Chemistry 410B **Exam 6** **Spring 2009**

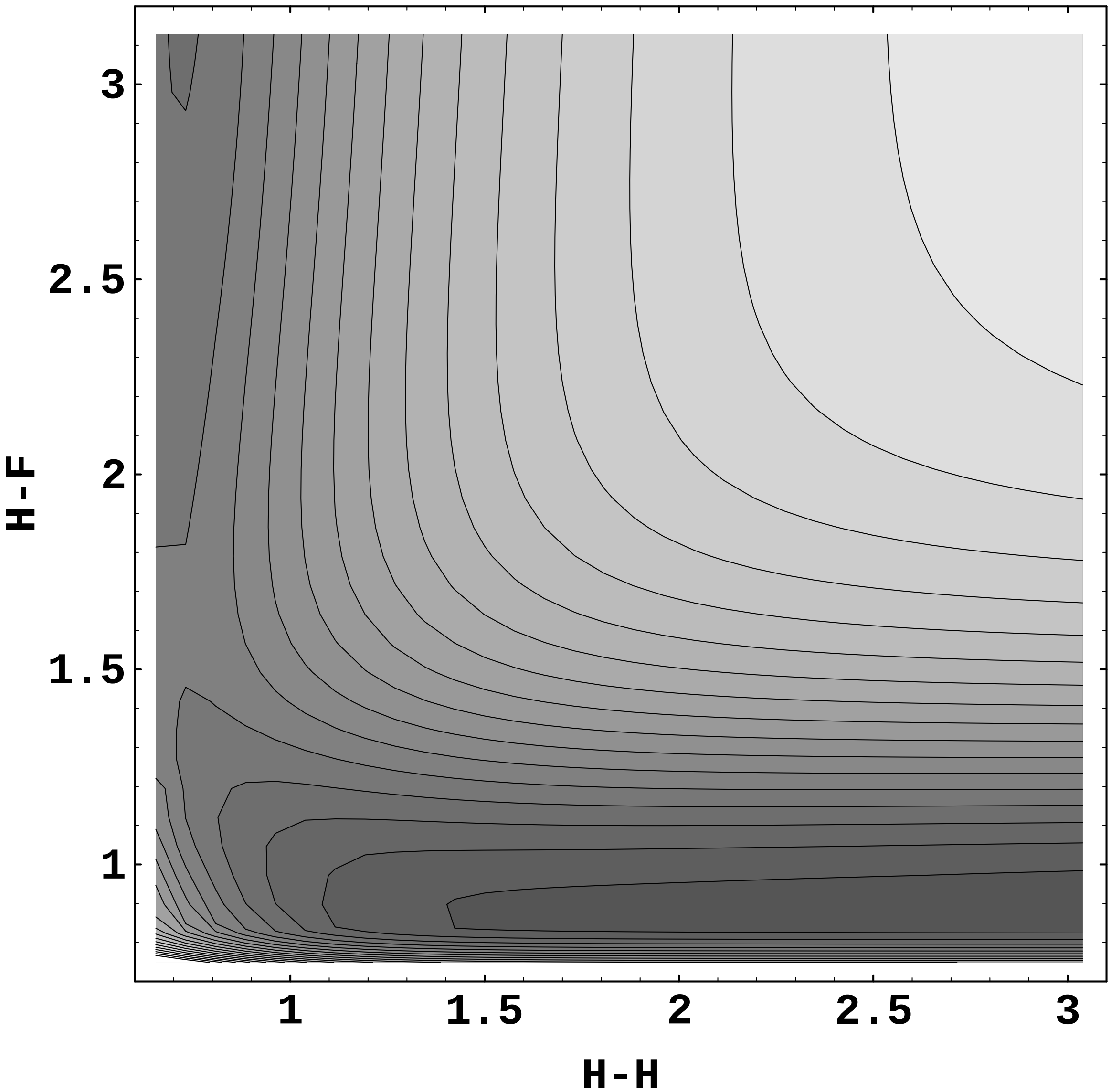
NAME:

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.**

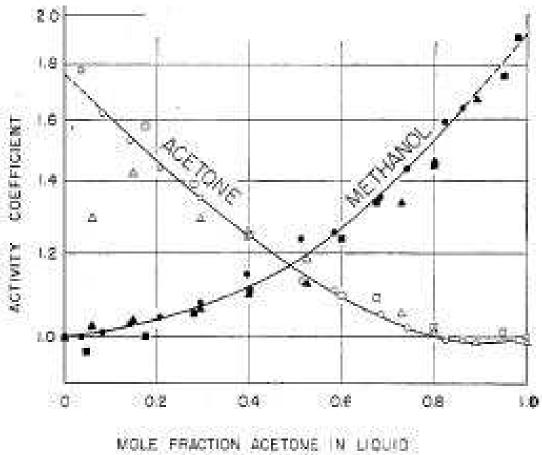
Other notes:

- **The first page portion of the exam 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.


