Surname (last name):______________________________

Given name (first name):______________________________

Student number:_____________________

Lab Section: (circle one)1 2 3 4 5 6 7 8

Lab Day: (circle one) Tues. Wed. Thurs. Fri.

Lab TA: _________________________________

Course: (circle one) 1301 1311B

Chemistry 1311B/1301

Test 2

November 1, 2006

Please keep your work covered and keep your eyes on your own paper! Cheating or any appearance of cheating will result in an F in the course and possible expulsion from the University.

There are 5 questions in this exam. A periodic table and formula sheet are provided at the end. You may rip these two pages off of the exam and use them to cover your work during the exam.

Any scratch work should be on the back of the exam pages and should be handed in with your exam.

Please show all work to receive partial credit.

You have 80 minutes to complete the exam.

1. At 1130 °C, for the reaction given below,

$$H_2(g) + S(g) \leftarrow\rightarrow H_2S(g)$$

the equilibrium concentrations are:

$[H_2S] = 4.8 \times 10^{-2}$ M; $[H_2] = 1.5 \times 10^{-5}$ M; $[S] = 1.37 \times 10^{-5}$ M

Given the molar enthalpies of formation:

$H_2S(g)\ \Delta G^\circ_f = -33.0$ kJ mole^{-1}; $H_2(g)\ \Delta G^\circ_f = 0.0$ kJ mole^{-1};
$S(g)\ \Delta G^\circ_f = 238.3$ kJ mole^{-1} $S_8(g)\ \Delta G^\circ_f = 49.63$ kJ mole^{-1};
$S_8\ (s)\ \Delta G^\circ_f = 0.0$ kJ mole^{-1}

a) (3 points) Determine the equilibrium constant (**that you would use to calculate ΔG°**) for the reaction at 1130 °C.

$Kc=[H_2S] / ([S]\ [H_2]) = 4.8\times10^{-2} / (1.5\times10^{-5} * 1.37\times10^{-5}) = 2.34 \times 10^8$

$Kp = Kc/(RT) = 2.34 \times 10^8 / (0.08206*(1130+273)) =$ **2.0×10^6**

b) (3 points) Determine the equilibrium constant for the reaction at 298 K.

ΔG°(at 298K) = $-33 -(238.3 + 0) = -271.3$ kJ mol^{-1}

$= -RT \ln K$

$\ln K = -(-271.3\times10^3)/(8.314*298) = 109.5$

$K = 3.6 \times 10^{47}$

c) (3 points) Determine the enthalpy, ΔH°_f, of the reaction.

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

$$\ln\left(\frac{3.6e47}{2e6}\right) = \frac{\Delta H}{8.414}\left(\frac{1}{1403} - \frac{1}{T298}\right)$$

$\Delta H^\circ_f = -299$ kJ mol^{-1}

d) (1 point) Is the reaction endothermic or exothermic?

exothermic

2. Write the equilibrium expression for K you would use to calculate ΔG^O for the following reactions:

a) **(2 points)** $P_4(s) + 6Cl_2(g) \leftarrow\rightarrow 4PCl_3\ (l)$

$K_p = P^{-6}_{Cl2}$

b) **(2 points)** $2NO(g) + O_2(g) \leftarrow\rightarrow 2NO_2\ (g)$

$K_p = P^2_{NO2} / (P^2_{NO} P_{O2})$

c) **(2 points)** $CoCl_4^{2-}(aq) + 6H_2O(l) \leftarrow\rightarrow Co(H_2O)_6^{2+}(aq) + 4\ Cl^-(aq)$

$K_c = [Cl^-]^4\ [Co(H_2O)_6^{2+}] / [CoCl_4^{2-}]$

d) **(2 points)** $2\ Fe(s) + 6\ H_3O^+(aq) \leftarrow\rightarrow 2\ Fe^{3+}(aq) + 6H_2O\ (l) + 3H_2(g)$

$K_{eq} = P^2_{H2}\ [Fe^{3+}]^2 / [H_3O^+]^6$

3. An 0.10 M solution of acetic acid was found to be 1.3 % ionized.

a) (1 point) Write the chemical equation illustrating acid ionization for acetic acid in water:

$H_2O + CH_3COOH \leftarrow\rightarrow H_3O^+ + CH_3COO^-$

b) **(4 points)** What are the equilibrium concentrations of all species in the above reaction?

