

In addition to Atkins and the primer, you may (or may not!) find some of the following books useful:

- F. C. Andrews, Equilibrium Statistical Mechanics 2nd edition (John Wiley and Sons, Inc 1975)
- Peter A. Rock, Chemical Thermodynamics, Principles and Applications (The Macmillan company, - Collier Macmillan Canada, Ltd., Toronto, Ontario 1969)
- Oscar K. Rice, Statistical Mechanics, Thermodynamics and Kinetics (W. H. Freeman and Company 1967)
- M. H. Everdell, Statistical Mechanics and its Chemical applications (Academic Press, London, 1975)
- Robert J. Finkelstein, Thermodynamics and Statistical Physics, a Short Introduction (W. H. Freeman and Company, San Francisco 1959)
- Walter Greiner, Ludwig Neise, Horst Stocker, Thermodynamics and Statistical Mechanics (Springer-Verlag New York 1995)
- Donald A. McQuarrie, Statistical Mechanics (Harper and Row, 1976)

Section A

Make notes on the following.

1. The Boltzmann distribution and its derivation.
2. What is a molecular partition function? What is its physical significance and why is it important in chemistry?
3. Show how the molecular partition function can be written as the product of contributions from independent modes of motion of a molecule and derive analytical expressions for the translational, rotational and vibrational partition functions (stating any approximations you make).
4. What is a canonical partition function and why is it used? How is it related to the molecular partition function?
5. By using standard equations from thermodynamics, show how the canonical partition function can be used to calculate the following macroscopic thermodynamic properties for a system of interacting particles:
 - a) Internal energy U
 - b) Entropy S
 - c) Helmholtz energy A
 - d) Pressure P
 - e) Enthalpy H
 - f) Gibbs free energy G
 - g) Heat capacity C_v

Section B

Question 1

- State the relationship between the translational energy of a particle inside a cubic container, the mass m of the particle, the dimension L of the container, and the associated quantum numbers.
- By using this relationship, show that the translational partition function q_{tr} is given by the expression

$$q_{tr} = \frac{V}{\Lambda^3} \text{ where } \Lambda = \frac{h}{\sqrt{2\pi mk_B T}} \text{ and } V = L^3$$

You may need the integral

$$\int_0^\infty \exp[-ax^2] dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

- Explain why the expression for q_{tr} is invalid for small values of L and estimate the dimension where the invalidity will become significant for oxygen molecules at 298 K.

Question 2

- Using your expression for the vibrational partition function, show that the contribution to the molar specific heat at constant volume from the vibrational motion of a diatomic molecule is

$$C_v^{vib} = R \left(\frac{\theta_{vib}}{T} \right)^2 \frac{\exp[-\frac{\theta_{vib}}{T}]}{(\exp[-\frac{\theta_{vib}}{T}] - 1)^2} \text{ where } \theta_{vib} = \frac{hc\omega_e}{k_B}$$

What are the limiting values of C_v^{vib} in the limits as $T \rightarrow 0$ and at high temperature? Explain the significance of these two results.

- The molar specific heat at constant volume of chlorine at 300K is $25.44 \text{ JK}^{-1}\text{mol}^{-1}$. By trial and error or other means, use this value to estimate the harmonic vibrational wavenumber for chlorine.
- In reality, diatomic molecules are anharmonic oscillators. How will this anharmonicity modify the way in which C_v^{vib} changes as the temperature increases from low values?

Question 3

The two lowest electronic states of a fluorine atom are separated in energy by $\Delta\epsilon \sim 400 \text{ cm}^{-1}$.

- Deduce term symbols for these states, specify their respective electronic degeneracies, and explain which of the two has the lower energy.
- With the assumption that only these electronic states are thermally accessible, write down an expression for the molecular electronic partition function q_{el} .
- Obtain an expression for the electronic contribution $E_{el}(T)$ to the internal energy. Explain physically why, for temperatures $T \gg \Delta\epsilon/k$, $\Delta E_{el}(T) = E_{el}(T) - E_{el}(0)$ tends to the value $1/3 N\Delta\epsilon$, where N is the total number of fluorine atoms.
- Show that the electronic contribution, $C_{el}(T)$, to the specific heat is given by

$$\frac{C_{el}(T)}{Nk_B} = 2 \left(\frac{T_e}{T} \right)^2 \frac{\exp\left[\frac{T_e}{T}\right]}{\left(1 + 2\exp\left[\frac{T_e}{T}\right]\right)^2}$$

where $T_e = \Delta\epsilon/k_B$ is thus defined. Sketch $C_{el}(T)$ as a function of T/T_e , and comment on the limiting behaviour of $C_{el}(T)$ at low and high temperatures.