Chemistry 210

Exam 4

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number =
$$6.022 \times 10^{23} \text{ units}/_{mol}$$

 $32.00^{\circ}\text{F} = 0.000^{\circ}\text{C} = 273.15\text{K}$
Density of Water = $1.000^{\text{g}}/_{\text{mL}}$
 $R = 0.08206^{\text{L-atm}}/_{mol-\text{K}} = 8.314^{\text{J}}/_{mol-\text{K}}$
 $PV=nRT$
 $\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot \text{m} \cdot \text{i}$
For water: $k_{\text{fp}} = -1.86^{\circ\text{C}}/_{\text{m}}$
 $k_{\text{bp}} = 0.512^{\circ\text{C}}/_{\text{m}}$
 $P_1 = X_1 P_1^{\circ}$
 $\Pi = MRTi$
 $C_1 V_1 = C_2 V_2$
Quadratic formula:
 $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{b^2 - 4ac}$

$$=\frac{-b\pm\sqrt{b^2-2}}{2a}$$

232.04

231.04

238.03

Integrated Rate Laws:

$$\begin{array}{ll} 0^{th} \text{ order } & [A]_t = -kt + [A]_o \\ 1^{st} \text{ order } & \ln[A]_t = -kt + \ln[A]_o \\ 2^{nd} \text{ order } & 1/[A]_t = kt + 1/[A]_o \\ k = Ae^{-Ea/RT} \\ \ln(k) = \left(\frac{-E_a}{R}\right) \left(\frac{1}{T}\right) + \ln(A) \\ \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right) \end{array}$$

$$\begin{split} E_{cell} &= E^{o}_{cell} - {^{RT}}/_{nF} lnQ \\ E^{o}_{cell} &= {^{RT}}/_{nF} lnK^{o} \\ K^{o} &= e^{(nF}/_{RT} E^{o}_{cell}) \end{split}$$
 $F=96485~^J\!/_{V^{\bullet}mol~of~electrons}$ $\Delta G^{\circ} = \Delta H^{\circ}_{system} - T\Delta S^{\circ}_{system}$ $\Delta G^{\circ} = -nFE^{\circ}_{cell} = -RTlnK^{\circ}$ $\Delta G = \Delta G^{o} + RT lnQ$ $F = 96485 ^{C}/_{mol \ electrons}$ 1A = 1 C / sec

1																	2
Η																	He
1.0079																	4.0026
3	4]										5	6	7	8	9	10
Li	Be											В	С	Ν	0	F	Ne
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	Р	S	Cl	Ar
22.990	24.305											26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.91	137.33	138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111	112		114		116		
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									
(223)	226.03	227.03	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(277)						
														-		-	
		58	59	60	61	62	63	64	65	66	67	68	69	70	71	1	
		Ce	Pr	Nd	Pm	Sm 150.36	Eu	Gd 157.25	Tb 158.93	Dy	Ho	Er	Tm 168.94	Yb	Lu		
		140.12 90	140.91 91	144.24 92	(145) 93	94	95	96	97	162.50 98	164.93 99	167.26 100	108.94	173.04 102	174.97 103	1	
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

(247)

(251)

(252)

(258)

(258)

(259)

(243)

(247)

(244)

237.05

(260)

Multiple Choice (5pts each)

- 1. A large negative change in free energy means:
 - a. The reaction is very slow
 - b. The reaction is exothermic
 - c. The reaction is not spontaneous
 - d. The system is becoming more disordered
 - e. The reaction is spontaneous
- 2. For a reaction with a small negative ΔS :
 - a. Heat is liberated by the reaction
 - b. The system is becoming more ordered
 - c. The reaction is not spontaneous
 - d. The order of the system is increasing
 - e. The reaction proceeds very quicky
- 3. A reaction will be product-favored/spontaneous if:
 - $a. \quad \varDelta G^o < 0$
 - b. $K_{eq} < 1$
 - c. $\Delta H > 0$
 - d. $\Delta S^{o} < 0$
 - e. $E^{\circ}_{cell} < 0$
- 4. A reaction will be spontaneous at relatively high temperature if:
 - a. $\Delta H^{o}_{system} > 0$ and $\Delta S^{o}_{system} > 0$
 - b. $\Delta H^{o}_{system} < 0$ and $\Delta S^{o}_{system} > 0$
 - c. $\Delta H^{\circ}_{system} > 0$ and $\Delta S^{\circ}_{system} = 0$
 - d. $\Delta H^{o}_{system} > 0$ and $\Delta S^{o}_{system} < 0$
 - e. $\Delta H^{o}_{system} < 0$ and $\Delta S^{o}_{system} < 0$
- 5. In a spontaneous electrochemical voltaic cell, which of the following is *true*?
 - a. The cell potential is zero
 - b. Oxidation occurs at the cathode
 - c. Electrons flow from the cathode to the anode
 - d. Cations flow through the salt bridge from the cathode to the anode
 - e. The metal cathode gains mass as the cell reaction proceeds
- 6. For a spontaneous redox reaction, which of the following is *false*?
 - a. Oxidation is the process of losing electrons
 - b. Gaining electrons is reduction
 - c. Electrons appear on the left side of the oxidation half reaction
 - d. Water molecules are added to balance any extra oxygen atoms
 - e. ΔG is negative.

