Chemistry 410B **Exam 4** **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.

1. **40 points.**

   (a) For each of the following, write a **single** thermodynamic parameter equal to the expression:

      i. $\frac{nRT}{V}$ for ideal gas

      ii. $\left(\frac{\partial H}{\partial P}\right)_{S,n}$

      iii. $\left(\frac{\partial H}{\partial T}\right)_{P,n}$

      iv. $F + TS$

   (b) Rank the following gas-phase compounds (by letter) in order of **increasing** molar heat capacity C_{Pm} (from lowest value on the left, to highest value on the right). (A) C_3H_8 (B) HCCH (C) C_3H_7I (D) H_2CO

   (c) A leak in a container allows an ideal gas to escape our sample irreversibly and isothermally at constant pressure. For each of the following parameters, **circle** any that stay unchanged (for the sample) during this process, put a **square** around any that decrease, and **underline** any that increase.

S	n	V	E
S_{tot}	T	H	μ

   (d) If $\Omega = AV^N$, find $\Delta S = S(V_2) - S(V_1)$ in terms of R when $V_2 = 2V_1$ and $N = \mathcal{N}_A$.

2. (a) Find an expression for $\left(\frac{\partial P}{\partial T}\right)_{F,n}$ of any material in terms of any of α, C_P, C_V, or the compressibilities κ, where

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S .$$

(b) Evaluate this expression when the material is an ideal gas.

3. Start from 0.100 mol of a monatomic ideal gas at a volume of 5.00 L at 298 K. Find the final pressure if we change the volume adiabatically to bring the gas to a final temperature of 410 K.

4. The heat capacity gives the heat transfer per unit temperature change, $\partial q/\partial T$, and we define these at constant V or at constant P. In the same way, we can define "work capacities" at constant T or S, B_T and B_S, by

$$B_T = \left(\frac{\partial w}{\partial P}\right)_T \qquad\qquad B_S = \left(\frac{\partial w}{\partial P}\right)_S .$$

Find an expression for B_T in terms of B_S, replacing any remaining partial derivatives by common thermodynamic parameters.

equipartition $E = \frac{1}{2} N_{\rm ep} N k_B T = \frac{1}{2} N_{\rm ep} n R T$

virial/van der Waals $P = RT\left[V_m + B_2(T) V_m^2\right]$ $\qquad RT = \left(P + \frac{a}{V_m^2}\right)(V_m \; - \; b)$

$$B_2(T) = -\mathcal{N}_A \frac{1}{2}\mathcal{I}(\beta) \equiv -2\pi\mathcal{N}_A \int_0^{V^{1/3}} (e^{-u(R)/(k_BT)} - 1) R^2 dR$$

$$a \approx \frac{16\pi\mathcal{N}_A^2 \epsilon R_{\rm LJ}^3}{9} \qquad b \approx \frac{2\mathcal{N}_A \pi R_{\rm LJ}^3}{3}$$

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

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

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_x \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

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

isothermal exp: $w_{\rm rev} = -nRT \ln\left(\frac{V_2}{V_1}\right)$ $\qquad w_{\rm irr} = -P_{\rm ex}\,\Delta V$

rev. adiabatic exp: $w_{\rm rev} = C_V \Delta T$ $\qquad V_2 = V_1\left(\frac{P_2}{P_1}\right)^{-C_V/(C_V + nR)}$

Joule-Thompson: $\left(\frac{\partial T}{\partial P}\right)_H = \frac{\frac{2a}{RT} - b}{C_{Pm}}$

Partial derivative identities

reciprocal rule	$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z$	$= 1$
slope rule	$dz(x,y)$	$= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$
cyclic rule	$\left(\frac{\partial x}{\partial y}\right)_z$	$= -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$
chain rule	$\left(\frac{\partial x}{\partial y}\right)_z$	$= \left(\frac{\partial x}{\partial w}\right)_z \left(\frac{\partial w}{\partial y}\right)_z$
	$\left(\frac{\partial x}{\partial y}\right)_z$	$= \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z$

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