% ionization = $[H_3O^+]$ / [initial acid concentration]

$[H_3O^+] = (1.3/100)0.1 = 0.0013\ M = [CH_3COO^-]$

$[CH_3COOH] = 0.1 - 0.0013 = 0.0987\ M$

c) **(3 points)** Write the equilibrium expression, K_a for the reaction in part a and determine the acid dissociation (equilibrium constant) K_a for a 0.10 M acetic acid solution.

$Ka = [CH_3COO^-][H_3O^+] / [CH_3COOH] = 0.0013*0.0013/0.0987 = 1.7\times10^{-5}$

d) **(1 point)** Write the chemical reaction that corresponds to the ionization of the conjugate base of acetic acid, (acetic acid = CH_3COOH) (ie. the reaction for which K_b is the equilibrium constant)

$CH_3COO^- + H_2O \leftarrow\rightarrow OH^- + CH_3COOH$

e) **(1 point)** What is the base dissociation constant K_b for the acetate anion in aqueous solution?

$Kb = Kw/Ka = 10^{-14}/1.7\times10^{-5} = 5.9\times10^{-10}$

4. **(8 points)** A mixture of 0.94 g of H_2 and 3.59 moles of HCl is heated to 2800°C. Calculate the mole fraction of H_2, Cl_2 and HCl given that $K_p = 193$ at 2800°C for:

$$H_2(g) + Cl_2(g) \leftarrow\rightarrow 2HCl(g)$$

Moles of H_2 = 0.94/2 = 0.47 moles

	H_2	**Cl_2**	**2HCl**
I	.47 moles	0 moles	3.59 moles
C	+x	+x	-2x
E	0.47+x	x	3.59 -2x

In terms of pressure

E	$(0.47 + x)P_T/n_T$	$(x)P_T/n_T$	$(3.59-2x)P_T/n_T$

$Kp = 193 = [(3.59-2x)P_T/n_T]^2 / [(0.47 + x)P_T/n_T * (x)P_T/n_T]$

$= [(3.59-2x)]^2 / [(0.47 + x) * (x)]$

$= (12.88 - 14.36x + 4x^2) / (0.47\ x + x^2)$

$0 = 189\ x^2 + 105\ x - 12.88$

x = 0.102 or -0.661 (this root is not meaningful)
moles H_2 = .47 + .1 = 0.57; moles Cl_2 0.1; moles HCl = 3.59 – 2(.1) = 3.39
total moles = 0.57+0.1+3.39 = 4.06

X_{H2}=0.140; X_{Cl2}=0.025; X_{HCl}= 0.835

b) If the partial pressure of Cl_2, at equilibrium, is 0.102 atm, what is the total pressure of the gas mixture at equilibrium?
$P_{Cl2} = P_T X_{Cl2}$; 0.102 atm = P_T (0.025)
P_T = 4 atm

4. The following equilibrium constants were obtained at 1123K:
$2CO(g) \leftarrow\rightarrow C(s) + CO_2(g)$ $K_p = 7.7\times10^{-15}$ rxn 1
$CO(g) + Cl_2(g) \leftarrow\rightarrow COCl_2(g)$ $K_p = 6.0 \times 10^{-3}$ rxn 2
a) **(4 points)** Calculate K_c at 1123 K for
$C(s) + CO_2(g) + 2Cl_2(g) \leftarrow\rightarrow 2COCl_2(g)$ rxn 3
Rxn 3 = 2*rxn 2 + (-rxn1)
$K_3 = (K_2)^2/K_1 = (6\times10^{-3})^2/(7.7\times10^{-15}) = 4.7\times10^{-9} = K_p$
$K_p = K_c(RT)^{2-3} = Kc/RT$; $Kc = Kp(RT) = 4.7\times10^{-9} * 0.08206 * 1123 = 4.3\times10^{11}$
b) **(1 point)** Is this reaction spontaneous under standard conditions at 1123 K? Explain.
Since Kp is very much larger than 1, the reaction is product favoured, so under standard conditions it will be spontaneous (also if K>1, $\Delta G° < 0$)
c) **(3 point)** Do you expect $\Delta H°$ and $\Delta S°$ to be positive or negative? Explain.
$\Delta S°$ will be negative because you are going from 3 moles of gas (and one mole of solid) down to 2 moles of gas.
$\Delta H°$ must be –ve because $\Delta G°$ is negative at 1123, and $-T\Delta S°$ is positive.
d) **(2 points)** Under what temperature conditions will the reaction be product favoured? Explain briefly
Under low T conditions. If T gets too large then the positive ($-T\Delta S°$) will "swamp" the negative $\Delta H°$ and $\Delta G°$ will become positive.
e) **(3points)** You have a non equilibrium mixture at 1123K of 0.2 moles of $COCl_2$, 1×10^{-4} moles of Cl_2 and 1.0×10^{-4} moles of CO_2 (total pressure 1 atm). Determine Q and based on this value predict if the reaction will be spontaneous in the forward direction.
$C(s) + CO_2(g) + 2Cl_2(g) \leftarrow\rightarrow 2COCl_2(g)$
$K = P^2_{COCl2} / (P^2_{Cl2} * P_{CO2}) = X^2_{COCl2} P_{total} / (X^2_{Cl2} * (P_T)^2 * X_{CO2} * P_T)$

