

Key

Chemical Physics  
ANNOUNCED Cumulative Examination  
Monday, 24 January 2005

This examination is concerned with the examples of partition functions for atoms and small molecules as discussed in Chapters 17 & 18 of the text by McQuarrie and Simon. There are five major questions on this exam (parts A-E) with 60 total points; the point values are indicated for each problem. A list of potentially useful equations is given on pages 3 and 4.

A. The canonical partition function for a system composed of independent atoms is written by McQuarrie and Simon as:  $Q(N,V,\beta) = [q_{atomic}(V,\beta)]^N / N!$  where  $N$  is the number of atoms,  $V$  is the (macroscopic) volume of the system, and  $\beta$  is the usual function of temperature.

(A-1) (2 points) Describe in words the two contributions to the atomic partition function,  $q_{atomic}$ , of a system only composed of helium atoms (or any other pure noble gas).

(A-2) (2 points) Which of the two terms just described that contribute to  $q_{atomic}$  can be ignored at room temperature and why?

(A-3) (6 points) Using the assumption that only one contribution to  $Q(N,V,\beta)$  is important and information in the equation sheet, show that the difference of the Helmholtz free energy for one mole of helium atoms (4 g/mol) from that for one mole of argon atoms (40 g/mol) is a constant times temperature if each sample is confined in the same volume. What is the value of the constant?

correct

(A-4) (2 points) Describe the property of a system composed of "N" helium atoms (or any other pure noble gas) that leads to the factor of  $N!$  in the denominator of the expression for  $Q(N,V,\beta)$  given above.

(A-5) (3 points) Given that the average energy of a system in terms of  $Q(N,V,\beta)$  is:

$$\langle E \rangle = - \left( \frac{\partial \ln Q(N, V, \beta)}{\partial \beta} \right)_{N, V}$$

and the definition of  $\beta$ , change variables and show that the average energy can also be written as:

$$\langle E \rangle = k_B T^2 \left( \frac{\partial \ln Q(N, V, T)}{\partial T} \right)_{N, V}$$

- B. (10 points) Show that the internal energy of a mole of helium atoms is  $3/2 RT$  and thus independent of  $V$  using the assumption that you justified in (A-2) that one term contributes to  $Q[N,V,\beta]$ .
- C. (10 points) Show that  $P = RT/V$  for a mole of helium atoms with the same assumption made in (A-2).
- D. A collection of molecules generally has a more complicated canonical partition function compared to that for the same number of atoms due to the additional degrees of freedom present in a molecule.
- (D-1) (2 points) Describe two degrees of freedom that any molecule, even the simplest diatomic, has that are not present in an atom, even the most complicated atom.
- (D-2) (3 points) What is the total number of degrees of freedom for an ammonia molecule,  $NH_3$ ? Divide these degrees of freedom into the usual three categories and give the number in each category for ammonia.
- (D-3) (3 points) Consider the simple diatomic molecule carbon monoxide,  $CO$ . Calculate the total rotational contribution to the internal energy,  $\langle E \rangle$ , at  $T=300$  K if the rotation temperature,  $\Theta_{rot}=2.78$  K,  $\sigma = 1$  for this heterodiatom molecule.
- (D-4) (2 points) Calculate the total rotational contribution to the constant Volume heat capacity,  $C_V$ , for one mole of carbon monoxide,  $CO$ , at 300 K if the rotation temperature,  $\Theta_{rot}=2.78$  K.
- (D-5) (5 points) Estimate the probability that a carbon monoxide molecule,  $CO$ , will be in its ground rotational state,  $J=0$ , at  $T=300$  K. The rotation temperature for  $CO$  is still  $\Theta_{rot}=2.78$  K. For reference, the degeneracy of a rotational state  $g_J=(2J)+1$ .
- E. (10 points) Consider a peculiar molecule that has a singlet ground electronic state and a low-lying triplet excited state with an energy of 1 eV. Estimate the fraction of molecules in the excited state if the entire sample is heated to 1000 K and if other higher lying excited states are ignored.

