Chemistry 1212 Name KEY
April 16, 2012
Exam #4

Write very clearly and **show all of your work** for partial credit. A list of equations and constants as well as a periodic table are on the last two pages of your exam.

1. (20 points) Place a correct response in each blank.

(a.) What is K if $\Delta G^\circ = 1.2\times10^{-2}$? $\boxed{1.0}$

(b.) If $\Delta H^\circ_{rxn} = -84.9\,kJ$, what is ΔS°_{surr} in $\frac{J}{K}$? $\boxed{285\frac{J}{K}}$

(c.) Which law is related to ΔE, q, and w? $\boxed{1^{st}}$

(d.) Is the S_f^0 for graphite zero (yes or no)? $\boxed{\text{no}}$

(e.) Write the line/short notation for the redox reactions given below.

i.) $Sn^{4+}_{(aq)} + Tl_{(s)} \rightleftharpoons Sn^{2+}_{(aq)} + Tl^{+}_{(aq)}$ $\boxed{Tl_{(s)}, Tl^{+}_{(aq)} \| Sn^{4+}_{(aq)}, Sn^{2+}_{(aq)} | Pt}$

ii.) $Au^{3+}_{(aq)} + Hg_{(l)} \rightleftharpoons Au^{+}_{(aq)} + Hg^{+}_{(aq)}$ $\boxed{Pt | Hg_{(l)}, Hg^{+}_{(aq)} \| Au^{3+}_{(aq)}, Au^{+}_{(aq)} | Pt}$

(f.) What conditions for Gibbs and cell potential will never give a spontaneous process?

$\boxed{\Delta G > 0, E < 0}$

(g.) What do we call the cell described in f.)?

$\boxed{\textit{electrolytic}}$

(h.) What do we call the process in f.)? $\boxed{\text{endergonic/nonspontaneous}}$

(i.) What is the n for the cell given in (e.) ii.)? $\boxed{2}$

(j.) For electrons to flow nonspontaneously is the potential positive or negative? $\boxed{-}$

2. (20 points) Balance the following redox reaction under <u>acidic</u> conditions. Identify which reagent is the oxidizing agent and which is the reducing agent.

$$H_2C_2O_{4(aq)} + BrO_{3(aq)} \rightarrow CO_{2(g)} + Br_{2(l)}$$

$$\underbrace{H_2C_2O_{4(aq)}}_{ON=+6} \rightarrow \underbrace{2CO_{2(g)}}_{ON=+3} + 2e^-$$

(5 pts)

$$12e^- + \underbrace{2BrO_{3(aq)}}_{ON=+6} \rightarrow \underbrace{Br_{2(l)}}_{ON=0}$$

$$\underbrace{H_2C_2O_{4(aq)}}_{\text{charge}=0} \rightarrow \underbrace{\underbrace{2CO_{2(g)} + 2e^-}_{\text{charge}=0-2=-2} + 2H^+_{(aq)}}_{-2+2=0}$$

(5 pts)

$$\underbrace{12H^+_{(aq)} + \underbrace{12e^- + 2BrO_{3(aq)}}_{\text{charge}=0-12=-12}}_{-12+12=0} \rightarrow \underbrace{Br_{2(l)}}_{\text{charge}=0}$$

$$H_2C_2O_{4(aq)} \rightarrow 2CO_{2(g)} + 2e^- + 2H^+_{(aq)}$$

(5 pts)

$$12H^+_{(aq)} + 12e^- + 2BrO_{3(aq)} \rightarrow Br_{2(l)} + 6H_2O_{(l)}$$

$$6\left(H_2C_2O_{4(aq)} \rightarrow 2CO_{2(g)} + 2e^- + 2H^+_{(aq)}\right)$$

$$12H^+_{(aq)} + 12e^- + 2BrO_{3(aq)} \rightarrow Br_{2(l)} + 6H_2O_{(l)}$$

$$\cancel{12H^+_{(aq)}} + 6H_2C_2O_{4(aq)} + \cancel{12e^-} + 2BrO_{3(aq)} \rightarrow 12CO_{2(g)} + \cancel{12e^-} + 6H_2O_{(l)} + Br_{2(l)} + \cancel{12H^+_{(aq)}}$$

$$\boxed{\begin{array}{l} 6H_2C_2O_{4(aq)} + 2BrO_{3(aq)} \rightarrow 12CO_{2(g)} + 6H_2O_{(l)} + Br_{2(l)} \quad \text{(3 pts)} \\ H_2C_2O_{4(aq)} = reducing\ agent\ \&\ BrO_{3(aq)} = oxidizing\ agent \quad \text{(2 pts)} \end{array}}$$

3.(25 points) Consider the following reaction and corresponding thermodynamic data

$$2H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(s)} + 2H_2O_{(g)} \quad \Delta H^\circ_{rxn} = -154.6\ kJ$$

