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 $= 6.022 \times 10^{23}$ $^{units}/_{mol}$

$32.00^{o}F = 0.000^{o}C = 273.15K$

Density of Water $= 1.000^{g}/_{mL}$

$R = 0.08206$ $^{L \cdot atm}/_{mol \cdot K} = 8.314$ $^{J}/_{mol \cdot K}$

$1 atm = 760 torr = 760 mmHg = 101.325 kPa$

$PV = nRT$

$\Delta T_{fp/bp} = k_{fp/bp} \cdot m \cdot i$

For water: $k_{fp} = -1.86$ $^{oC}/_{m}$

                $k_{bp} = 0.512$ $^{oC}/_{m}$

$P_1 = X_1 P_1^{o}$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

$E = C_s \cdot g \cdot \Delta T$

Quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrated Rate Laws:

0th $[A]_t = -kt + [A]_o$

1st $\ln[A]_t = -kt + \ln[A]_o$

2nd $1/[A]_t = kt + 1/[A]_o$

$k = Ae^{-Ea/RT}$

$$\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right)$$

$E_{cell} = E^{o}_{cell} - {}^{RT}/_{nF} \, lnQ$

$E^{o}_{cell} = {}^{RT}/_{nF} \, lnK^{o}$

$K^{o} = e^{\wedge}({}^{nF}/_{RT} E^{o}_{cell})$

$F = 96485$ $^{J}/_{V \cdot mol \ of \ electrons}$

$\Delta G^{o} = \Delta H^{o}_{system} - T\Delta S^{o}_{system}$

$\Delta G^{o} = -nFE^{o}_{cell} = -RTlnK^{o}$

$\Delta G = \Delta G^{o} + RTlnQ$

$F = 96485$ $^{C}/_{mol \ electrons}$

$1A = 1 \ C / sec$

1 H 1.0079																		2 He 4.0026
3 Li 6.941	4 Be 9.0122												5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305												13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39		31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41		49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59		81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)			114		116		

| 58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.94	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (258)	101 Md (258)	102 No (259)	103 Lr (260)

Score

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. 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. $\Delta H^o_{system} < 0$ and $\Delta S^o_{system} > 0$
   c. $\Delta H^o_{system} > 0$ and $\Delta S^o_{system} = 0$
   d. $\Delta H^o_{system} > 0$ and $\Delta S^o_{system} < 0$
   e. $\Delta H^o_{system} < 0$ and $\Delta S^o_{system} < 0$

3. 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 disorder of the system is increasing
   e. The reaction proceeds very quickly

4. If the change in enthalpy for a reaction is positive and the change in entropy is negative:
   a. The system is becoming more disordered
   b. The reaction releases heat
   c. The reaction will be spontaneous at all temperatures
   d. The reaction will be non-spontaneous at all temperatures
   e. The reaction will be spontaneous only at low temperatures

5. 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. $E^\circ_{cell} < 0$

6. 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. The value of ΔG is equal to (-logK)
   c. As ΔG gets more positive, K approaches 1
   d. They're not.
   e. As ΔG gets more negative, K gets very large

7. 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

Score

8. 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.

9. Give the oxidation number for each atom in the following formulas. (15pts)

Na_3PO_3

Na → +1
P → +3
O → -2

SO_2

S → +4
O → -2
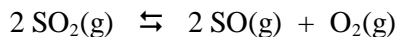
SiH_4
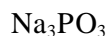
Si → -4
H → +1

10. For each of the following reactions, predict whether the sign if $\Delta S°$ will be positive or negative and explain your answer. (15pts)

$$Pb(NO_3)_2(aq) + 2\,Na_2SO_4(aq) \rightleftarrows PbSO_4(s) + 2\,NaNO_3(aq)$$
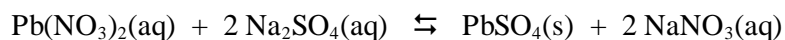
$\Delta S°$ should be negative
The reaction is becoming more ordered because a solid (very ordered) is being formed from aqueous solutions.

$$2\,SO_2(g) \rightleftarrows 2\,SO(g) + O_2(g)$$

$\Delta S°$ should be positive
Since all of the reactants and products are gases, more particles on the product side means that the products are more disordered/disperse than the reactants.

$$MgCO_3(s) + 2\,HNO_3(aq) \rightleftarrows Mg(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

$\Delta S°$ should be positive
The reaction is becoming more disordered/disperse because a gas (very disordered/disperse) is being formed from aqueous solution and solid.