$$k_B = R/N_A = 1.38066 \times 10^{-23} \text{ J } \text{ } ^\circ\text{K}^{-1}$$

$$1. \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$$

$$R = 0.08314 \text{ } \ell\text{-bar/K-mole} = 8.314 \text{ J/K-mole}$$

$$\pi = 3.1415927$$

$$1 \text{ atm} = 760 \text{ torr} = 101,325 \text{ Pa}$$

$$N_A = 6.0221 \times 10^{23} \text{ mole}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J sec}$$

$$c = 2.99792 \times 10^8 \text{ m sec}^{-1}$$

$$\hbar = h/2\pi = 1.054 \times 10^{-34} \text{ J sec}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$\text{proton mass} = 1.67263 \times 10^{-27} \text{ kg}$$

$$\text{electron mass} = 9.1094 \times 10^{-31} \text{ kg}$$

$$\text{neutron mass} = 1.67493 \times 10^{-27} \text{ kg}$$

$$\text{electron charge} = 1.60218 \times 10^{-19} \text{ Coul}$$

$$E_{\text{photon}} = h\nu$$

$$\lambda \nu = c$$

$$\lambda = hc / E_{\text{photon}}$$

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$E(n) = n^2 h^2 / 8mL^2$$

$$E(n,l,m) = \left( \frac{n^2}{L_x^2} + \frac{l^2}{L_y^2} + \frac{m^2}{L_z^2} \right) h^2 / 8m$$

$$\omega = \sqrt{k/m_{\text{eff}}}$$

$$\nu = (1/2\pi) \sqrt{k/m_{\text{eff}}}$$

$$E_{\text{vib}} = \hbar\omega(v + \frac{1}{2}) = h\nu(v + \frac{1}{2})$$

$$\text{Modes} = 3N - (5 \text{ or } 6)$$

$$\Delta E_v = \hbar\omega$$

$$m_{\text{eff}} = m_1 m_2 / (m_1 + m_2)$$

$$E_R = \hbar^2 j(j+1) / 2I$$

$$I = m_{\text{eff}} R^2$$

$$T = \lim_{P \rightarrow 0} (P\bar{V}/R)$$

$$p_j = a_j / A$$

$$\sum_{j=1} a_j = A$$

$$\sum_{\text{states}} p_j = 1$$

$$\langle E \rangle = \sum_{\text{states}} (p_j E_j)$$

$$\langle x \rangle = \sum_{\text{states}} (p_j x_j)$$

$$\langle x^2 \rangle = \sum_{\text{states}} (p_j x_j^2)$$

$$Q(N, V, \beta) = \sum_{\text{states}} \text{Exp}(-\beta E_j(N, V))$$

$$p_j(N, V, \beta) = \text{Exp}(-\beta E_j(N, V)) / Q(N, V, \beta)$$

$$\beta = 1/k_B T$$

$$\langle E \rangle = -(\partial \ln Q / \partial \beta)_{N, V} = k_B T^2 (\partial \ln Q / \partial T)_{N, V}$$

$$\langle P \rangle = k_B T (\partial \ln Q / \partial V)_{T, N}$$

$$C_V = (\partial \langle E \rangle / \partial T)_{N, V} = -1 / (k_B T^2) (\partial \langle E \rangle / \partial \beta)_{N, V}$$

$$Q(N, V, \beta) = \prod_{i=1, N} q_i(V, \beta)$$

$$q(V, \beta) = \sum_j g_j \text{Exp}(-\beta \epsilon_j)$$

$$Q(N, V, \beta) = q(V, \beta)^N / N! \quad q(V, \beta) = q_{\text{trans}} q_{\text{elec}} q_{\text{vib}} q_{\text{rot}}$$

