## CHEM 1423 Chapters 21 Homework Solutions

#### **TEXTBOOK HOMEWORK**

**Note:** In various homework questions, the author is assuming that you're looking up the Reduction Potential in Appendix D. On a test, you will be given the required Reduction Potentials. In addition, the table will be displayed on the web site.

- 21.5 (a) Cl<sup>-</sup> is oxidized
  - (b) MnO<sub>4</sub> is reduced
  - (c) MnO<sub>4</sub> is the oxidizing agent
  - (d) Cl<sup>-</sup> is the reducing agent
  - (e) Electrons flow from Cl<sup>-</sup> which is losing electrons, to MnO<sub>4</sub><sup>-</sup> which is gaining electrons
  - (f)  $8 \text{ H}_2\text{SO}_4(\text{aq}) + 2 \text{ KMnO}_4(\text{aq}) + 10 \text{ KCl}(\text{aq}) \square$  $2 \text{ MnSO}_4 + 5 \text{ Cl}_2(\text{g}) + 8 \text{ H}_2\text{O}(\text{l}) + 6 \text{ K}_2\text{SO}_4(\text{aq})$

**21.9** (a) 
$$Sb + NO_3^- \rightarrow Sb_4O_6 + NO$$
 (acid)

### **Initial Half Reactions**

Red:  $NO_3^- \rightarrow NO$ 

 $Oxid: Sb \rightarrow Sb_4O_6$ 

### **Balanced Half Reactions**

Red: 
$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$

$$Oxid: 4Sb + 6H_2O \rightarrow Sb_4O_6 + 12H^+ + 12e^-$$

## Mult Red Rxn. by 4, Oxid. Rxn. by 1 and add

$$4 \text{ NO}_{3}^{-} + 16 H^{+} + 12 e^{-} + 4 Sb + 6 H_{2}O \rightarrow$$

$$4NO + 8H_2O + Sb_4O_6 + 12H^+ + 12e^-$$

### Cancel to get final balanced reaction

$$4 \text{ NO}_{3}^{-} + 4 H^{+} + 4 Sb \rightarrow 4 NO + 2 H_{2}O + Sb_{4}O_{6}$$

(b) 
$$Mn^{2+} + BiO_3^- \to MnO_4^- + Bi^{3+}$$
 (acid)

