Chemistry 366
Thermodynamics
FINAL Exam
MAY 17, 2006

Name ______________

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This is a closed book exam, and you are responsible to be sure that your exam has no missing pages 7 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

GATE RULES

Rule7

Before you were born, your parents weren't as boring as they are now. They got that way from paying your bills, cleaning your clothes, and listening to you talk about how cool you are. So before you save the rain forest from the parasites of your parents generation, try delousing the closet in your own room.

Rule 8

Your school may have done away with winners and losers, but life has not. In some schools they have abolished failing grades and they'll give you as many times as you want to get the right answer. This doesn't bear the slightest resemblance to anything in real life.

Rule 9

Life is not divided into semesters. You don't get the summers off and very few employers are interested in helping you find yourself. Do that in your own time.

Rule 10

Television is NOT real life. In real life people actually have to leave the coffee shop and go to jobs.

Rule11

Be nice to nerds. Chances are you'll end up working for one.

Once you start the exam, you have up to 2.5 hours to solve it.

Honor Statement

I have neither give nor received aid in this examination.

Full signature ______________________________

Problem 1 (50 points)

P5.15) The heat capacity of α-quartz is given by $\frac{C_{P,m}(\alpha\text{-quartz}, s)}{\text{J K}^{-1}\text{ mol}^{-1}} = 46.94 + 34.31\times10^{-3}\frac{T}{\text{K}} - 11.30\times10^{-5}\frac{T^2}{\text{K}^2}$. The coefficient of thermal expansion is given by $\beta = 0.3530 \times 10^{-4}\text{ K}^{-1}$ and $V_m = 22.6\text{ cm}^3\text{ mol}^{-1}$. Calculate ΔS_m for the transformation α-quartz (25°C, 1 atm) → α-quartz (225°C, 1000 atm).

From Equations (5.23) and (5.24)

$$\Delta S = \int_{T_i}^{T_f} C_P \frac{dT}{T} - V\beta\left(P_f - P_i\right)$$

$$= \left[46.94\ln\frac{498\text{ K}}{298\text{ K}} + 34.31\times10^{-3}\times(498-298) - 5.65\times10^{-5}\times\left(498^2 - 298^2\right)\right]\text{J K}^{-1}\text{ mol}^{-1}$$

$$-22.6\text{ cm}^3\text{ mol}^{-1}\times\frac{1\text{ m}^3}{10^6\text{ cm}^3}\times0.3530\times10^{-4}\text{ K}^{-1}\times999\text{ atm}\times\frac{1.0125\times10^5\text{Pa}}{\text{atm}}$$

$$= 22.11\text{ J K}^{-1}\text{ mol}^{-1} - 0.0807\text{ J K}^{-1}\text{ mol}^{-1} = 21.88\text{ J K}^{-1}\text{ mol}^{-1}$$

Problem 2 An equation of state for a rubber band is either:

$$S = L_o \gamma (\theta\, U / L_o)^{1/2} - L_o \gamma \left[\left[\frac{1}{2}\right] \left(\frac{L}{L_o} \right)^2 + \frac{L}{L_o} - \frac{3}{2} \right]$$

$$S = L_o \gamma \exp(\theta\, n U / L_o) - L_o \gamma \left[\left[\frac{1}{2}\right] \left(\frac{L}{L_o} \right)^2 + \frac{L}{L_o} - \frac{3}{2} \right]$$

$$with \quad L_o = n\, l_o$$

where. γ, Lo, and θ are constants L is the length of the rubber band, and the other symbols have their usual meaning.

(10 Points) Of the two possibilities the first expression is acceptable? Why?

