Chemistry 410B **Exam 6** **Fall 2016**

NAME:

Instructions:

1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- **The first portion of the exam (problem 1) is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. **40 points.**

(a) The vapor pressure of tetrahydrofuran (THF) at 293 K is 0.173 bar. Use Raoult's law to estimate the partial pressure at equilibrium of THF over a solution of 5.0 M $LiBH_4$ in THF. (The molarity of pure THF is 12.33 M. Assume the molarity is not affected by the solute.)

(b) Calculate the osmotic pressure **in bar** across the membrane when the concentration inside the osmotic cell is 0.100 M at 298 K.

(c) Indicate whether each of the following reactions has a $\Delta_{\text{rxn}}S$ value that is large (**L**) or small (**S**) in magnitude, where large is $> 80\,\text{J K}^{-1}\,\text{mol}^{-1}$ and small is $< 40\,\text{J K}^{-1}\,\text{mol}^{-1}$. Also indicate whether the value is positive (+) or negative (−).

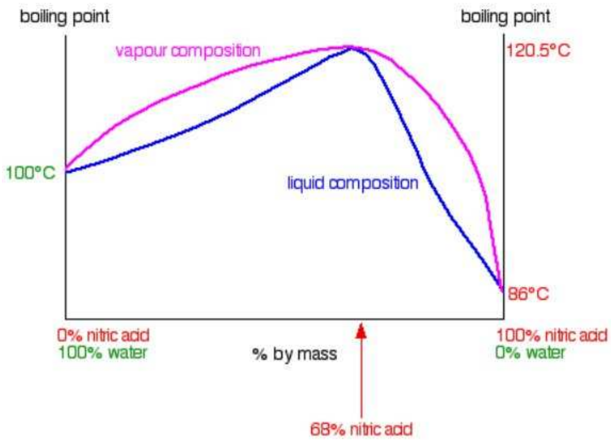
$$I_2(s) \longrightarrow 2I(g)$$

$$2CH_3OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(g)$$

$$2H_2CCO(g) + 4O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$$

(d) In a calorimetry experiment, 0.100 mol of $Br_2(l)$ evaporates with ΔH° of 3.091 kJ. Find the final temperature of the 1.00 L ($c_P = 4.184\,\text{J K}^{-1}\,\text{g}^{-1}$, $C_{Pm} = 75.3\,\text{J K}^{-1}\,\text{mol}^{-1}$) water bath if the initial temperature was 298.15 K.

2. The phase diagram for a mixture of water and nitric acid is shown below.



(a) What is the boiling point of pure nitric acid?

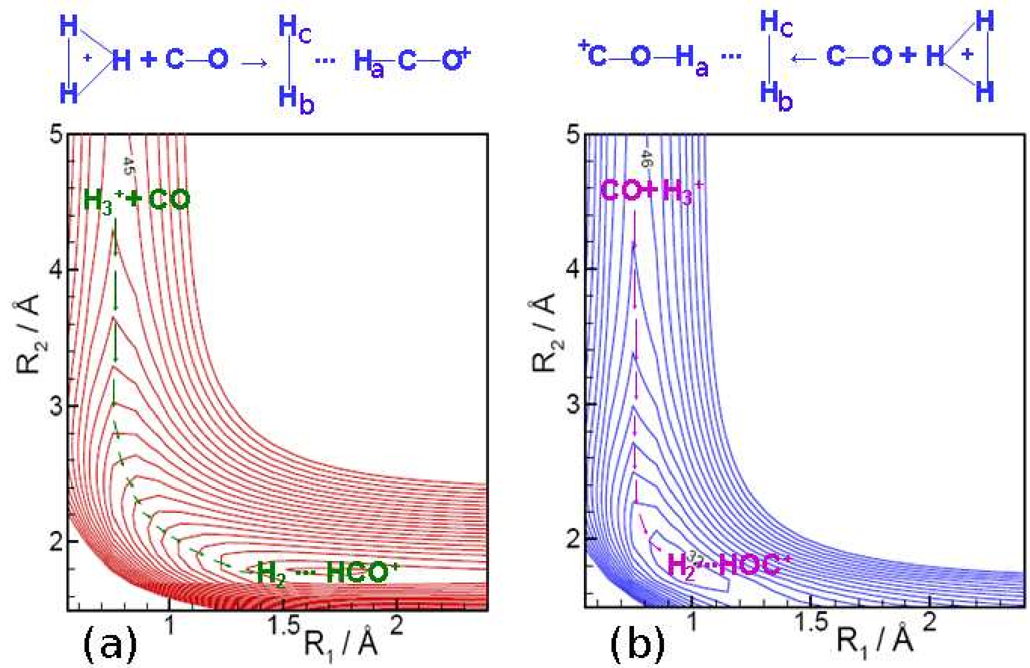
(b) At what temperature is the azeotrope?

(c) Would this mixture show a positive, negative, or zero deviation from Raoult's law?

(d) In one sentence, explain what process or structure at the molecular scale would justify your answer to the previous question.