### **Initial Half Reactions**

Red:  $BiO_3^- \rightarrow Bi^{3+}$ 

 $Oxid: Mn^{2+} \rightarrow MnO_4^-$ 

### **Balanced Half Reactions**

Red:  $BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{3+} + 3H_2O$ 

 $Oxid: Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$ 

# Mult Red Rxn. by 5, Oxid. Rxn. by 2 and add

 $5BiO_3^- + 30H^+ + 10e^- + 2Mn^{2+} + 8H_2O \rightarrow$ 

 $5Bi^{3+} + 15H_2O + 2MnO_4^- + 16H^+ + 10e^-$ 

## Cancel to get final balanced reaction

 $5BiO_3^- + 14H^+ + 2Mn^{2+} \rightarrow 5Bi^{3+} + 7H_2O + 2MnO_4^-$ 

# (c) $Fe(OH)_2 + Pb(OH)_3^- \rightarrow Fe(OH)_3 + Pb$ (basic)

### **Initial Half Reactions**

Red:  $Pb(OH)_3^- \rightarrow Pb$ 

 $Oxid: Fe(OH)_2 \rightarrow Fe(OH)_3$ 

### **Balanced Half Reactions**

Red:  $Pb(OH)_3^- + 3H^+ + 2e^- \rightarrow Pb + 3H_2O$ 

 $Oxid: Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^-$ 

# Mult Red Rxn. by 1, Oxid. Rxn. by 2 and add

 $Pb(OH)_{3}^{-} + 3H^{+} + 2e^{-} + 2Fe(OH)_{2} + 2H_{2}O \rightarrow$ 

 $Pb + 3H_2O + 2Fe(OH)_3 + 2H^+ + 2e^-$ 

# Cancel to get final balanced reaction IN ACID SOLUTION

 $Pb(OH)_{3}^{-} + H^{+} + 2 Fe(OH)_{2} \rightarrow Pb + H_{2}O + 2 Fe(OH)_{3}$ 

# Add OH to each side and cancel waters to get final balanced reaction in BASIC SOLUTION

 $Pb(OH)_3^- + 2Fe(OH)_2 \rightarrow Pb + 2Fe(OH)_3 + OH^-$ 

**21.27** 
$$2Se^{2-} + 2SO_3^{2-} + 3H_2O \rightarrow 2Se + 6OH^- + S_2O_3^{2-}$$

(a) Balanced Half Reactions

## **Initial Half Reactions**

Red: 
$$SO_3^{2-} \to S_2O_3^{2-}$$

$$Oxid: Se^{2+} \rightarrow Se$$

## Half Reactions balanced in basic solution

Red: 
$$2SO_3^{2-} + 3H_2O + 4e^- \rightarrow S_2O_3^{2-} + 6OH^-$$

$$Oxid: Se^{2-} \rightarrow Se + 2e^{-}$$

(b) Given 
$$E_{cell}{}^o$$
 = +0.35 V and  $E_{red}{}^o$  ( $SO_3{}^{2-}$ ) = -0.57 V, what is  $E_{red}{}^o$  ( $Se$ )?

$$E_{cell}^{o} = +0.35V = E_{red}^{o} \lceil SO_{3}^{-} \rceil + E_{ox}^{o} [Se^{2-}] = -0.57 \text{ V} + E_{ox}^{o} [Se^{2-}]$$

$$E_{ox}^{o}[Se^{2-}] = +0.35 + 0.57 = +0.92V$$

$$E_{red}^{o}[Se] = -E_{ox}^{o}[Se^{2-}] = -0.92V$$

### **21.33** Reduction potentials are taken from Appendix D.

$$2Ag + Cu^{2+} \rightarrow 2Ag^{+} + Cu$$

$$E_{cell}^{o} = E_{red}^{o}(Cu^{2+}) + E_{oxid}^{o}(Ag) = E_{red}^{o}(Cu^{2+}) - E_{red}^{o}(Ag^{+})$$
  
= +0.34 - 0.80 = -0.46V

This reaction is NOT spontaneous.

# (b) Unlike (a) [and c)], this reaction cannot be readily balanced by inspection.

### **Initial Half Reactions**

$$\operatorname{Re} d: Cr_2O_7^{2-} \to Cr^{3+}$$

$$Oxid: Cd \rightarrow Cd^{2+}$$

### **Balanced Half Reactions**

Re 
$$d: Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$Oxid: Cd \rightarrow Cd^{2+} + 2e^{-}$$

# Mult Red Rxn. by 1, Oxid. Rxn. by 3 and add

$$Cr_2O_7^{2-} + 14H^+ + 3Cd \rightarrow 2Cr^{3+} + 7H_2O + 3Cd^{2+}$$

$$E_{cell}^{o} = E_{red}^{o}(Cr_{2}O_{7}^{2-}) + E_{oxid}^{o}(Cd) = E_{red}^{o}(Cr_{2}O_{7}^{2-}) - E_{red}^{o}(Cd^{2+})$$
  
= +1.33 - (-0.40) = +1.73V

This reaction IS Spontaneous

(c)  

$$Ni^{2+} + Pb \rightarrow Ni + Pb^{2+}$$
  
 $E_{cell}^{o} = E_{red}^{o}(Ni^{2+}) + E_{oxid}^{o}(Pb) = E_{red}^{o}(Ni^{2+}) - E_{red}^{o}(Pb^{2+})$   
 $= -0.25 - (-0.13) = -0.12V$ 

This reaction is NOT spontaneous.

- **21.36** For a reaction to be spontaneous, the species with the higher reduction potential must be reduced, while the species with the lower reduction potential must be oxidized.
- a. N<sub>2</sub>O is reduced, Au is oxidized.