(40 points) For the acceptable choice deduce the dependence of the tension f, upon T and L/n; that is, determine f(T, L/n)

Problem 3 (50 points)

P31.15) ^{14}N is a spin 1 particle such that the energy levels are at 0 and $\pm\gamma B\hbar$, where γ is the magnetogyric ratio and B is the strength of the magnetic field. In a 4.8-T field, the energy splitting between any two spin states expressed as the resonance frequency is 14.45 MHz. Determine the occupation numbers for the three spin states at 298 K.

$$\Delta E = \frac{freq.}{c} = \frac{1.445\times10^{7}\ \text{s}^{-1}}{3.00\times10^{10}\ \text{cm s}^{-1}} = 4.82\times10^{-4}\ \text{cm}^{-1}$$

With this energy gap, the partition function becomes:

$$q = \sum_{n} e^{-\beta\varepsilon_n} = e^{-\beta\varepsilon_-} + e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_+} = e^{-\left(\frac{-4.82\times10^{-4}\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1}\ \text{K})(298\ \text{K})}\right)} + 1 + e^{-\left(\frac{4.82\times10^{-4}\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1}\ \text{K})(298\ \text{K})}\right)} \cong 3.00$$

With the partition function, the occupation numbers are readily determined:

$$a_- = \frac{e^{-\beta\varepsilon_-}}{q} = \frac{e^{-\left(\frac{-4.82\times10^{-4}\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1}\ \text{K})(298\ \text{K})}\right)}}{3.00} = \frac{1.00000233}{3.00} = 0.333334$$

$$a_0 = \frac{e^{-\beta\varepsilon_0}}{q} = \frac{1}{3.00} = 0.333333$$

$$a_+ = \frac{e^{-\beta\varepsilon_+}}{q} = \frac{e^{-\left(\frac{4.82\times10^{-4}\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1}\ \text{K})(298\ \text{K})}\right)}}{3.00} = \frac{0.999998}{3.00} = 0.333333$$

Problem 4 (50 points)

P32.23)

a) In this chapter, the assumption was made that the harmonic oscillator model is valid such that anharmonicity can be neglected. However, anharmonicity can be included in the expression for vibrational energies. The energy levels for an anharmonic oscillator are given by

$$E_n = hc\tilde{\nu}\left(n+\frac{1}{2}\right) - hc\tilde{\chi}\tilde{\nu}\left(n+\frac{1}{2}\right)^2 + \ldots$$

Neglecting zero point energy, the energy levels become $E_n = hc\tilde{\nu}n - hc\tilde{\chi}\tilde{\nu}n^2 + \ldots$.

Using the preceding expression, demonstrate that the vibrational partition function for the anharmonic oscillator is

$$q_{V,anharmonic} = q_{V,harm}\left(1 + \beta hc\tilde{\chi}\tilde{\nu}q_{V,harm}^2\left(e^{-2\beta\tilde{\nu}n} + e^{-\beta\tilde{\nu}n}\right)\right)$$

In deriving the preceding result, the following series relationship will prove useful:

$$\sum_{n=0}^{\infty} n^2 x^n = \frac{x^2 + x}{(1-x)^3}$$

b) For H_2, $\tilde{\nu} = 4401.2\ \text{cm}^{-1}$ and $\tilde{\chi}\tilde{\nu} = 121.3\ \text{cm}^{-1}$. Use the result from part (a) to determine the percent error in q_V if anharmonicity is ignored.

a)

$$q=\sum_n e^{-\beta E_n}=\sum_n e^{-\beta\left(hc\tilde{\nu}n-hc\tilde{\chi}\tilde{\nu}n^2\right)}=\sum_n e^{-\beta hc\tilde{\nu}n}e^{\beta hc\tilde{\chi}\tilde{\nu}n^2}$$

