Chemistry 410B **Exam 5** **Spring 2012**

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.

1. **40 points.**

(a) Calculate the entropy of mixing when we combine 0.100 mol of neon with 0.900 mol of argon at 298 K and 1.00 bar, assuming both are ideal gases.

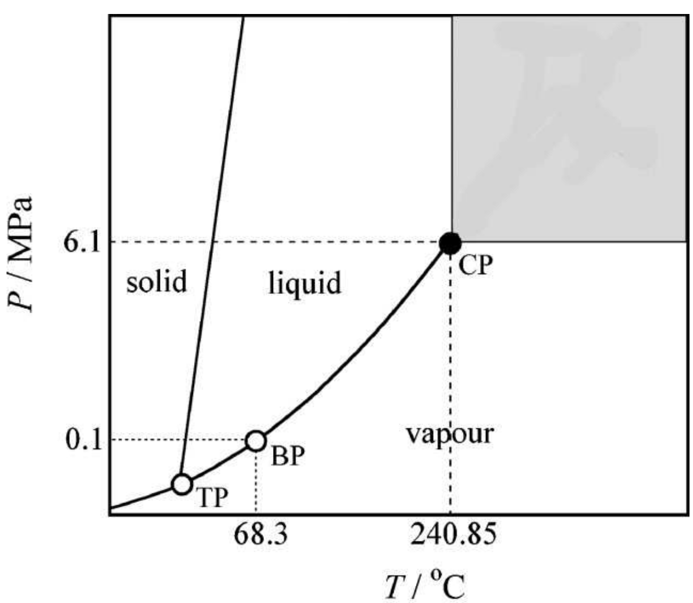
(b) In a dewar filled with liquid nitrogen, we have an equilibrium mixture of N_2, O_2, and argon, with each substance present in both liquid and vapor phases. Give any *complete* set of intensive parameters that can be independently adjusted while maintaining this equilibrium (in other words, list as many as the number of free parameters).

(c) Find $\Delta_{\mathrm{fus}}H^{\circ}$, $\Delta_{\mathrm{fus}}S^{\circ}$, and $\Delta_{\mathrm{fus}}G^{\circ}$ for water at its normal freezing point of 273.15 K.

(d) Find $\Delta_{\mathrm{vap}}H^{\circ}$ of n-pentane if $T_b^{\circ} = 309.2\,\mathrm{K}$ and the compound boils at a pressure of 0.680 bar at 298.15 K.

2. Estimate $\Delta_{\mathrm{vap}}E^{\ominus}$ for carbon tetrachloride at its standard boiling point.

3. Based on the phase diagram shown below for ethanol, estimate the ethanol-ethanol binding energy in cm^{-1} and the critical number density ρ_c in cm^{-3}. Pay close attention to all units, and note that $1\,\mathrm{MPa}=10^6\,\mathrm{Pa}$.



4. If we mix 10.0 mol of water initially at 273.15 K with 10.0 mol of liquid nitrogen initially at 77.36 K and allow the mixture to come to equilibrium, what do we get? Give the phase or phases of each substance and how many moles in each phase, and the final temperature T_f.

   (a) final state of N_2:

   (b) final state of H_2O:

   (c) T_f:

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}= 0.6950 cm^{-1}/K
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

entropy $S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -Nk_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$

partition func.s $q(T) = \sum_\epsilon g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)} \qquad q_{\text{rot}} \approx \frac{k_{\text{B}}T}{B} \qquad q_{\text{vib}} \approx \frac{1}{1 - e^{-\omega_e/(k_{\text{B}}T)}}$

$$q_{\text{trans}}(T,V) = q'_K q'_U = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \quad \text{(ideal gas)}$$

collisions $v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} \qquad \langle v \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} \qquad \langle v_{\text{AB}} \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi \mu}}$

$$\gamma = \rho \sigma \langle v_{AA} \rangle \qquad \lambda = \frac{1}{\sqrt{2}\rho\sigma} \qquad \rho = \frac{N}{V} = \frac{P\mathcal{N}_A}{RT}$$

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

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

isobaric heating: $\Delta S = nC_{P\text{m}} \ln \left(\frac{T_f}{T_i}\right)$

isothermal exp: $w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1}\right) \qquad w_{\text{irr}} = -P_{\text{min}} \Delta V \qquad \Delta S = nR \ln \left(\frac{V_f}{V_i}\right)$

adiabatic exp: $w_{\text{rev}} = C_V \Delta T \qquad \frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)^{-C_{V\text{m}}/R} = \left(\frac{P_2}{P_1}\right)^{-C_{V\text{m}}/C_{P\text{m}}}$

Sackur-Tetrode: $S_m = R \left\{ \frac{5}{2} + \ln \left[\left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} \frac{RT}{\mathcal{N}_A P} \right] \right\}$

Clausius/Clapeyron: $\frac{dP}{dT} = \frac{\Delta_\phi H}{T \Delta_\phi V} \qquad \ln P(\text{ bar}) = \frac{\Delta_{\text{vap}} H}{R} \left[\frac{1}{T_b} - \frac{1}{T} \right]$

Gibbs phase: $d = k - p + 2$

Raoult's law: $P_{\text{A}} = P^{\bullet}_{\text{A}} X_{\text{A}}$

Henry's law: $P_{\text{B}} = k_X, X_{\text{B}} \qquad k_X = \lim_{X_{\text{B}} \to 0} \left(\frac{P_{\text{B}}}{X_{\text{B}}}\right)$

colligative props. $\Delta T_f = -\frac{RT^{\bullet 2}_f X_{\text{B}}}{\Delta_{\text{fus}} H} \qquad \Pi = RT[\text{B}]$

reactions: $\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^{\ominus} + RT \ln \Xi$

$$\ln K_{\text{eq}}(T) = -\frac{\Delta_{\text{rxn}} G^{\ominus}}{RT} = -\frac{\Delta_{\text{rxn}} H^{\ominus}}{RT} + \frac{\Delta_{\text{rxn}} S^{\ominus}}{R}$$

rate constants: $k_{\text{SCT}} = p \sigma_{AB} \left(\frac{8k_{\text{B}}T}{\pi \mu}\right)^{1/2} e^{-E_a/(RT)} \mathcal{N}_A \qquad k_{\text{TST}} = \frac{k_{\text{B}}T}{Ch} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/(RT)}$