$$q_{\text{rot}} = T / \Theta_{\text{rot}}$$

$$\Theta_{\text{rot}} = \hbar^2 / 2Ik_B$$

$$q_{\text{elec}} = g_1 + g_2 e^{-\beta \epsilon_2}$$

$$q_{\text{vib}} = e^{-\Theta_v / 2T} / (1 - e^{-\Theta_v / T})$$

$$\Theta_{\text{vib}} = h\nu / k_B$$

$$q_{\text{trans}} = (2\pi m k_B T / h^2)^{3/2} V$$

$$dS = \delta q_{\text{rev}} / T$$

$$\Delta S_{\text{Univ}} = \Delta S + \Delta S_{\text{surr}}$$

$$S = k_B \ln W$$

$$S = U/T + k_B \ln Q$$

$$S = k_B T (\partial \ln Q / \partial T)_{N, V} + k_B \ln Q$$

$$\ln N! \approx N \ln N - N$$

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} (C_v / T) dT$$

$$A = -k_B T \ln Q$$

A-1  $q_{\text{atomic}} = q_{\text{electronic}} * q_{\text{translational}}$   
 → electronic partition func ↔ electronic excitation  
 → translational partition func ↔ translational energy

A-2 Electronic part. func. can often be taken to be 1 because electronic excited states require ~1 eV or more of energy which is much larger than typical thermal energies of ~1/40 eV

A-3  $A = -k_B T \ln Q$ ;  $Q(N, V, T) = [q_{\text{atomic}}(V, T)]^N / N!$ ;  $q_{\text{atomic}} \sim q_{\text{TRANS}}$

$$A(\text{He}) - A(\text{Ar}) = -k_B T \ln \left[ \frac{q(\text{He})^N}{N!} \right] - k_B T \ln \left[ \frac{q(\text{Ar})^N}{N!} \right]$$

$$= -k_B T \ln \left[ \frac{q(\text{He})^N}{N!} \frac{N!}{q(\text{Ar})^N} \right]$$

$$= -k_B T N \ln \left[ \frac{q(\text{He})}{q(\text{Ar})} \right]; \quad q_{\text{TRANS}} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

$$= -k_B T N \ln \left[ \frac{\left( \frac{2\pi m_{\text{He}} k_B T}{h^2} \right)^{3/2} V}{\left( \frac{2\pi m_{\text{Ar}} k_B T}{h^2} \right)^{3/2} V} \right] = -k_B T N \frac{3}{2} \ln \left[ \frac{m(\text{He})}{m(\text{Ar})} \right]$$

$$= +k_B T N \frac{3}{2} \ln 10 \quad \checkmark$$

$$(A-4) \quad Q(N, V, T) = (\text{atomic})^N / N!$$

The factor in the denominator ~~is~~ occurs due to overcounting the number of states for indistinguishable particles.

$$(A-5) \quad \langle E \rangle = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_{N, V} \quad \beta = \frac{1}{k_B T} \quad \frac{d\beta}{dT} = \frac{1}{k_B} \left( -\frac{1}{T^2} \right)$$

$$\left( \frac{\partial \ln Q}{\partial \beta} \right)_{N, V} = \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V} \left( \frac{\partial T}{\partial \beta} \right)_{N, V} \quad \text{chain rule}$$

$$\langle E \rangle = - \left[ \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V} \cdot \left( -k_B T^2 \right) \right] = + k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V} \quad \checkmark$$

=

$$(B) \quad \langle E \rangle = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V} \quad Q = \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V \right]^N / N!$$

$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} \left( \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} T^{3N/2} \right] - \ln V^{3N/2} - \ln N! \right)$$

only  $T^{3N/2}$  term will survive derivative

$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} \left( \frac{3N}{2} \ln T \right) \quad \frac{d}{dx} \ln(x) = \frac{1}{x}$$

$$= k_B T^2 \left( \frac{3N}{2} \left( \frac{1}{T} \right) \right)$$

$$= \frac{3}{2} N k_B T \quad \text{one mole } N = N_A$$

$$= \frac{3}{2} N_A k_B T = \frac{3}{2} R T \quad \checkmark$$

$$(C) \langle P \rangle = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}, \quad Q = \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V \right]^N / N!$$