$$\begin{split} N_2O + 2\,H^+ + 2\,Au &\to 2N_2 + 2\,H_2O + 2\,Au^+ \\ E^o_{cell} &= E^o_{red}(N_2O) + E^o_{oxid}(Au) = E^o_{red}(N_2O) - E^o_{red}(Au^+) \\ &= +1.77 - (+1.69) = +0.08V \end{split}$$

b. N<sub>2</sub>O is reduced, Cr is oxidized

$$3N_2O + 6H^+ + 2Cr \rightarrow 3N_2 + 3H_2O + 2Cr^{2+}$$

$$E^o_{cell} = E^o_{red}(N_2O) + E^o_{oxid}(Cr) = E^o_{red}(N_2O) - E^o_{red}(Cr^{2+})$$

$$= +1.77 - (-0.74) = +2.51V$$

c. Au<sup>+</sup> is reduced, Cr is oxidized

$$3Au^{+} + Cr \rightarrow 3Au + Cr^{2+}$$

$$E_{cell}^{o} = E_{red}^{o}(Au^{+}) + E_{oxid}^{o}(Cr) = E_{red}^{o}(N_{2}O) - E_{red}^{o}(Cr^{2+})$$

$$= +1.69 - (-0.74) = +2.43V$$

# **Ranking Ozidizing Agents**

Because an oxidizing agent is reduced, the strongest oxidizing agent will have the highest Reduction Potential

Therefore:  $N_2O > Au^+ > Cr^{3+}$ 

### **Ranking Reducing Agents**

Because the reducing agent is oxidized, the strongest reducing agent will have the highest Oxidation Potential, which corresponds to the lowest Reduction Potential; i.e. the order is exactly the opposite from the order of oxidizing agents

Therefore:  $Cr > Au > N_2$ 

### 20.45 Reduction Potentials taken from Appendix D

### (a) Ni and Ag+

 $\operatorname{Re} d: Ag^+ + e^- \to Ag$ 

 $Oxid: Ni \rightarrow Ni^{2+} + 2e^{-}$ 

Balanced Reaction:  $2Ag^+ + Ni \rightarrow 2Ag + Ni^{2+}$ 

n = 2

$$E_{cell}^{o} = E_{red}^{o}(Ag^{+}) + E_{oxid}^{o}(Ni) = E_{red}^{o}(Ag^{+}) - E_{red}^{o}(Ni^{+})$$
  
= +0.80 - (-0.25) = 1.05 V

$$E_{cell}^o = \frac{0.0592}{n} \log(K)$$

$$\log(K) = \frac{n \cdot E_{cell}^o}{0.0592} = \frac{2(1.05)}{0.0592} = 35.47$$

$$K = 10^{35.47} = 3.0x10^{35}$$

# (b) Fe and $Cr^{3+}$

 $\operatorname{Re} d: Cr^{3+} + 3e^{-} \rightarrow Cr$ 

$$Oxid: Fe \rightarrow Fe^{2+} + 2e^{-}$$

Balanced Reaction:  $2Cr^{3+} + 3Fe \rightarrow 2Cr + 3Fe^{2+}$ 

$$n = 6$$

$$E_{cell}^{o} = E_{red}^{o}(Cr^{3+}) + E_{oxid}^{o}(Fe) = E_{red}^{o}(Cr^{3+}) - E_{red}^{o}(Fe^{2+})$$
$$= -0.74 - (-0.44) = -0.30V$$

$$E_{cell}^o = \frac{0.0592}{n} \log(K)$$

$$\log(K) = \frac{n \cdot E_{cell}^o}{0.0592} = \frac{6(-0.30)}{0.0592} = -30.41$$

$$K = 10^{30.41} = 3.9x10^{-31} \approx 4x10^{-31}$$

# **21.50** n = 2, K = 0.065

$$E_{cell}^{o} = \frac{0.0592}{2}\log(0.065) = -0.035V$$

$$\Delta G^o = -nFE^o_{cell} = -(2 \, mol)(96,500 \, C \, / \, mol)(-0.035 \, V)$$
  
= +6780  $C \cdot V = +6780 \, J \approx +6.8 \, kJ$ 

**21.52 Note:** The problem as written doesn't tell you which species is being oxidized and and which is being reduced. As written, you are supposed to write the reaction so that it is spontaneous (i.e. positive  $E_{cell}^{o}$ ). However, on a test, I would tell you the reaction; e.g. this reaction is  $Mn|Mn^{2+}||Pb^{2+}||Pb||$ 

$$\operatorname{Re} d: Pb^{2+} + 2e^{-} \rightarrow Pb$$

$$Oxid: Mn \rightarrow Mn^{2+} + 2e^{-}$$

Balanced Re action:  $Pb^{2+} + Mn \rightarrow Pb + Mn^{2+}$ 

$$E_{cell}^{o} = E_{red}^{o}(Pb^{2+}) + E_{oxid}^{o}(Mn) = E_{red}^{o}(Pb^{2+}) - E_{red}^{o}(Mn^{2+})$$
$$= -0.13 - (-1.18) = +1.05V$$
$$n = 2$$