11. For liquid water $S° = +69.91\,^J/_{mol·K}$ and for solid water $S° = +41.3\,^J/_{mol·K}$. Explain this difference. (10pts)

S is a measure of disorder/dispersion in a system. The molecules in liquid water can move around more than the molecules in solid water so they should be more disordered/disperse. More positive values of S imply more disorder/dispersion, so the $S°$ should be more positive for liquid water. And it is!!

Score

12. You are studying a process for which $\Delta H° = -28.38^{kJ}/_{mol}$ and $\Delta S° = -137.62^{J}/_{mol\cdot K}$. What is $\Delta G°$ for this process at 25.00°C? Will the reaction be more or less spontaneous at 20.00°C? (10pts)

$$\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$$
$$\Delta G°_{rxn} = (-28.38^{kJ}/_{mol}) - (298.15K)(-0.13762^{kJ}/_{mol\cdot K}) = +12.65^{kJ}/_{mol}$$

$$\Delta G°_{rxn} = (-28.38^{kJ}/_{mol}) - (293.15K)(-0.13762^{kJ}/_{mol\cdot K}) = +11.96^{kJ}/_{mol}$$
Slightly less positive means slightly more spontaneous.

13. Ammonia $\{NH_3(g)\}$ can burn in oxygen to form nitrogen dioxide and water. How much {Gibb's Free} energy can be liberated by burning 23.948g of ammonia in an unlimited supply of oxygen? (10pts)

$$4\,NH_3(g) + 7\,O_2(g) \Leftrightarrow 4\,NO_2(g) + 6\,H_2O(g)$$
$$\Delta G°_{rxn} = 4(+16.45^{kJ}/_{mol}) + 7(+0^{kJ}/_{mol}) + 4(+51.31^{kJ}/_{mol}) + 6(-228.6^{kJ}/_{mol}) = -1100.56^{kJ}/_{mol}$$
$$\{(23.948g\ NH_3) / (17.031^{g}/_{mol})\}\ (1mol\ rxn / 4mol\ NH_3)\ (1100.56^{kJ}/_{mol\ rxn}) = 386.89kJ$$
If you chose to produce liquid water instead of gaseous water, it would be pretty close to the same…
$$\Delta G°_{rxn} = 4(+16.45^{kJ}/_{mol}) + 7(+0^{kJ}/_{mol}) + 4(+51.31^{kJ}/_{mol}) + 6(-237.2^{kJ}/_{mol}) = -1152.16^{kJ}/_{mol}$$
$$\{(23.948g\ NH_3) / (17.031^{g}/_{mol})\}\ (1mol\ rxn / 4mol\ NH_3)\ (1152.16^{kJ}/_{mol\ rxn}) = 405.03kJ$$

14. You are studying the reaction of propanoic acid $\{C_2H_5CO_2H(l)\}$ with ethyl amine $\{C_2H_5NH_2(l)\}$ to produce N-ethylpropanamide $\{C_5H_{11}NO(l)\}$ and water. When you run the reaction at 23.61ºC, you find that ΔG for this reaction is $-18.62^{kJ}/_{mol}$ and $\Delta S = +61.37\ ^{J}/_{mol\cdot K}$ (12pts)
   a. Is the reaction endothermic or exothermic? (*Explain your answer with explicit calculations.*)
   b. Over what temperature range is this reaction spontaneous?

$$-18.62^{kJ}/_{mol} = \Delta H_{rxn} - (296.76K)(0.06137^{kJ}/_{mol\cdot K})$$
$$\Delta H_{rxn} = -0.41^{kJ}/_{mol}$$
Since ΔH is negative, the reaction must be exothermic.
Since ΔH is negative and ΔS is positive, the rxn is spontaneous at all temperatures.

15. You have burned 72.612g of ethane $\{C_2H_6(g)\}$ in oxygen to form carbon dioxide and water. If all of the Gibb's Free Energy liberated by this reaction is used to decompose iron(III) chloride to iron metal and chlorine gas, how many grams of iron metal will be formed? (16pts)

$$2\,C_2H_6(g) + 7\,O_2(g) \Leftrightarrow 4\,CO_2(g) + 6\,H_2O(g)$$
$$\Delta G°_{rxn} = 2(+32.0^{kJ}/_{mol}) + 7(+0^{kJ}/_{mol}) + 4(-394.4^{kJ}/_{mol}) + 6(-228.6^{kJ}/_{mol}) = -2885.2^{kJ}/_{mol}$$
$$\{(72.612g\ C_2H_6) / (30.069^{g}/_{mol})\}\ (1mol\ rxn / 2mol\ C_2H_6)\ (2885.2^{kJ}/_{mol\ rxn}) = 3483.66kJ$$

$$2\,FeCl_3(s) \Leftrightarrow 2\,Fe(s) + 3\,Cl_2(g)$$
$$\Delta G°_{rxn} = 2(+334.18^{kJ}/_{mol}) + 2(0^{kJ}/_{mol}) + 3(0^{kJ}/_{mol}) = +668.36^{kJ}/_{mol}$$
$$\{ (3483.66kJ) / 668.36^{kJ}/_{mol\ rxn}) \}\ (2mol\ Fe(s) / 1mol\ rxn)\ (55.847^{g}/_{mol}) = 582.18g\ Fe(s)$$

