

Lecture 13
Objectives

1. Be able to compute the following:

- (a) Populations of ground and excited states
- (b) Thermodynamic quantities such as entropy

1. Example: Electronic partition function and excited states.

Nitric oxide has a low-lying electronic excited state. The data are $\omega_1 = 4$ and $\epsilon_1 = 121.1 \text{ cm}^{-1}$ ($\Theta_{e,1} = 174.24 \text{ K}$). Compute the population of the ground and excited states at room temperature and 1000 K.

$$\mathcal{P}(i) = \frac{\omega_i \exp(-\beta\epsilon_i)}{\sum_j \omega_j \exp(-\beta\epsilon_j)}$$

Assume only ground and first states are occupied.

$$\mathcal{P}(0) = \frac{2 \exp(0)}{2 \exp(0) + 4 \exp(-174.24/T)}$$

$$\mathcal{P}(1) = 1 - \mathcal{P}(0) \text{ True if only states 0, 1 are occupied.}$$

For $T = 298.15 \text{ K}$,

$$\mathcal{P}(0) = \frac{2}{2 + 2.2298} = 0.473$$

$$\mathcal{P}(1) = 1 - 0.473 = 0.527$$

At $T = 1000 \text{ K}$,

$$\mathcal{P}(0) = \frac{2}{2 + 3.36} = 0.373$$

$$\mathcal{P}(1) = 1 - 0.373 = 0.627$$

2. Example: Compute the molar entropy of HCl at 25° C and 1 atm.

- (a) This is a linear molecule, so use Table 3.6
- (b) Break down the problem into S_t , S_n , S_{ev} , and S_r .
- (c) Translational

$$\frac{S_t}{R} = \frac{5}{2} + \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{p} \right]$$

where we have used

$$\frac{V}{N} = \frac{kT}{p}$$

$$m = 36.458 \text{g/mol} = 0.036458 \text{kg/mol} \rightarrow 6.0541 \times 10^{-26} \text{kg/molecule.}$$

$$\begin{aligned} \frac{S_t}{R} &= \frac{5}{2} + \ln \left\{ \left[\frac{2\pi(6.0541 \times 10^{-26} \text{kg})(1.38066 \times 10^{-23} \text{J/K})(298.15 \text{K})}{(6.62618 \times 10^{-34} \text{J}\cdot\text{s})^2} \right]^{3/2} \right\} \\ &\quad + \ln \left[\frac{(1.38066 \times 10^{-23} \text{J/K})(298.15 \text{K})}{1.01325 \times 10^5 \text{N/m}^2} \right] \\ &= \frac{5}{2} + \ln \left[(2.1298 \times 10^{32} \text{m}^{-3})(4.0626 \times 10^{-26} \text{m}^3) \right] \\ &= \frac{5}{2} + 15.973 = 18.473 \end{aligned}$$

$$\begin{aligned} \frac{S_r}{R} &= \ln \left(\frac{Te}{\sigma\Theta_r} \right) \\ &= 1 + \ln \left(\frac{298.15}{1 \cdot 15.02} \right) \\ &= 3.9882 \end{aligned}$$

Note that

$$\frac{T}{\Theta_r} = 19.9 > 5$$

So, the classical approximation is valid.

$$\begin{aligned} \frac{S_{e,v}}{R} &= \frac{\Theta_v/T}{e^{\Theta_v/T} - 1} - \ln \left(1 - e^{-\Theta_v/T} \right) + \ln \omega_{e,0} \\ &= \frac{\frac{4227}{298.15}}{e^{4227/298.15} - 1} - \ln \left(1 - e^{-4227/298.15} \right) + 0 \\ &= 1.05 \times 10^{-5} \end{aligned}$$

$$\frac{S}{R} = 18.473 + 3.9882 = 22.462$$

$$S = 186.75 \text{ J}/(\text{mol}\cdot\text{K})$$

The experimental value is 186.6 J/(mol·K)

3. Heat Capacities.

Ideal gas heat capacities are often used in engineering thermodynamic calculations. For example, they are useful for computing changes in real fluid properties through the use of residual functions. We can compute the molar heat capacity for ideal gases by using the following equation

$$\tilde{C}_V = RT \left[2 \left(\frac{\partial \ln q}{\partial T} \right)_V + T \left(\frac{\partial^2 \ln q}{\partial T^2} \right)_V \right] \quad (1)$$

As an example, we will compute the heat capacities for ammonia and carbon dioxide. Since ammonia is a nonlinear molecule we must substitute the correct expressions for nonlinear molecules into equation (1). The final result, after some algebra, is

$$\tilde{C}_V = R \left[\frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{N_{\text{vib}}} \left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{\left(1 - e^{-\Theta_{\text{vib},j}/T} \right)^2} \right] \quad (2)$$

The first term comes from the translational contribution to the heat capacity, the second term is the rotational contribution, and the last term is due to the vibrational degrees of freedom. We have implicitly assumed that the high temperature approximation is valid for the rotational partition function. If we were considering a linear molecule, such as carbon dioxide, then the second term in equation (2) would be 2/2 rather than 3/2.

