  $V^{3+}$ :

In+ Al Ag Ce

d. Circle the species that will oxidize  $Cr^{2+}$  but not  $Mn^{2+}$ :

$$Pb^{4+}$$
  $Zn^{2+}$   $Fe^{2+}$   $O_3$ 

11. For each of the reactions below, circle all those that will have positive voltages. Assume all molecules are in their standard state concentrations unless otherwise given. The table below has standard reduction potentials and may be useful.

		Half-Reaction		$E^{\circ}_{red}(V)$	
a.	Fe <sup>3+</sup> is able to oxidize Ag.	Ag+   Ag		0.80	
		Fe <sup>3+</sup>	Fe <sup>2+</sup>	0.77	
b.	Ag <sup>+</sup> is able to oxidize Fe <sup>2+</sup> .	Fe <sup>2+</sup>   Fe		-0.44	

- c. Fe<sup>2+</sup> is able to oxidize Ag.
- d. Write the line notation for the cell with most positive standard cell potential:
- 12. 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.

 $2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g) E^{\circ}_{red} = 0 V$ PbSO<sub>4</sub>(s) + 2e<sup>-</sup>  $\rightarrow$  Pb(s) + SO<sub>4</sub><sup>2-</sup> (aq)  $E^{\circ}_{red} = -0.360 V$ 

# $Pt(s) | H_2(g) | H_3O^+(aq) || PbSO_4(s) | SO_4^{2-}(aq) | Pb(s)$

Anode half-reaction:

Cathode half-reaction:

NET reaction:

 $\rm E^{o}_{cell} =$ 

# Things you should know and review:

- Oxidation Reduction Reactions
  - i. Oxidation is <u>loss</u> of electrons (acts as a reducing agent)
  - ii. Reduction is gain of electrons (acts as a oxidizing agent)
- Assigning Oxidation numbers
  - i. Oxidation number is 0 for atoms in an element.
  - ii. The sum of all oxidation numbers in a molecule or ion must add up to the total charge.
  - iii. In compounds, alkalis (group 1) have oxidation number +1; alkaline earths (group 2) have oxidation number +2.
  - iv. In compounds, fluorine (F) always has oxidation number -1. Other halogens (Cl ext.) have oxidation number -1, *except when bonded to elements that are more electronegative* such as fluorine or oxygen, where they can have positive oxidation numbers.
  - v. In compounds, hydrogen has oxidation number +1 (*when bonded to elements with higher electronegativity*). When bonded to metals hydrogen has oxidation number -1 (*when bonded to elements with lower elecronegativity*).
  - vi. In compounds, oxygen has oxidation number -2, except when bonded to fluorine, where fluorine's rule takes precedence (in  $OF_2$  oxygen has oxidation number +2), and if there are 0-0 (peroxide) bonds. (in  $H_2O_2$  or  $Na_2O_2$  oxygen has oxidation number -1).
- Steps for Balancing Redox reactions in Acidic or Basic media (always start with acidic).
  - 1. Write the two half reactions.
  - 2. Balance all the elements except for 0 and H.
  - 3. Balance O by adding H<sub>2</sub>O.
  - 4. Balance H by adding H<sup>+</sup>.
  - 5. Balance charge by adding electrons to the side of the half reaction that is most positive.
  - 6. Balance electrons lost in one half reactions with electrons gained in the other half reaction.
  - 7. Add half reactions together canceling what can be canceled.
  - 8. Determine if your answer should be in acidic media or basic media
    - If in acidic media: Add water to both sides in order to convert all  $H^+$  to  $H_3O^+$ a) Combine  $H^+$  and  $H_2O$  to form  $H_3O^+$ 
      - b) Simplify the reaction by canceling the H<sub>2</sub>O that appear on both sides
      - If in basic media: Add enough OH- to neutralize H+ to both sides of the reaction.
        - a) Combine  $OH^{-}$  and  $H^{+}$  to form  $H_2O$ .
      - b) Simplify the reaction by canceling  $H_2O$  that appear on both sides.
- http://quantum.bu.edu/courses/ch102-spring-2016/notes/BalancingRedoxEquations.pdf
- 1. Balance the following reaction:  $MnO_4^{-}(aq) + C_2O_4^{2-}(aq) \rightarrow MnO_2(aq) + CO_2(g)$ .