Chem 210 – Exam 4a Spring 2011

- 7. How are the change in Gibb's Free Energy and the equilibrium constant for a reaction related?
 - a. As K approaches zero, ΔG approaches zero
 - b. They're not.
 - c. The value of ΔG is equal to (-logK)
 - d. As ΔG gets more positive, K approaches 1
 - e. As ⊿G gets more negative, K gets very large

Problems:

8. For each of the following reactions, predict the sign of ΔS° and explain your answer (5pts each): H₂SO₄(aq) + Mg(OH)₂(aq) \Leftrightarrow MgSO₄(s) + 2 H₂O(l)

Negative. Aqueous solutions are significantly more disordered than solids and more disordered than pure solvent.

```
2 \operatorname{NO}_2(g) \Leftrightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)
```

Positive. Two gas particles are reacting to form three gas particles, so this system is probably getting more disordered.

9. Give the oxidation number for each atom in the following formulas. (5pts each formula)

Na ₃ PO ₄	CH ₃ OH
$Na \rightarrow +1$ P \rightarrow +5 O \rightarrow -2	$\begin{array}{c} C \rightarrow -2 \\ H \rightarrow +1 \\ O \rightarrow -2 \end{array}$

10. Ammonia {NH₃(g)} can burn in oxygen to form nitrogen dioxide and water. How much energy can be liberated by burning 21.964g of ammonia in an unlimited supply of oxygen? (20pts)

11. You would like to plate 4.38g of chromium (atomic # = 24) using an electrolytic cell containing a solution of chromium(III) nitrate and operating at 2.37A. How long will you have to run the cell? (20pts)

$$\operatorname{Cr}^{3+}(\operatorname{aq}) + 3 \operatorname{e}^{-} \rightarrow \operatorname{Cr}(\operatorname{s})$$

$$(4.38 \operatorname{g} \operatorname{Cr} \left(\frac{1 \operatorname{mol} \operatorname{Cr}}{51.996 \operatorname{g} \operatorname{Cr}} \right) \left(\frac{3 \operatorname{mol} \operatorname{e}^{-}}{1 \operatorname{mol} \operatorname{Cr}} \right) \left(\frac{96485 \operatorname{C}}{1 \operatorname{mol} \operatorname{e}^{-}} \right) \left(\frac{1 \operatorname{sec}}{2.37 \operatorname{C}} \right) = 10300 \operatorname{sec} = 171 \operatorname{minutes} = 2.86 \operatorname{hours}$$

Name:

- 12. You are studying the reaction of acetic acid {CH₃CO₂H(l)} with iso-propanol {C₃H₈O(l)} to produce isopropylacetate {C₅H₁₀O₂(l)} and water. When you run the reaction at 22.67°C, you find that ΔG for this reaction is -27.39^{kJ}/_{mol} and $\Delta S = +34.18^{J}/_{mol\cdot K}$ (20pts)
 - a. Is the reaction endothermic or exothermic? (Explain your answer with explicit calculations.)

$$\Delta G = \Delta H - T\Delta S$$

-27.39^{kJ}/_{mol} = $\Delta H - (22.67+273.15K)(0.03418^{kJ}/_{mol}K)$
 $\Delta H = -17.28^{kJ}/_{mol}$

Since ΔH is negative, the reaction is exothermic

b. Over what temperature range is this reaction spontaneous?

Since ΔH is negative and ΔS is positive, this reaction will be spontaneous at all temperatures.

13. For each of the following pairs of half-reactions/half-cells, determine the voltage of the spontaneous reaction/cell and write a balanced equation for the reaction that occurs, identifying the oxidation and reduction half-reactions. (18pts each)

 $Au^{3+}(aq)|Au(s) \text{ and } Br_2(l)|Br^{-1}(aq)$

 $MnO_2(s)|Mn^{2+}(aq) \ and \ Cr_2O_7^{-2}(aq)|Cr^{3+}(aq)$

From the standard reduction potentials, manganese(II) ion will be oxidized in the spontaneous cell. $14 \text{ H}^{+}(\text{aq}) + 6 \text{ e}^{-} + \text{Cr}_2 \text{O}_7^{-2}(\text{aq}) \rightarrow 2 \text{ Cr}^{+3}(\text{aq}) + 7 \text{ H}_2 \text{O}(1)) \qquad \text{E}^{\circ}_{\text{red}} = +1.33 \text{V}$ $3 (2 \text{ H}_2 \text{O}(1) + \text{Mn}^{+2}(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) + 2 \text{ e}^{-} + 4 \text{ H}^{+}(\text{aq})) \text{ E}^{\circ}_{\text{ox}} = -1.21 \text{V}$ $2 \text{ H}^{+}(\text{aq}) + 3 \text{ Mn}^{+2}(\text{aq}) + \text{Cr}_2 \text{O}_7^{-2}(\text{aq}) \rightarrow 3 \text{ MnO}_2(\text{s}) + 2 \text{ Cr}^{+3}(\text{aq}) + \text{H}_2 \text{O}(1) \qquad \text{E}^{\circ}_{\text{cell}} = +0.12 \text{V}$

Substance	$\Delta H^{o}_{f} (^{kJ}/_{mol})$	$S^{o}(J_{mol \cdot K})$	$\Delta G^{o}_{f} (^{kJ}/_{mol})$
$NH_3(g)$	-46.11	192.45	-16.45
$O_2(g)$	0	205.138	0
$NO_2(g)$	33.18	240.06	51.31
$H_2O(g)$	-241.8	188.8	-228.6

Standard Reduction Potentials at 25°C:

Half cell	E ^o _{red} (volts)	Half cell	E ^o _{red} (volts)
$Cr^{3+}(aq) Cr(s)$	-0.74	$MnO_2(s) Mn^{2+}(aq)$	+1.21
Au ³⁺ (aq) Au(s)	+1.50	$Cr_2O_7^{-2}(aq) Cr^{3+}(aq) $	+1.33
$Br_2(l) Br^{-1}(aq)$	+1.09		