$= [n^2_{COCl2} / (n^2_{Cl2} * n_{CO2})] * (n_{total}/P_{total})$ (n = number of moles)

$= .2^2(0.2002)/[(1\times10^{-4})^3 *1 \text{ atm}] = 8.0 \times 10^9$

$K_p = 4.7\times10^9$

Since Q > K, you have too much products, so the reaction is not spontaneous in the forward direction.

f) **(4 points)** Determine ΔG for the reaction under the conditions described in part e above. Is your answer reasonable?

$\Delta G=\Delta G^\circ + RT\ln Q = -RT\ln K + RT \ln Q$

$=-(8.314*1123)\ln 4.7\times10^9 + (8.314*1123)\ln 8.0\times10^9 = 4.98 \text{ kJ}$

Since ΔG > 0, rxn is not spontaneous and yes it makes sense because in e) above we said it shouldn't be spontaneous.

Bonus: You have 3 M standard solutions of HCl and benzoic acid, C_6H_5COOH collecting dust on a shelf in the laboratory. You are required to make up 100 ml solutions of pH = 2 from each of the HCl and benzoic acid. Given the K_a of benzoic acid = 6.5×10^{-5}, how many more ml of the benzoic acid (than HCl) 3M standard will you use?

To make a pH 2 solution from HCl

pH =2; $[H_3O^+] = 10^{-2}$ M

To make 100ml of 10^{-2} M from your 3M stock:

$100 * 10^{-2} = x * 3M$; x = 0.33ml (you need 0.33 ml of 3M HCl)

To make a pH 2 solution from benzoic acid:

$C_6H_5COOH + H_2O \leftrightarrow C_6H_5COO^- + H_3O^+$

At Equilibrium: x 10^{-2} 10^{-2}

$Ka = 6.5 \times 10^{-5} = (10^{-2})^2 / x$

x = 1.54 M

So initial concentration of C_6H_5COOH = 1.54 M + 0.01 M = 1.55 M

1.55 (100) = 3 (x)

x = 51.67 ml (you need 51.67 ml of 3M benzoic acid)

ΔV = 51.67 -0.33= 51.33 ml You need 51.33 ml more benzoic acid than HCl

EQUATIONS SHEET

$\Delta H^o_{rxn} = \Sigma n \Delta H^o_f$ (products) – $\Sigma m \Delta H^o_f$ (reactants)

$\Delta G^o_{rxn} = \Sigma n \Delta G^o_f$ (products) – $\Sigma m \Delta G^o_f$ (reactants)

$\Delta S^o_{rxn} = \Sigma n S^o$ (products) – $\Sigma m S^o$ (reactants)

$PV = nRT$ $\qquad \Delta G = \Delta H - T\Delta S$ $\qquad \Delta G^o = -RT\ln K$

$\upsilon_{rms} = (3RT/MM)^{1/2}$ $\qquad \Delta E = q + w$ $\qquad \Delta G = \Delta G^o + RT\ln Q$

$\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\qquad q = ms\Delta T$ $\qquad q = C\Delta T$

