Chemistry 410B **Exam 4** **Spring 2008**

NAME:

Instructions:

1. Keep this exam closed until instructed to begin. Please write your name on this page but not on any other page.
2. Please silence any noisy electronic devices you have.
3. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam if you prefer.
4. To receive full credit for your work, please
    - (a) show all your work, using the back of this sheet if necessary,
    - (b) specify the correct units, if any, for your final answers,
    - (c) stop writing and close your exam immediately when time is called.

Other notes:

- **Your best scores on 4 of the 5 questions will contribute to your grade.**
- Partial credit is usually available for all problems, so try each problem and do not erase any of your work.
- Each question is worth 25 points.

1. The absorbed power for the spectroscopic transition from 1 → 2 is proportional to the difference in the number of molecules in the upper and lower states of the transition, $D \equiv N_1 - N_2$. Find an expression for D in terms of the Einstein coefficients, the total number of molecules N, and the radiation density $\rho(\nu_{12})$. Assume this is a two-state system in steady state, and that both states are non-degenerate.

2. A process is carried out such that $\Delta H = -6.2$ kJ mol^{-1}, $\Delta G = +23.7$ kJ mol^{-1}, and $\Delta F = +27.6$ kJ mol^{-1}. Find ΔE.

3. Circle the letter for *each* of the following which is equal to the pressure P of the sample:

a. $k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,n}$

b. $T \left(\frac{\partial S}{\partial E}\right)_{T,n}$

c. $-\left(\frac{\partial F}{\partial V}\right)_{T,n}$

d. $\frac{1}{\kappa_T}\frac{dV}{V}$

e. $\frac{k_B T}{\rho}$ for an ideal gas

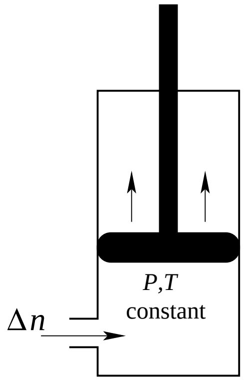
f. $-\frac{dw_{\text{rev}}}{dV}$

4. For the non-linear triatomic molecule FNO, the average vibrational energy per molecule between 280 K and 320 K is given roughly by the equation

$$\langle \epsilon_{\text{vib}} \rangle \approx k_B \left[a + b(T - T_0) + c(T - T_0)^2\right]$$

where $a = 33.71$ K, $b = 0.630$, $c = 0.00232\ \text{K}^{-1}$, and $T_0 = 222.2$ K. This includes all of the vibrational modes. Find the *total* molar heat capacity C_{Pm} of FNO at 298 K, assuming the sample otherwise behaves like an ideal gas.

5. For a monatomic ideal gas, set $\mu = \frac{3}{2}RT$. We add Δn moles of a monatomic ideal gas to a sample at constant pressure P and temperature T. Find an equation for the work w during this process in terms of P, T, and/or Δn. Because adding the gas invloves net motion of the molecular mass, the $\mu\, dn$ term contributes to the work in this problem.



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

Einstein coefficients $\frac{A_{21}}{B_{21}} = \frac{8h\pi\nu^3}{c^3} \qquad \frac{g_1 B_{12}}{g_2 B_{21}} = 1$

linewidths: $\delta\nu_{\text{Doppler}} = \frac{4\nu_0}{c}\sqrt{\frac{2k_B T \ln 2}{m}} \qquad \delta\nu_{\text{collision}} = 4\gamma$

thermo derivatives:

$$\begin{aligned} dE &= TdS - PdV + \mu_1 dn_{\text{‘}} + \ldots \\ dH &= TdS + VdP + \mu_1 dn_{\text{‘}} + \ldots \\ dF &= -SdT - PdV + \mu_1 dn_{\text{‘}} + \ldots \\ dG &= -SdT + VdP + \mu_1 dn_{\text{‘}} + \ldots \end{aligned}$$

Maxwell relations:

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

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

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

statistical thermo:

$$E = k_B T^2 \left(\frac{\partial \ln Q(T)}{\partial T}\right)_{V,n} \qquad \mu = -k_B T \left(\frac{\partial \ln Q}{\partial n}\right)_{T,V}$$

$$F = -k_B T \ln Q(T) \qquad P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,n}$$

$$S = k_B \ln Q(T) + k_B T \left(\frac{\partial \ln Q(T)}{\partial T}\right)_{V,n}$$

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

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

rev. isothermal exp: $w_{\text{rev}} = -nRT \ln\left(\frac{V_2}{V_1}\right)$

irr. isothermal exp: $w_{\text{irr}} = -P_{\text{ex}}\,\Delta V$

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

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