If you chose to produce liquid water instead of gaseous water, it would be pretty close to the same…

Score

16. 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)

$Al^{3+}(aq)|Al(s)$ and $Pb^{4+}(aq)|Pb^{2+}(aq)$

Oxidation: $\quad\quad\quad\quad\quad\quad\quad 2 \{ Al(s) \Leftrightarrow Al^{+3}(aq) + 3e^{-1}(aq) \}$	$E°_{ox} = +1.676V$
Reduction: $\quad\quad 3 \{ 2e^{-1}(aq) + Pb^{+4}(aq) \Leftrightarrow Pb^{+2}(aq) \}$	$E°_{red} = +1.69V$
Net Rxn: $\quad\quad 2 Al(s) + 3 Pb^{+4}(aq) \Leftrightarrow 3 Pb^{+2}(aq) + 2 Al^{+3}(aq)$	$E°_{cell} = +3.37V$

$GeO_2(s)|GeO(s)$ and $Br_2(l)|Br^{-1}(aq)$

Oxidation: $\quad\quad\quad H_2O(l) + GeO(s) \Leftrightarrow GeO_2(s) + 2e^{-1}(aq) + 2 H^+(aq)$	$E°_{ox} = +0.370V$
Reduction: $\quad\quad\quad 2e^{-1}(aq) + Br_2(l) \Leftrightarrow 2 Br^{-1}(aq)$	$E°_{red} = +1.06V$
Net Rxn: $\quad H_2O(l) + GeO(s) + Br_2(l) \Leftrightarrow 2 Br^{-1}(aq) + GeO_2(s) + 2 H^+(aq)$	$E°_{cell} = +1.43V$

$NO_3^{-1}(aq)|NO(g)$ and $Cr_2O_7^{-2}(aq)|Cr^{3+}(aq)$

Oxidation: $\quad\quad\quad 2 \{ 2 H_2O(l) + NO(g) \Leftrightarrow NO_3^{-1}(aq) + 3e^{-1}(aq) + 4 H^+(aq) \}$	$E°_{ox} = -0.96V$
Reduction: $\quad 14 H^+(aq) + 6e^{-1}(aq) + Cr_2O_7^{-2}(aq) \Leftrightarrow 2 Cr^{+3}(aq) + 7 H_2O(l)$	$E°_{red} = +1.33V$
Net Rxn: $14 H^+(aq) + 4 H_2O(l) + 2 NO(g) + Cr_2O_7^{-2}(aq) \Leftrightarrow 2 Cr^{+3}(aq) + 2 NO_3^{-1}(aq) + 8 H^+(aq) + 7 H_2O(l)$	$E°_{cell} = +0.37V$
Net Rxn: $\quad 6 H^+(aq) + 2 NO(g) + Cr_2O_7^{-2}(aq) \Leftrightarrow 2 Cr^{+3}(aq) + 2 NO_3^{-1}(aq) + 3 H_2O(l)$	$E°_{cell} = +0.37V$

Thermodynamic Values at 25ºC:

Substance	$\Delta H°_f$ ($^{kJ}/_{mol}$)	$S°$ ($^{J}/_{mol\cdot K}$)	$\Delta G°_f$ ($^{kJ}/_{mol}$)
$NH_3(g)$	-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
$FeCl_3(s)$	-400.39	+142.3	-334.18
$Fe(s)$	0	+27.15	0
$Cl_2(g)$	0	+222.96	0

Standard Reduction Potentials at 25ºC:

Half cell	$E°_{red}$ (volts)	Half cell	$E°_{red}$ (volts)
$Al^{3+}(aq)|Al(s)$	-1.676	$Br_2(g)|Br^{-1}(aq)$	+1.06
$Pb^{4+}(aq)|Pb^{2+}(aq)$	+1.69	$NO_3^{-1}(aq)|NO(g)$	+0.96
$GeO_2(s)|GeO(s)$	-0.370	$Cr_2O_7^{-2}(aq)|Cr^{3+}(aq)$	+1.33

Score