Performing a series expansion for the second exponential term, and keeping only the first two terms since the exponent will be small for limited anharmonicity:

$$\begin{aligned}q&=\sum_n e^{-\beta hc\tilde{\nu}n}e^{\beta hc\tilde{\chi}\tilde{\nu}n^2}=\sum_n e^{-\beta hc\tilde{\nu}n}\left(1+\beta hc\tilde{\chi}\tilde{\nu}n^2\right)\\&=\sum_n e^{-\beta hc\tilde{\nu}n}+\sum_n\left(\beta hc\tilde{\chi}\tilde{\nu}n^2\right)e^{-\beta hc\tilde{\nu}n}\\&=q_{harm}+\beta hc\tilde{\chi}\tilde{\nu}\sum_n n^2e^{-\beta hc\tilde{\nu}n}\\&=q_{harm}+\beta hc\tilde{\chi}\tilde{\nu}\sum_n n^2\left(e^{-\beta hc\tilde{\nu}}\right)^n\end{aligned}$$

Using series expression provided in the problem to evaluate the second term in the preceding expression:

$$\begin{aligned}q&=q_{harm}+\beta hc\tilde{\chi}\tilde{\nu}\sum_n n^2\left(e^{-\beta hc\tilde{\nu}}\right)^n=q_{harm}+\left(\beta hc\tilde{\chi}\tilde{\nu}\right)\left[\frac{e^{-2\beta hc\tilde{\nu}}+e^{-\beta hc\tilde{\nu}}}{\left(1-e^{-\beta hc\tilde{\nu}}\right)^3}\right]\\&=q_{harm}+\left(\beta hc\tilde{\chi}\tilde{\nu}\right)\left(q_{harm}^3\right)\left(e^{-2\beta hc\tilde{\nu}}+e^{-\beta hc\tilde{\nu}}\right)\\&=q_{harm}\left(1+\left(\beta hc\tilde{\chi}\tilde{\nu}\right)\left(q_{harm}^2\right)\left(e^{-2\beta hc\tilde{\nu}}+e^{-\beta hc\tilde{\nu}}\right)\right)\end{aligned}$$

b) First, the partition function in the harmonic-oscillator limit is:

$$q_{harm}=\frac{1}{1-e^{-\beta hc\tilde{\nu}}}=\frac{1}{1-e^{-\frac{(6.626\times10^{-34}\text{ J s})(3.00\times10^{10}\text{ cm s}^{-1})(4401.2\text{ cm}^{-1})}{(1.38\times10^{-23}\text{ J K}^{-1})(1000\text{ K})}}}=1.0018$$

Next, evaluating the expression for the anharmonic oscillator:

$$\begin{aligned}q_{anharm}&=q_{harm}\left(1+\left(\beta hc\tilde{\chi}\tilde{\nu}\right)\left(q_{harm}^2\right)\left(e^{-2\beta hc\tilde{\nu}}+e^{-\beta hc\tilde{\nu}}\right)\right)\\&=(1.0018)\left(1+\left(\frac{(6.626\times10^{-34}\text{ J s})(3.00\times10^{10}\text{ cm s}^{-1})(121.3\text{ cm}^{-1})}{(1.38\times10^{-23}\text{ J K}^{-1})(1000\text{ K})}\right)\times\left(e^{-\frac{2(6.626\times10^{-34}\text{ J s})(3.00\times10^{10}\text{ cm s}^{-1})(4401.2\text{ cm}^{-1})}{(1.38\times10^{-23}\text{ J K}^{-1})(1000\text{ K})}}+e^{-\frac{(6.626\times10^{-34}\text{ J s})(3.00\times10^{10}\text{ cm s}^{-1})(4401.2\text{ cm}^{-1})}{(1.38\times10^{-23}\text{ J K}^{-1})(1000\text{ K})}}\right)\right)\\&=(1.0018)\left(1+(0.175)\left(3.12\times10^{-6}+1.76\times10^{-3}\right)\right)\\&=1.0021\end{aligned}$$

The percent error is :

$$\%error=\frac{q_{anharm}-q_{harm}}{q_{anharm}}\times100\%=0.03\%$$

Problem 5 (50 points)