3. Let the reaction $2\mathrm{F}(g) \longrightarrow \mathrm{F}_2(g)$ occur adiabatically, starting at an initial temperature of 298 K. Use the properties in the attached table of thermodynamic properties (including the heat capacities) to calculate the final temperature *and* the value of K_{eq} at the final temperature.

4. The two reaction surfaces drawn below describe the two reactions shown. There is no transition state for either reaction. The contour lines are drawn every 3 kJ mol^{-1}. The H atoms are labeled in half of each reaction. The CO bond axis is always perpendicular to and bisects the H_aH_b bond.



(a) R_2 in surface (a) is measuring the distance between what two atoms?

(b) Find $\Delta_{\text{rxn}}E$ for reaction (a): $H_3^+ + CO \longrightarrow H_2 + HCO^+$.

(c) Find $\Delta_{\text{rxn}}E$ for the reaction $HCO^+ \longrightarrow HOC^+$.

(d) How many vibrational coordinates would we need to describe the *entire* reaction surface?

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_B	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^8$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	erg	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-24}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-21}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-18}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-16}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-16}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^{2}$	83.59	1	0.2390	$1.661 \cdot 10^{-14}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^{2}$	$3.498 \cdot 10^{2}$	4.184	1	$6.948 \cdot 10^{-14}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^{4}$	$8.066 \cdot 10^{3}$	96.49	23.06	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^{5}$	$2.195 \cdot 10^{5}$	$2.625 \cdot 10^{3}$	$6.275 \cdot 10^{2}$	$4.360 \cdot 10^{-11}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	1	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	10^{7}	10^{-3}
dm^3 bar =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	$1.000 \cdot 10^{9}$	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{10}	1

distance	1 Å=	10^{-10} m	
mass	1 amu =	$1.66054 \cdot 10^{-27}$ kg	
energy	1 J =	1 kg m^2 s^{-2}	= 10^7 erg
force	1 N =	1 kg m s^{-2}	= 10^5 dyn
electrostatic charge	1 C =	1 A s	= $2.9979 \cdot 10^9$ esu
	1 D =	$3.3357 \cdot 10^{-30}$ C m	= $1 \cdot 10^{-18}$ esu cm
magnetic field strength	1 T =	1 kg s^{-2} A^{-1}	= 10^4 gauss
pressure	1 Pa =	1 N m^{-2}	= 1 kg m^{-1} s^{-2}
	1 bar =	10^5 Pa	= 0.98692 atm

Gibbs phase	$d = k - p + 2$
colligative props.	$\Delta T_f = -\frac{RT^{\bullet 2}_f X_B}{\Delta_{fus}H}$ $\qquad \Pi = RT[B]$
reactions	$T_{ad} = T_1 \; - \; \frac{\Delta H_{,rxn}(T_1)}{C_P(\text{products})}$
	$\Delta_{rxn}G = \Delta_{rxn}G^{\circ} + RT \ln \Xi$
	$\ln K_{eq} = -\frac{\Delta_{rxn}G}{RT}$

	S°_m (J K^{-1} mol^{-1})	$\Delta_f H^{\circ}$ (kJ mol^{-1})	$\Delta_f G^{\circ}$ (kJ mol^{-1})	C_{Pm} (J K^{-1} mol^{-1})
$CO(g)$	197.674	–110.525	–137.168	29.142
$CO_2(g)$	213.74	–393.509	–394.359	37.11
$CS_2(g)$	237.84	117.36	67.12	45.40
$CS_2(l)$	151.34	89.70	65.27	75.7
$CH_4(g)$	186.264	–74.81	–50.72	35.309
$CHCl_3(l)$	201.7	–134.47	–73.66	113.8
$CH_2Cl_2(g)$	270.23	–92.47	–65.87	50.96
$CH_3Cl(g)$	234.58	–80.83	–57.37	40.75
$CCl_4(g)$	309.85	–102.9	–60.59	83.30
$CCl_4(l)$	216.40	–135.44	–65.21	131.75
$CF_4(g)$	261.61	–925.	–879.	61.09
$F(g)$	158.754	78.99	61.91	22.744
$F_2(g)$	202.78	0.	0.	31.30
$H(g)$	114.713	217.965	203.247	20.786
$H_2(g)$	130.684	0.	0.	28.824
$H_2O(g)$	188.825	–241.818	–228.572	33.577
$H_2O(l)$	69.91	–285.830	–237.129	75.291
$H_2S(g)$	205.79	–20.63	–33.56	34.23
$HF(g)$	173.779	–271.1	–273.2	29.133
$HCl(g)$	186.908	–92.307	–95.299	29.12
$HBr(g)$	198.695	–36.40	–53.45	29.142
$HI(g)$	206.594	26.48	1.70	29.158
$I(g)$	180.791	106.838	70.250	20.786
$I_2(g)$	260.69	62.438	19.327	36.90
$I_2(s)$	116.135	0.	0.	54.438
$N_2(g)$	191.49	0	0	29.088
$O(g)$	161.055	249.170	231.731	21.912
$O_2(g)$	205.138	0.	0.	29.355
$O_3(g)$	238.93	142.7	163.2	39.20