Chemistry 410B **Exam 4** **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) Write the symbol (*not* the mathematical formula) that we use for each of the following parameters:

      i. **example:** Gibbs free energy: $\boxed{G}$

      ii. heat capacity at constant pressure:

      iii. isothermal compressibility:

      iv. chemical potential:

      v. heat:

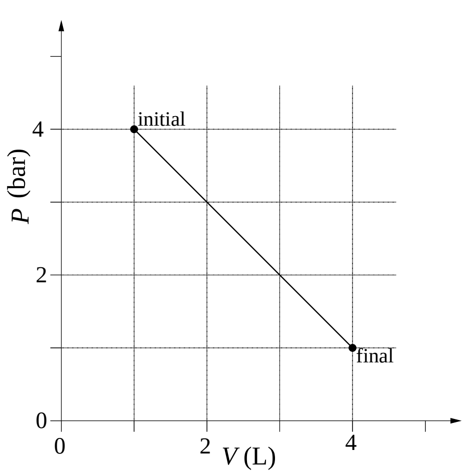
   (b) During an irreversible isothermal expansion of an ideal gas in a closed system, 255 J of work is done.

      i. What is ΔE for the process?

      ii. What is q?

   (c) Estimate the molar heat capacity at constant pressure (in SI units) of hexabromoethane (C_2Br_6), assuming that all of the vibrational motions contribute completely.

   (d) What is the work (in **kJ**) done by the process illustrated in this graph?



2. Define the adiabatic coefficient of thermal expansion α_S to be

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{S,n}.$$

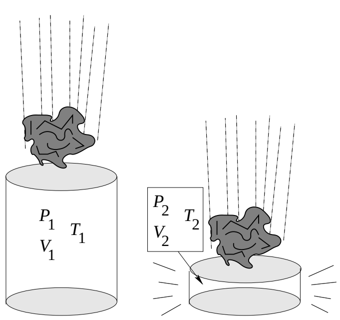
Simplify the expression below to get a function of only α and α_S:

$$\frac{\kappa_T C_P}{TV\alpha} =$$

3. Let's estimate the temperature change associated with a meteor entering the atmosphere. A column of air in the upper atmosphere has initial conditions $P_1 = 1.0 \cdot 10^3\,\mathrm{Pa}$ and $T_1 = 200\,\mathrm{K}$. A meteor with mass $m_\mathrm{M} = 1.0 \cdot 10^3$ kg and cross-section area $A = 1.0\,\mathrm{m}^2$ enters at a constant speed $v_\mathrm{M} = 15\,\mathrm{km\,s^{-1}}$ and **adiabatically** compresses the air column to new pressure P_2:

$$P_2 = \frac{F}{A} \approx \frac{m_\mathrm{M} v_\mathrm{M}}{A\Delta t} = \frac{1.5 \cdot 10^7\ \mathrm{Pa \cdot s}}{\Delta t},$$

where p is the meteor's momentum and Δt is the time we wait for the pressure to build up. Calculate the final temperature T_2 after 1.0 s. Let $C_{Pm} = 7R/2$.



4. In our derivation of the Joule-Thomson coefficient, we obtained the following expression for α:

$$\alpha = \frac{1}{V} \frac{\frac{V}{T} + \frac{nRT}{P}\frac{n}{V}\left(\frac{\partial B_2}{\partial T}\right)_P}{1 + \frac{nRT}{P}\frac{n}{V^2}B_2}. \approx \frac{\frac{V_m}{T} + \left(\frac{\partial B_2}{\partial T}\right)_P}{V_m + B_2}.$$

Your final expressions for each of the parts below should depend on some combination of the temperature, the molar volume, and/or one or two of the van der Waals coefficients. If you get the ideal gas result, you've approximated too much.

(a) Rewrite this last form of the equation in terms of the van der Waals coefficients.

(b) Find an expression for α in the limit of high temperature.

(c) Find an expression for α in the limit of low temperature.

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

virial/van der Waals $P = RT\left[V_m^{-1} + B_2(T)V_m^{-2}\right]$ $RT = \left(P + \frac{a}{V_m^2}\right)(V_m - b)$

$$B_2(T) \approx b - \frac{a}{RT} \qquad a \approx \frac{16\pi\mathcal{N}_A^2\epsilon R_{\rm LJ}^3}{9} \qquad b \approx \frac{2\mathcal{N}_A\pi R_{\rm LJ}^3}{3}$$

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

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

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

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

$$C_V = \left(\frac{T\partial S}{\partial T}\right)_{V,n} = \left(\frac{\partial E}{\partial T}\right)_{V,n} \qquad C_P = \left(\frac{T\partial S}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial T}\right)_{V,n}$$

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

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

Einstein equation $C_{Vm} = \frac{3\mathcal{N}_A\omega_E^2 e^{\omega_E/(k_{\rm B}T)}}{k_{\rm B}T^2(e^{\omega_E/(k_{\rm B}T)} - 1)^2}$

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

adiabatic exp: $w_{\rm rev} = C_V\Delta T$ $\frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)^{-C_{Vm}/R} = \left(\frac{P_2}{P_1}\right)^{-C_{Vm}/C_{Pm}}$

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

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	$\left(\frac{\partial x}{\partial y}\right)_z$	=	$\left(\frac{\partial x}{\partial w}\right)_z\left(\frac{\partial w}{\partial y}\right)_z$
	$\left(\frac{\partial x}{\partial y}\right)_z$	=	$\left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y\left(\frac{\partial w}{\partial y}\right)_z$