Chemistry 410B **Exam 4** **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:

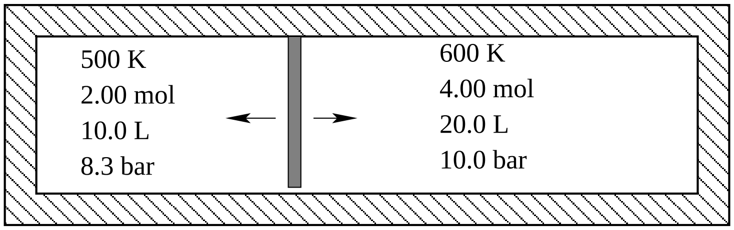
- **The first page portion of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase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

1. **40 points.**

   (a) Use the Sackur-Tetrode equation to predict the standard molar entropy of *atomic* iodine I(g) at 573 K and 1.00 bar.

   (b) Calculate the entropy change when we heat calcium chloride from 298 K to 323 K, assuming that the heat capacity remains a constant 72.59 $\mathrm{J\,K^{-1}\,mol^{-1}}$ over this temperature range.

   (c) The container shown below separates an ideal gas into two compartments with a movable, thermally conducting wall between them. The conditions in each compartment are labeled.



   Circle **each** statement below that correctly describes how the system will change.

   i. the wall will move to the right
   ii. the wall will move to the left
   iii. heat will flow to the right
   iv. heat will flow to the left
   v. until the volume on both sides is the same
   vi. until the temperature on both sides is the same
   vii. until the pressure on both sides is the same
   viii. until the number of moles on both sides is the same

2. In the text, we described the reversible, isothermal expansion of 1.00 mol of an ideal gas from 2.48 L at 10.00 bar and 298 K to a final pressure of 1.00 bar. Repeat the process from the same starting point, but this time set the final pressure P_2 to 0.100 bar. Calculate the following parameters:

   (a) $V_2 =$

   (b) $\Delta E =$

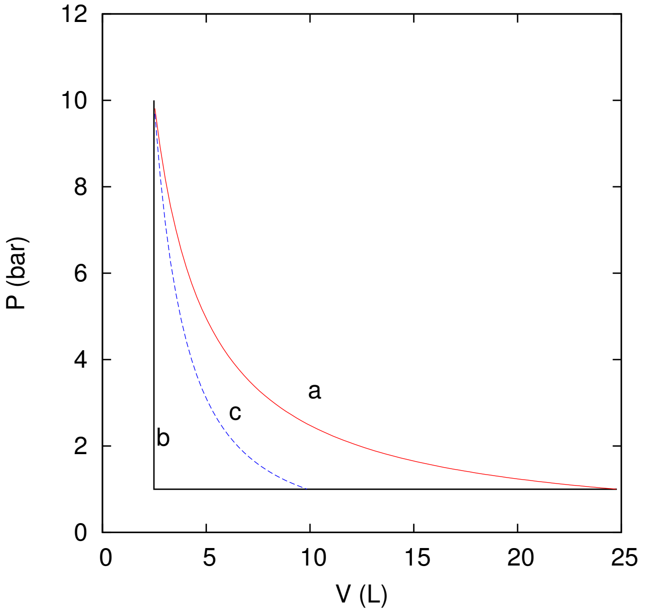
   (c) $w =$

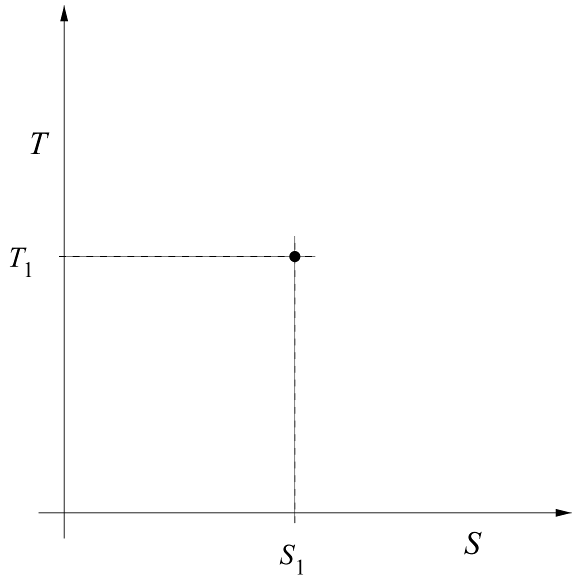
   (d) $\Delta S =$

   (e) $\Delta F =$

3. In many systems, the canonical distribution accurately describes populations in each degree of freedom (translations, rotations, and vibrations), but the effective temperature for each degree of freedom is different. Consider a sample of I_2 gas ($\omega_e = 214.5\,\mathrm{cm}^{-1}$, $B_e = 0.0559\,\mathrm{cm}^{-1}$) that initially has a vibrational temperature $T_{\mathrm{vib}} = 653\,\mathrm{K}$, a rotational temperature $T_{\mathrm{rot}} = 437\,\mathrm{K}$, and a translational temperature $T_{\mathrm{trans}} = 298\,\mathrm{K}$. We then isolate the sample, and wait for these different degrees of freedom to exchange energy until the temperatures are equal. What is the final temperature (now the same for all motions) of the sample?

4. Figure 17.17 from the book (reproduced at left below) shows the P vs V graphs of three expansions: (a) the reversible isothermal, (b) the irreversible isothermal, and (c) the reversible adiabatic. In the empty graph at right, plot the corresponding curves for T vs S of these three processes, letting all three processes start from the same initial point (T_1, S_1). Be quantitative if possible, otherwise sketch an approximate curve. Label the curves a, b, and c.





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