Example: Calculation of the Heat Capacity of Ammonia at Room Temperature.

The vibrational temperatures (calculated from the frequencies) for ammonia are 1360, 2330(2), 4800, and 4880(2) K, where the number in parentheses is the degeneracy of the vibrational mode. That is, there are two different vibrational modes that have vibrational temperature of 2330 K and two with 4880 K. The total number of modes is $3 \times 4 - 6 = 6$, as it should be for a nonlinear molecule, but two of the modes are degenerate. The translational and rotational degrees of freedom each contribute a factor of $3/2 R$ to the heat capacity. The rotational temperatures for ammonia are all less than 14 K, so that at 298 K the high temperature approximation for the rotational modes is very accurate. We now compute the vibrational contribution to \tilde{C}_V .

$$\begin{aligned} \frac{\tilde{C}_V}{R} &= 3 + \left(\frac{1360}{298.15} \right)^2 \frac{e^{-1360/298.15}}{\left(1 - e^{-1360/298.15} \right)^2} + 2 \left(\frac{2330}{298.15} \right)^2 \frac{e^{-2330/298.15}}{\left(1 - e^{-2330/298.15} \right)^2} \\ &+ \left(\frac{4800}{298.15} \right)^2 \frac{e^{-4800/298.15}}{\left(1 - e^{-4800/298.15} \right)^2} + 2 \left(\frac{4880}{298.15} \right)^2 \frac{e^{-4880/298.15}}{\left(1 - e^{-4880/298.15} \right)^2} \\ &= 3 + 0.222 + 2(0.0247) + 2(2.64 \times 10^{-5}) + 2.09 \times 10^{-5} \\ &= 3.271 \end{aligned}$$

$$\tilde{C}_V = 27.20 \text{ J mol}^{-1} \text{ K}^{-1}$$

The value of 27.2 J/(mol K) compares very well with the literature value of 27.18 J/(mol K). Note that the vibrational contribution to the heat capacity is about 8% at room temperature. At 1200 K the heat capacity is computed to be 52.09 J/(mol K), 52% of which is due to vibrational contributions. This is to be expected, since the vibrational modes of the molecule are capable of absorbing more energy at higher temperatures.

Example: Calculation of the Heat Capacity of Carbon Dioxide and Comparison with Literature Data.

The same procedure as used in the above example can be used to compute \tilde{C}_V for carbon dioxide over a range of temperatures. We use equation (2) with the second term on the right hand side being 2/2 rather than 3/2. The vibrational constants for CO₂ are 952(2), 1890, and 3360 K, a total of $3N - 5 = 9 - 5 = 4$ vibrational degrees of freedom. It is helpful to use a computer to perform the calculations. Common software packages such as Mathcad, Matlab, or even

simple spreadsheet programs such as Excel can be used to do this. We can use statistical mechanics to compute the ideal gas heat capacity for CO_2 at any temperature. However, we must be careful at very low temperatures because we have used the high temperature approximation for the rotational partition function in equation (2). We can correct this by using the exact sum directly. At very high temperatures we must also be careful because the vibrational partition function was based on the harmonic oscillator approximation. When the temperatures are high then the harmonic approximation is not as accurate and we must include anharmonic effects to achieve high accuracy. In this example, we have computed \tilde{C}_V for CO_2 from 200 to 1200 K. The lowest temperature is high enough to justify use of the high temperature approximation for rotational degrees of freedom, because $\Theta_{\text{rot}} = 0.561$ K for CO_2 . We have not corrected for anharmonic effects at the high temperatures. A plot of \tilde{C}_V computed from statistical mechanics is shown in Figure 1 (solid line). We have also plotted highly accurate data for \tilde{C}_V from the NIST Webbook (shown as points in Figure 1) and a correlation from a standard thermodynamics text book (dashed line).