$w = -P\Delta V$ $\qquad [A] = -kt + [A]_o$ $\qquad t_{1/2} = 0.693/k$

$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\qquad 1/[A] = kt + 1/[A]_o$ $\qquad \ln[A] = -kt + \ln[A]_o$

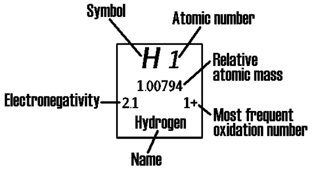
$P_A = X_A P_A^o$ $\qquad P_A = X_A P_{Total}$ $\qquad P_{total} = P_1 + P_2 + \ldots$

$K_P = K_C(RT)^{\Delta n}$

$pH = -\log[H_3O^+]$ $\qquad pOH = -\log[OH^-]$ $\qquad pH + pOH = 14$

$K_w = K_a \times K_b$ $\qquad pH = pKa + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$

Constants:		Conversion Factors :
Avogadro's Number (N_A)	6.02×10^{23}	1 A = 1 C s^{-1}
Faraday's constant (F)	96,500 C/mol e^-	1 C = 1 J V^{-1} mol^{-1}
Universal Gas Constant (R)	8.314 J mol^{-1} K^{-1}	
	8.314 kg m^2 mol^{-1} K^{-1} s^{-2}	
	0.08206 L atm mol^{-1} K^{-1}	1 nm = 10^{-9} m
Planck's constant (h)	6.626×10^{-34} J s	1 atm = 760 torr
Rydberg Constant (R_H)	2.18×10^{-18} J	= 760 mmHg
Speed of light(c)	3.00×10^8 m/s	= 101.3 kPa



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	*H 1* 1.00794 2.1 1+ Hydrogen																	*He 2* 4.002602 - - Helium
2	**Li 3** 6.941 1.0 1+ Lithium	**Be 4** 9.012182 1.5 2+ Beryllium											**B 5** 10.811 2.0 3+ Boron	**C 6** 12.011 2.5 4+,4- Carbon	*N 7* 14.00674 3.0 3+,3- Nitrogen	*O 8* 15.9994 3.5 2- Oxygen	*F 9* 18.9984032 4.0 1- Fluorine	*Ne 10* 20.1797 - - Neon
3	**Na 11** 22.989768 0.9 1+ Sodium	**Mg 12** 24.3050 1.2 2+ Magnesium											**Al 13** 26.981539 1.5 3+ Aluminum	**Si 14** 28.0855 1.8 4+ Silicon	**P 15** 30.973762 2.1 5+ Phosphorus	**S 16** 32.066 1.8 4+ Sulfur	*Cl 17* 35.4527 3.0 1- Chlorine	*Ar 18* 39.948 - - Argon
4	**K 19** 39.0983 0.8 1+ Potassium	**Ca 20** 40.078 1.0 2+ Calcium	**Sc 21** 44.955910 1.3 3+ Scandium	**Ti 22** 47.88 1.5 4+ Titanium	**V 23** 50.9415 1.6 5+ Vanadium	**Cr 24** 51.9961 1.6 3+ Chromium	**Mn 25** 54.93805 1.5 2+ Manganese	**Fe 26** 55.847 1.8 3+ Iron	**Co 27** 58.9332 1.8 2+ Cobalt	**Ni 28** 58.6934 1.8 2+ Nickel	**Cu 29** 63.546 1.9 2+ Copper	**Zn 30** 65.39 1.6 2+ Zinc	***Ga 31*** 69.723 1.6 3+ Gallium	**Ge 32** 72.61 1.6 4+ Germanium	**As 33** 74.92159 2.0 3+,3- Arsenic	**Se 34** 78.96 2.4 4+ Selenium	***Br 35*** 79.904 2.8 1- Bromine	*Kr 36* 83.80 - - Krypton
5	**Rb 37** 85.4678 0.8 1+ Rubidium	**Sr 38** 87.62 1.0 2+ Strontium	**Y 39** 88.90585 1.3 3+ Yttrium	**Zr 40** 91.224 1.4 4+ Zirconium	**Nb 41** 92.90638 1.6 5+ Niobium	**Mo 42** 95.94 1.8 6+ Molybdenum	Tc 43 98.9063 1.9 7+ Technetium	**Ru 44** 101.57 2.2 3+,4+ Ruthenium	**Rh 45** 102.9055 2.2 3+ Rhodium	**Pd 46** 106.42 2.2 2+ Palladium	**Ag 47** 107.8682 1.9 1+ Silver	**Cd 48** 112.411 1.7 2+ Cadmium	**In 49** 114.82 1.7 3+ Indium	**Sn 50** 118.71 1.8 4+ Tin	**Sb 51** 121.757 1.9 3+,3- Antimony	**Te 52** 127.60 2.1 4+ Tellurium	**I 53** 126.90447 2.5 1- Iodine	*Xe 54* 131.29 - - Xenon
6	***Cs 55*** 132.90543 0.7 1+ Cesium	**Ba 56** 137.327 0.9 2+ Barium	**La 57** 138.9055 1.1 3+ Lanthanum	**Hf 72** 178.49 1.3 4+ Hafnium	**Ta 73** 180.9479 1.5 5+ Tantalum	**W 74** 183.85 1.7 6+ Tungsten	**Re 75** 186.207 1.9 7+ Rhenium	**Os 76** 190.2 2.2 4+ Osmium	**Ir 77** 192.22 2.2 4+ Iridium	**Pt 78** 195.08 2.2 4+ Platinum	**Au 79** 196.96654 2.4 3+ Gold	***Hg 80*** 200.59 1.9 2+ Mercury	**Tl 81** 204.3833 1.8 1+ Thallium	**Pb 82** 207.2 1.8 2+ Lead	**Bi 83** 208.98037 1.9 3+ Bismuth	**Po 84** 208.9824 2.0 2+ Polonium	**At 85** 209.9871 2.2 1- Astatine	*Rn 86* 222.0176 - - Radon
7	***Fr 87*** 223.0197 0.7 1+ Francium	**Ra 88** 226.0254 0.9 2+ Radium	**Ac 89** 227.0278 1.1 3+ Actinium	Rf 104 261.11 - - Rutherfordium	Db 105 262.11 - - Dubnium	Sg 106 263.12 - - Seaborgium	Bh 107 262.12 - - Bohrium	Hs 108 264 - - Hassium	Mt 109 266.1378 - - Meitnerium	Uun 110 269 - - Ununnilium	Uuu 111 272 - - Unununium	Uu 112 277 - - Ununbium		Uuq 114 289 - - Ununquadium		Uuh 116 289 - - Ununhexium		Uuo 118 293 - - Ununoctium