P33.18) Determine the standard molar entropy of OClO, a nonlinear triatomic molecule where $B_A = 1.06\ \text{cm}^{-1}$, $B_B = 0.31\ \text{cm}^{-1}$, $B_C = 0.29\ \text{cm}^{-1}$ and $\tilde{\nu}_1 = 938\ \text{cm}^{-1}$, $\tilde{\nu}_2 = 450\ \text{cm}^{-1}$, and $\tilde{\nu}_3 = 1100\ \text{cm}^{-1}$.

$$U_m^\circ = U_{T,m}^\circ + U_{R,m}^\circ + U_{V,m}^\circ + U_{E,m}^\circ$$

$$= \frac{3}{2}RT + \frac{3}{2}RT + N_A hc\left[\left(\frac{\tilde{\nu}_1}{e^{\beta hc\tilde{\nu}_1}-1}\right)+\left(\frac{\tilde{\nu}_2}{e^{\beta hc\tilde{\nu}_2}-1}\right)+\left(\frac{\tilde{\nu}_3}{e^{\beta hc\tilde{\nu}_3}-1}\right)\right]+0$$

$$= 3R(298.15\ \text{K}) + 479\ \text{J mol}^{-1} = 7.92\ \text{kJ mol}^{-1}$$

$$S_m^\circ = \frac{U_m^\circ}{T} + k\ln Q = \frac{U_m^\circ}{T} + k\ln\left(\frac{q_{total}^N}{N!}\right) = \frac{U_m^\circ}{T} + Nk\ln(q_{total}) - k\ln(N!)$$

$$= \frac{7.92\ \text{kJ mol}^{-1}}{298.15\ \text{K}} + R\ln(q_T q_R q_V q_E) - R\ln((1\ \text{mol})N_A) + R$$

$$= -420\ \text{J mol}^{-1}\ \text{K}^{-1} + R\ln(q_T q_R q_V q_E)$$

$$q_T = \left(\frac{V}{\Lambda^3}\right) = \frac{0.0245\ \text{m}^3}{1.89\times10^{-33}\ \text{m}^3} = 1.30\times10^{31}$$

$$q_R = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{B_A}\right)^{1/2}\left(\frac{kT}{B_B}\right)^{1/2}\left(\frac{kT}{B_C}\right)^{1/2}$$

$$= \frac{\sqrt{\pi}}{2}\left(\frac{(0.695\ \text{cm}^{-1}\ \text{K}^{-1})(298.15\ \text{K})}{1.60\ \text{cm}^{-1}}\right)^{1/2}\left(\frac{(0.695\ \text{cm}^{-1}\ \text{K}^{-1})(298.15\ \text{K})}{0.31\ \text{cm}^{-1}}\right)^{1/2}$$

$$\times\left(\frac{(0.695\ \text{cm}^{-1}\ \text{K}^{-1})(298.15\ \text{K})}{0.29\ \text{cm}^{-1}}\right)^{1/2}$$

$$= 6.98\times10^3$$

$$q_V = \left(\frac{1}{1-e^{-\beta\nu_1}}\right)\left(\frac{1}{1-e^{-\beta\nu_2}}\right)\left(\frac{1}{1-e^{-\beta\nu_3}}\right)$$

$$= \left(\frac{1}{1-e^{-\frac{938\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1})(298.15\ \text{K})}}}\right)\left(\frac{1}{1-e^{-\frac{450\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1})(298.15\ \text{K})}}}\right)\left(\frac{1}{1-e^{-\frac{1100\ \text{cm}^{-1}}{(0.695\ \text{cm}^{-1})(298.15\ \text{K})}}}\right)$$

$$= 1.14$$

$$q_E = 2$$

$$S_m^\circ = -420\ \text{J mol}^{-1}\ \text{K}^{-1} + R\ln(q_T q_R q_V q_E) = -424\ \text{J mol}^{-1}\ \text{K}^{-1} + 676\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$$S_m^\circ = 256\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Problem 6 (50 points)
Consider an ensemble consisting of N particles having only two energy levels separated by an arbitrary amount of energy $h \nu$.
What can you tell me about this system?