3
2.5
2
1.5
1
H-F
1
1.5
2
2.5
3
H-H

1. **40 points.**

   (a) A graph of the activity coefficients γ for methanol and acetone is shown below, where $a_i = \gamma_i X_i$. Circle the region or regions of the graph where either liquid obeys Raoult's law.



   (b) On the F+H_2 reaction surface, shown on the opposite page, determine the energy in $\mathrm{kJ\,mol^{-1}}$ of the system, relative to the minimum energy of H+HF, when the F atom is 2.5 Å from the nearest H atom, and the H atoms are separated by 1.5 Å.

   (c) Identify the number of degrees of freedom contributed by each term in the following reaction of **linear** diacetylene (HC_4H), and indicate whether the overall $\Delta_{\mathrm{rxn}}S$ is likely to be positive or negative:

	$9O_2(g)$	+	$2HC_4H(g)$	$\longrightarrow$	$8CO_2(g)$	+	$2H_2O(g)$
translational							
rotational							
vibrational							
$\Delta_{\mathrm{rxn}}S$ + or −							

   (d) For the metabolism of methylamine to formaldehyde and ammonia, the enthalpy of reaction is $-201.8\,\mathrm{kJ\,mol^{-1}}$ and the entropy of reaction is $148.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Find the value of the equilibrium constant at 325 K.

2. From the corresponding Henry's law coefficient $k_X = 8.64 \cdot 10^4$ bar, estimate the **molarity** of $N_2(g)$ in water at 298 K when the water is in equilibrium with air at a total pressure of 1.10 bar.

Assume that the air is 78% N_2 by volume (*i.e.,* by mole number), and that the dissolved N_2 does not affect the volume of solution.

3. Calculate the Helmholtz free energy of reaction $\Delta_{\text{rxn}}F^{\ominus}$ for the formation of 1.00 mol $IF_5(g)$ from solid iodine and fluorine gas at 320 K and 1.00 bar. For IF_5 at 298 K, $\Delta_f H^{\ominus} = -822.49\,\text{kJ mol}^{-1}$ $\Delta_f S^{\ominus} = -237.32\,\text{J K}^{-1}\,\text{mol}^{-1}$, and $\Delta_f C_{Pm} = -6.27\,\text{J K}^{-1}\,\text{mol}^{-1}$.

4. (a) Write the chemical reaction for the combustion of ketene gas, $H_2C{=}C{=}O$, at 298 K.

   (b) If the enthalpy of combustion for ketene is $-1025.3\,\text{kJ mol}^{-1}$, what is the enthalpy of formation for ketene?

   (c) Estimate the adiabatic flame temperature of ketene, using the heat capacities at 298 K. For this calculation, assume water is a gas.

equipartition $$E = \frac{1}{2}N_{\text{ep}}Nk_BT = \frac{1}{2}N_{\text{ep}}nRT$$

thermo derivatives $$dE = TdS - PdV + \mu_1 dn_1 + \ldots \qquad dH = TdS + VdP + \mu_1 dn_1 + \ldots$$

$$dF = -SdT - PdV + \mu_1 dn_1 + \ldots \qquad dG = -SdT + VdP + \mu_1 dn_1 + \ldots$$

Maxwell relations $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + V\alpha\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) \qquad \Delta S = nC_{Pm}\ln\left(\frac{T_f}{T_i}\right)$$

Gibbs-Duhem $$\sum_i n_i\mu_i = 0$$

$$\Delta T_f = -\frac{RT^{\bullet 2}_f X_B}{\Delta_{\text{fus}}H} \qquad \Pi = \frac{RTX_2}{V_m} = RTx_2$$

$$T_{\text{ad}} = T_1 - \frac{\Delta H_{,\text{rxn}}(T_1)}{C_P(\text{products})}$$

$$\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^{\circ} + RT\ln\Xi$$

adiab. flame $$T_2 = T_1 - \frac{\Delta_{\text{rxn}}H(T_1)}{\bar{C}_P(\text{products})}$$

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