	$H_2S_{(g)}$	$SO_{2(g)}$	$S_{(s)}$	$H_2O_{(g)}$
$S^\circ\left(\frac{J}{mol \bullet K}\right)$	20.5	264.1	64.8	89.9
$\Delta_f H^\circ\left(\frac{kJ}{mol}\right)$		-256.8	0	-214.8

(a) Determine the heat of formation for $H_2S_{(g)}$. (*5pts*)

$$\Delta H^o_{rxn} = 3\Delta H^o_f(S) + 2\Delta H^o_f(H_2O) - \left[2\Delta H^o_f(H_2S) + \Delta H^o_f(SO_2)\right] \quad (2\,pts)$$

$$-154.6\ kJ = 3\Delta H^o_f(0) + 2\Delta H^o_f(-214.8) - \left[2\Delta H^o_f(H_2S) + \Delta H^o_f(-256.8)\right]$$

$$\Delta H^o_f(H_2S) = \boxed{-9.1\ kJ} \quad (3\,pts)$$

(b) Determine the entropy change for the above reaction. (*5pts*)

$$\Delta S^o_{rxn} = 3S^o_f(S) + 2S^o_f(H_2O) - \left[2S^o_f(H_2S) + S^o_f(SO_2)\right] \quad (2\,pts)$$

$$\Delta S^o_{rxn} = 3\bullet 64.8\tfrac{J}{K} + 2\bullet 89.9\tfrac{J}{K} - \left[2\bullet 20.5\tfrac{J}{K} + 264.1\tfrac{J}{K}\right] = \boxed{69.1\tfrac{J}{K}} \quad (3\,pts)$$

(c) Determine ΔG^0 for the above reaction. (*5pts*)

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn} \quad (2\,pts)$$

$$\Delta G^o_{rxn} = -154.6\,kJ - 298.15K \bullet \left(69.1\tfrac{J}{K}\right) \times \tfrac{1\,kJ}{1000\,J} = \boxed{-175\,kJ} \quad (3\,pts)$$

(d) Determine the equilibrium constant for the above reaction. (*5pts*)

{R = 8.314 J/K·mol and F = 96485 C/mol}

$$K = e^{-\Delta G^o_{rxn}/RT} \quad (2\,pts)$$

$$K = e^{-(-175\,kJ)/8.3145\frac{J}{K}\times\frac{1\,kJ}{1000\,J}\times 298.15K} = \boxed{4.94\times 10^{30}} \quad (3\,pts)$$

(e) Is the reaction spontaneous? Why or why not? (*5pts*)

Yes, Gibbs is less than zero.

4. (35 points) Given the data below:

$$BiO^+_{(aq)} + 2H^+_{(aq)} + 3e^- \rightarrow Bi_{(s)} + H_2O_{(l)} \qquad E^o = 0.32\,V$$

$$PbO_{2(s)} + 3H^+_{(aq)} + HSO^-_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \qquad E^o = 1.628\,V$$

a.) Write the balanced equation for a galvanic cell. (*5pts*)

$$3PbO_{2(aq)} + 5H^+_{(aq)} + 3HSO^-_{4(aq)} + 2Bi_{(s)} \rightarrow 3PbSO_{4(s)} + 4H_2O_{(l)} + 2BiO^+_{(aq)}$$

b.) State which half reaction is the cathode and the anode. (*5pts*)

$$PbO_{2(s)} + 3H^+_{(aq)} + HSO^-_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \qquad cathode$$

$$BiO^+_{(aq)} + 2H^+_{(aq)} + 3e^- \rightarrow Bi_{(s)} + H_2O_{(l)} \qquad anode$$

c.) State the species which is oxidized and reduced. (*5pts*)

$Bi_{(s)}$ is oxidized & $PbO_{2(s)}$ is reduced

d.) State the species which is the oxidizing and reducing agent. (*5pts*)

$PbO_{2(s)}$ is the oxidizing & $Bi_{(s)}$ is reducing agent

e.) Determine the standard emf, E°_{cell}. (*5pts*)

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \quad (2\,pts)$$

$$E^\circ_{cell} = 1.628 - 0.32 = \boxed{1.308\,V} \quad (3\,pts)$$

f.) Is the reaction spontaneous? Why? (*5pts*)

$yes, E^\circ_{cell} > 0$

g.) Determine the emf, E_{cell}, given: $\left[HSO_4^-\right] = 0.500M$, $\left[BiO^+\right] = 0.250M$, $pH = 5$ (*5pts*)

$$E_{cell} = E^\circ_{cell} - \tfrac{0.0592}{n}\log\frac{\left[Bi^{3+}\right]^2}{\left[H^+\right]^5\left[HSO_4^-\right]^3} \quad (2\,pts)$$

$$E_{cell} = 1.308V - \tfrac{0.0592}{6}\log\frac{[0.500]^2}{\left[10^{-5.00}\right]^5[0.250]^3} = \boxed{1.085\,V} \quad (3\,pts)$$