$$E_{cell} = E_{cell}^{o} - \frac{0.592}{n} \log(Q) = E_{cell}^{o} - \frac{0.592}{n} \log\left(\frac{[Mn^{2+}]}{[Pb^{2+}]}\right)$$

$$0.44V = 1.05V - \frac{0.0592}{2} \log \left( \frac{1.4M}{[Pb^{2+}]} \right)$$

$$\frac{0.0592}{2}\log\left(\frac{1.4M}{[Pb^{2+}]}\right) = 1.05 - 0.44 = +0.61V$$

$$\log\left(\frac{1.4\,M}{[Pb^{2+}]}\right) = (0.61) \cdot \frac{2}{0.0592} = 20.61$$

$$\frac{1.4M}{[Pb^{2+}]} = 10^{20.61} = 4.06x10^{20}$$

$$[Pb^{2+}] = \frac{1.4M}{4.06x10^{20}} = 3.5x10^{-21}M$$

**Note:** The above answer is correct. However, I don't think you would ever really have a 21 order of magnitude difference between half-cell reaction concentrations.

**21.76** M(Mg) = 24.3 g/mol

(a) 
$$Mg^{2+} + 2e^{-} \square Mg$$

$$n(Mg) = 45.6 g Mg \cdot \frac{1 mol Mg}{24.3 g Mg} = 1.865 mol Mg$$

$$n(e^{-}) = 1.865 \, mol \, Mg \cdot \frac{1 \, mol \, e^{-}}{1 \, mol \, Mg} = 3.75 \, mol \, e^{-}$$

(b) 
$$q = 3.75 \, mol \, e^{-} \cdot \frac{96,500 \, C}{1 \, mol \, e^{-}} = 3.62 \, x 10^{5} \, C$$

(c) 
$$t = 3.5 \text{ hr x } 3600 \text{ s/1 hr} = 12,600 \text{ s}$$
  
 $q = i \cdot t$ 

$$i = \frac{q}{t} = \frac{3.62 \times 10^5 C}{12.600 s} = 28.7 C / s = 28.7 A$$

**21.80** 
$$Zn^{2+} + 2 e^{-} \Box Zn$$
,  $M(Zn) = 65.4 \text{ g/mol}$ ,  $i = 21.0 \text{ A} = 21.0 \text{ C/s}$ 

$$n(Zn) = 65.5 g Zn \cdot \frac{1 mol Zn}{65.4 g Zn} = 1.0015 mol Zn$$

$$n(e^{-}) = 1.0015 \, mol \, Zn \cdot \frac{2 \, mol \, e^{-}}{1 \, mol \, Zn} = 2.003 \, mol \, e^{-}$$

$$q = 2.003 \, mol \, e^{-} \cdot \frac{96,500 \, C}{1 \, mol \, e^{-}} = 1.93 \, x 10^{5} \, C$$

$$q = i \cdot t$$

$$t = \frac{q}{i} = \frac{1.93x10^5 C}{21.0 C/s} = 9.20x10^3 s$$

**21.84** 
$$Zn^{2+} + 2e^{-} \square Zn$$
,  $M(Zn) = 65.4$  g/mol

 $i=0.855\;A=0.855\;C/s$  ,  $t=2.5\;days\;x\;24\;hr/1\;day\;x\;3600\;s\:/\:hr=2.16x10^5\;s$ 

$$q = i \cdot t = (0.855 \, C \, / \, s)(2.15 \, x 10^5 \, s) = 1.85 \, x 10^5 \, C$$

$$n(e^{-}) = 1.85 \times 10^{5} C \cdot \frac{1 \, mol \, e^{-}}{96,500 \, C} = 1.914 \, mol \, e^{-}$$

$$n(Zn) = 1.91 \, mol \, e^{-} \cdot \frac{1 \, mol \, Zn}{2 \, mol \, e^{-}} = 0.957 \, mol \, Zn$$

$$mass(Zn) = 0.957 \, mol \, Zn \cdot \frac{65.4 \, g \, Zn}{1 \, mol \, Zn} = 62.5 \, g \, Zn$$