$$\langle P \rangle = k_B T \frac{\partial}{\partial V} \left( \ln \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N - \ln N! \right) \quad \text{only } V^N \text{ term passes derivative}$$

$$\langle P \rangle = k_B T \frac{\partial (N \ln V)}{\partial V} = k_B T N \frac{\partial \ln V}{\partial V} = k_B T N \left( \frac{1}{V} \right)$$

$$\langle P \rangle = \frac{k_B T N}{V} \quad N = N_A \text{ for one mole} \rightarrow RT/V$$

(D-1) Molecules have rotational & vibrational energy states not possible w/ atoms

(D-2) NH3 → total DoF = 3N = 12  
 $\begin{matrix} & H & \\ & / \quad \backslash & \\ N & & \\ & \backslash \quad / & \\ & H & \end{matrix}$  translational = 3, rotational = 3, vib = 6

$$(D-3) \langle E \rangle = k_B T^2 \frac{\partial}{\partial T} \left( \ln (q_{\text{dec}} q_{\text{vib}} q_{\text{rot}} q_{\text{trans}})^N / N! \right)$$

only rotation

$$\langle E_{\text{rot}} \rangle = k_B T^2 \frac{\partial}{\partial T} \left( \ln \frac{q_{\text{rot}}^N}{N!} \right) \quad q_{\text{rot}} = \frac{T}{\sigma \Theta}$$

$$\langle E_{\text{rot}} \rangle = k_B T^2 \frac{\partial (N \ln T - N \ln \sigma \Theta - \ln N!)}{\partial T} \quad \text{again only one term}$$

$$\langle E_{\text{rot}} \rangle = k_B T^2 N \frac{\partial \ln T}{\partial T} = N k_B T^2 \left( \frac{1}{T} \right)$$

$$\langle E_{\text{rot}} \rangle = N k_B T = RT$$

(D-4)  $C_V = \left( \frac{d}{dT} \langle E \rangle \right)_{N,V} = \frac{2}{2T} (RT) = R$

(D-5)  $P_j(N,V,\beta) = \frac{g_j e^{-\beta \epsilon_j}}{q_{rot}}$   $\epsilon_j = \text{energy of state}$   
 $g_j = \text{statistical weight}$

$P_{j=0} = \frac{(2j+1) e^{-\beta \hbar^2(j(j+1)/2I)}}{q_{rot}}$   $j=0, \epsilon_j=0$

$P_{j=0} = \frac{(1) e^{-\beta(0)}}{T/5\theta}$   $q_{rot} = T/5\theta$

$P_{j=0} = \frac{1}{T/5\theta} = \frac{5\theta}{T} = \frac{1(2.78)}{300} \approx 10^{-2}$

(E)  $q_{elec} \approx g_{gs} e^{-0} + g_{1st} e^{-\beta \epsilon_{1st}}$

$q_{elec} \approx (1)(1) + (3) e^{-\beta(1eV)}$

$\text{frac}(1^{st} \text{ state}) = \frac{g_{1st} e^{-\beta \epsilon}}{q_{elec}} = \frac{3 e^{-\beta(1eV)}}{1 + 3 e^{-\beta(1eV)}}$

$\text{frac} = \frac{3 e^{-1eV \times 1.602 \times 10^{-19}} / 1.38 \times 10^{-23} \times 1000}{1 + 3 e^{-\uparrow}} = \frac{3 e^{-1.602/0.138}}{1 + 3 e^{-\uparrow}}$

$= \frac{3 e^{-\frac{11.6}{0.138}}}{1 + 3 e^{-\frac{11.6}{0.138}}} \rightarrow \text{tiny} \frac{3 \times 9.087 \times 10^{-6}}{1 + 3 \times 9.087 \times 10^{-6}} =$

$= \frac{4.7 \times 10^{-5}}{7.77 \times 10^{-5}}$