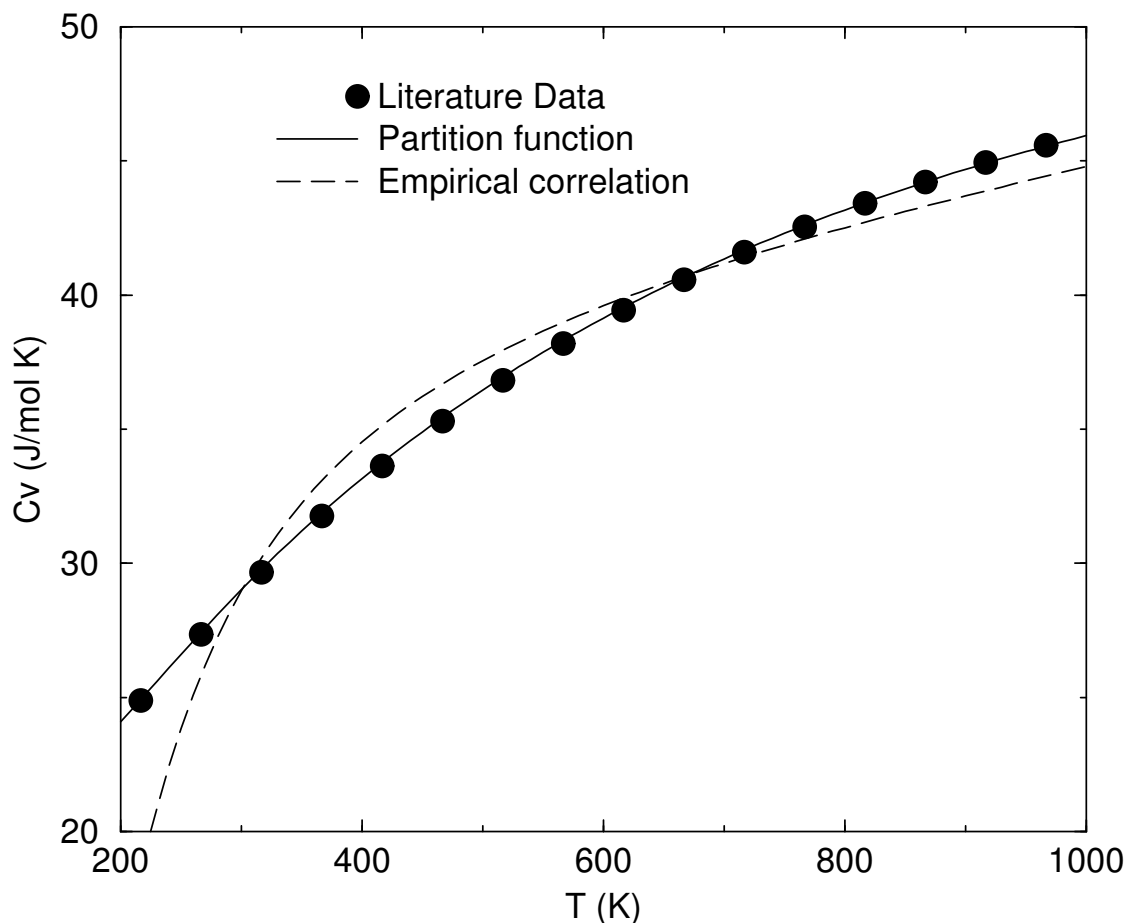


Figure 1: The heat capacity for carbon dioxide computed from statistical mechanics (solid line) compared with accurate data from the NIST Webbook (points), and with an empirical engineering correlation (dashed line).

The values of \tilde{C}_V computed from statistical mechanics are in excellent agreement with the data from the NIST Webbook over the entire range of temperatures. The NIST data are only

available from 216.6 to 1100 K, while statistical mechanics can give \tilde{C}_V over a much wider temperature range. The empirical correlation has the form

$$\tilde{C}_V = A + BT + CT^{-2} \quad (3)$$

where A , B , and C are adjustable parameters regressed from a least-squares fit to experimental data. The range of validity of equation (3) for CO_2 is reported to be from 298 to 2000 K. We have used equation (3) from 200 K in order to illustrate what happens when empirical equations for heat capacities are used outside their range of validity. The \tilde{C}_V values computed from the empirical correlation are seriously in error at the lowest temperatures because the correlation does not have any physical basis. The partition function, however, always provides a prediction for \tilde{C}_V that is at least physically reasonable. This is another advantage of using statistical mechanics rather than an empirical correlation to compute thermodynamic properties of materials.