6	**Ce 58** 140.115 1.1 3+ Cerium	**Pr 59** 140.90765 1.1 3+ Praseodymium	**Nd 60** 144.24 1.1 3+ Neodymium	Pm 61 144.9127 1.1 3+ Promethium	**Sm 62** 150.36 1.2 3+ Samarium	**Eu 63** 151.965 1.2 3+ Europium	**Gd 64** 157.25 1.2 3+ Gadolinium	**Tb 65** 168.92534 1.2 3+ Terbium	**Dy 66** 162.50 1.2 3+ Dysposium	**Ho 67** 164.93032 1.2 3+ Holmium	**Er 68** 167.26 1.2 3+ Erbium	**Tm 69** 168.93421 1.2 3+ Thulium	**Yb 70** 173.04 1.1 3+ Ytterbium	**Lu 71** 174.967 1.2 3+ Lutetium
7	**Th 90** 232.0381 1.3 4+ Thorium	**Pa 91** 231.03588 1.5 5+ Protactinium	**U 92** 238.0289 1.4 6+ Uranium	Np 93 237.082 1.3 5+ Neptunium	Pu 94 244.0642 1.3 4+ Plutonium	Am 95 243.0614 1.3 3+ Americium	Cm 96 247 1.3 3+ Curium	Bk 97 247.0703 1.3 3+ Berkelium	Cf 98 251.0796 1.3 3+ Californium	Es 99 252.03 1.3 - Einsteinium	Fm 100 257.0951 1.3 - Fermium	Md 101 258.01 1.3 - Mendelevium	No 102 259.1009 1.3 - Nobelium	Lr 103 260.1053 - - Lawrencium

Under normal conditions, bold symbols correspond to solid state, bold italic correspond to liquid state, italic correspond to gaseous state and normal correspond to synthetic elements.