Oxidation half-reaction:

Reduction half-reaction:

Net reaction in acidic media:

Net reaction in basic media:

2. Balance the following reaction:  $IO_{3}(aq) + I_{2}(aq) \rightarrow I_{2}(aq)$ .

Oxidation half-reaction:

Reduction half-reaction:

Net reaction in acidic media:

Net reaction in basic media:

- 3. Balance the redox reaction of  $H_2$  (g) reducing  $Au^{3+}$  (aq) to produce solid gold in an acidic solution.
- 4. Balance the following reaction in basic media:  $Fe^{2+}(aq) + MnO_{4^{-}}(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$
- 5. Write down the balanced oxidation half-reaction for the complete combustion of glucose,  $C_6H_{12}O_6$ , in aqueous acidic solution.
- 6. Use the steps provided to balance following oxidation reduction reactions in acidic and basic media.

a.  $Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$ 

b.  $S^{2-}(aq) + I_{2}(aq) \rightarrow SO_{4^{2-}}(aq) + I^{-}(aq)$ 

## **Numerical Answers**

1. 12·10<sup>−5</sup>M 2. 1.1·10<sup>-20</sup> M 3. 7.5·10<sup>−6</sup> M 4. 5.  $Fe^{2+}(aq) + H_2(g) + 2H_2O(l) \rightarrow Fe(s) + 2H_3O^+(aq)$  $Pt(s) | H_2(g) | H_3O^+(aq) || Fe^{2+}(aq) || Fe(s)$  $E_{cell}^{o} = -0.44V$ 6.  $Cr_2O_7^{2-}(aq) + 2NO(g) + 6 H_3O^+(aq) \rightarrow 2Cr^{3+}(aq) + 2NO_3^{-}(aq) + 9H_2O$  $Pt(s) | NO(g) | NO_{3}(aq) || Cr_2O_{7}(aq) , Cr^{3+}(aq) | Pt(s)$ 7. <u>Anode:</u>  $2H_2O(l) + 2Zn(s) \rightarrow 2ZnO(s) + 4H^+(aq) + 4e^{-1}$ <u>Cathode:</u>  $4H^+(aq) + 4e^- + O_2(g) \rightarrow 2H_2O(l)$ Net RXN:  $O_2 + 2 Zn(s) = 2ZnO(s)$ Zn(s),  $ZnO(s) || O_2(g) | H_2O(aq) | Pt(s)$ 8. 0.46V 9. Al (s)  $|A|^{3+}$  (aq)  $||Pb^{2+}_{(aq)}||Pb(s)$ , 1.53V 10. a. Pb4+ b. Al c. Ag d.  $0_3$ 11. a. No b. Yes c. No d.  $Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) || Ag^{+}(aq) || Ag(s)$ 

12.  $H_2(g) + PbSO_4(s) \rightarrow Pb(s) + SO_{4^2}(aq) + 2H^+(aq); E^{\circ}_{cell} = -0.36$ 

#### Extra balancing problems:

- 1. Acidic:  $3C_2O_{4^2}(aq) + 2MnO_{4^-}(aq) + 8H_3O^+ \rightarrow 6CO_2(g) + 2MnO_2(aq) + 12H_2O$ Basic:  $3C_2O_{4^{2^-}}(aq) + 2MnO_{4^-}(aq) + 8H_2O \rightarrow 6CO_2(g) + 2MnO_2(aq) + 8OH^-$
- 2. Acidic:  $12 H_3O^+ + 2 IO_3^-(aq) + 10 I^-(aq) \rightarrow 6I_2(aq) + 18H_2O$ Basic:  $6H_2O + 2IO_3^-(aq) + 10I^-(aq) \rightarrow 6I_2(aq) + 12OH^-$
- 3.  $2Au^{3+}(aq) + 3H_2(g) + 6H_2O(l) \rightarrow 2Au(s) + 6H_3O^+(aq)$
- 4.  $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H_3O^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 12H_2O(l)$
- 5.
- a. Acidic:  $4H_3O^+(aq) + 2NO_3^-(aq) + Cu(s) \rightarrow 2NO_2(g) + 6H_2O(l) + Cu^{2+}(aq)$ Basic:  $2H_2O(l) + 2NO_3^-(aq) + Cu(s) \rightarrow 2NO_2(g) + 4OH^-(aq) + Cu^{2+}(aq)$
- b. Acidic:  $4I_2(aq) + 12H_2O(l) + S^{2-}(aq) \rightarrow SO_{4^{2-}}(aq) + 8H_3O^+(aq) + 8I^-(aq)$ Basic:  $4I_2(aq) + 8OH^-(aq) + S^{2-}(aq) \rightarrow SO_{4^{2-}}(aq) + 8I^-(aq) + 4H_2O(l)$
- 6.  $30H_2O + C_6H_{12}O_6(s) \rightarrow 6CO_2(g) + 24H_3O^+(aq) + 24e^{-1}$