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 = $1.000^{\text{g}}/_{\text{mL}}$
 $R = 0.08206^{\text{L*atm}}/_{\text{mol}*\text{K}} = 8.314^{\text{J}}/_{\text{mol}*\text{K}}$
 $PV=nRT$
 $\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot \text{m} \cdot \text{i}$
For water: $k_{\text{fp}} = -1.86^{\circ}\text{C}/_{\text{m}}$
 $k_{\text{bp}} = 0.512^{\circ}\text{C}/_{\text{m}}$
 $P_1 = X_1P_1^{\circ}$
 $\Pi = MRTi$
 $C_1V_1 = C_2V_2$
Quadratic formula:
 $r = -b \pm \sqrt{b^2 - 4ac}$

2a

Th

232.04

Pa

231.04

U

238.03

Integrated Rate Laws:

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

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

	_																
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	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		140.12 90	140.91 91	144.24 92	(145) 93	150.36 94	151.97 95	157.25 96	158.93 97	162.50 98	164.93 99	167.26 100	168.94 101	173.04 102	174.97 103	1	
		20	71	92	73	24	75	20	31	70	39	100	101	102	105		

Bk

(247)

Cm

(247)

Cf

(251)

Es

(252)

Fm

(258)

Md

(258)

No

(259)

Lr

(260)

Am

(243)

Pu

(244)

Np

237.05

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Multiple Choice (4pts each): Circle the letter of the most correct response.

- 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 temperature of the system is increasing
 - e. The reaction proceeds very quicky
- 3. A reaction will be product-favored/spontaneous if:
 - a. $\Delta G^{o} < 0$
 - 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 and non-spontaneous at relatively low temperature if:
 - a. $\Delta H^{o}_{system} > 0$ and $\Delta S^{o}_{system} > 0$
 - b. $\Delta H^{\circ}_{system} < 0 \text{ and } \Delta S^{\circ}_{system} > 0$
 - c. $\Delta H^{o}_{system} > 0$ and $\Delta S^{o}_{system} = 0$
 - d. $\Delta H^{\circ}_{system} > 0 \text{ and } \Delta S^{\circ}_{system} < 0$
 - e. $\Delta H^{\circ}_{system} < 0$ and $\Delta S^{\circ}_{system} < 0$
- 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.
- 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 ΔG gets more negative, K gets very large

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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)

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

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

K₂SO₃ CH₃OH

- 10. 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 -35.19^{kJ}/_{mol} and $\Delta S = +79.18^{J}/_{mol \cdot K}$ (10pts)
 - a. Is the reaction endothermic or exothermic? (Explain your answer with explicit calculations.)
 - b. Over what temperature range is this reaction spontaneous?

11. The alkaline earth metals (Be, Mg, Ca, Sr, Ba) all appear in your Standard Reduction Potential tables in half-cells of the type:

 $M^{+2}(aq) + 2e^{-} \rightarrow M(s)$ (10 pts)

Explain the trend in E^{o}_{red} for these metals. (10 pts)

12. You are studying a process for which $\Delta H^\circ = +30.71^{kJ}/_{mol}$ and $\Delta S^\circ = +192.44^{J}/_{mol \cdot K}$. What is ΔG° for this process at 25.00°C? Will the reaction be more or less spontaneous at 20.00°C? (8pts)

13. Ammonia {NH₃(g)} can burn in oxygen to form nitrogen dioxide and water. How much {Gibb's Free} energy can be liberated by burning 15.772g of ammonia in an unlimited supply of oxygen? (10pts)

14. 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 spontaneous reaction, identifying the oxidation and reduction half-reactions. (10pts each)

 $Au^{3+}(aq)|Au(s)$ and $Sn^{4+}(aq)|Sn^{2+}(aq)|$

 $Al^{3+}(aq)|Al(s) \text{ and } F_2(g)|F^{-1}(aq)$

 $PbO_2(s)|Pb(s) \text{ and } Cr_2O_7^{-2}(aq)|Cr^{3+}(aq)|$

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15. After a strong storm, you are without electricity and would like to construct a flashlight from some materials you have found in your garage. You have a lightbulb that will produce light if you apply a voltage greater than 0.80 V. You have found the following materials: a box of iron (Fe) nails, a silver (Ag) necklace, Fe(NO₃)₃, FeSO₄, and AgNO₃. What cell(s) can you construct to power your flashlight? Explain your choices. (12 pts)

16. How many grams of ethane $\{C_2H_6(g)\}$ would you have to burn to liberate enough Gibb's Free Energy to break 14.227g of CaO(s) into Ca(s) and O₂(g)? (Assume 100% efficiency.) (12 pts)

17. When nitrogen gas and oxygen gas are sealed in a vessel, reactions occur that generate $N_2O_4(g)$ and $N_2O_5(g)$. If these are the only products, and ΔG° is the only factor that affects the composition of this mixture, which of these products would you expect to be present in higher quantity at the end of the reaction? (Explain your answer with explicit calculations/numbers.) (10 pts)

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Thermodynamic Values at 25°C:

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
$H_2O(l)$	-285.8	+69.91	-237.2
$C_2H_6(g)$	-84.68	+229.2	-32.0
$CO_2(g)$	-393.5	+213.6	-394.4
CaO(s)	-635.1	+39.75	-604.0
Ca(s)	0	+41.4	0
$N_2O_4(g)$	+9.16	+304.2	-81.7
$N_2O_5(g)$	+11.3	+355.6	-94.4

Standard Reduction Potentials at 25°C:

•••											
	Half cell	E ^o _{red} (volts)	Half cell	E ^o _{red} (volts)							
	$Au^{3+}(aq) Au(s)$	-1.50	$Be^{+2}(aq) Be(s)$	-1.97							
	$Sn^{4+}(aq) Sn^{2+}(aq) $	+0.15	$Mg^{+2}(aq) Mg(s)$	-2.36							
	$Al^{3+}(aq) Al(s)$	-1.676	$Ca^{+2}(aq) Ca(s)$	-2.84							
	$F_2(g) F^{-1}(aq)$	+2.87	$Sr^{+2}(aq) Sr(s)$	-2.89							
	$PbO_2(s) Pb(s)$	+1.93	$Ba^{+2}(aq) Ba(s)$	-2.92							
	$Cr_2O_7^{-2}(aq) Cr^{3+}(aq) $	+1.33	$Fe^{2+}(aq) Fe(s)$	-0.44							
	$Fe^{3+}(aq) Fe(s)$	-0.04	$Ag^{+}(aq) Ag(s)$	+0.799							