

Chemistry 21b – Spectroscopy & Statistical Thermodynamics

Lecture # 24 – Two Level Systems and the Translational Partition Function

Now that we have set up the machinery to examine statistical thermodynamics from a quantum mechanical perspective, the treatment of actual systems is possible. Before turning to the properties of polyatomic molecules, let's first look at the behavior of two of the simplest models: (1) An isolated two-level quantum system, and (2) The translational behavior of a perfect monatomic gas with no low-lying electronic states.

Examples of the former include spin $\frac{1}{2}$ particles in a magnetic field (NMR and ESR are the two spectroscopic approaches we have covered in these notes), atoms or molecules with an excited electronic state that is well removed from all others, or rotational and vibrational degrees of freedom in which nearly all of the molecules are in the ground state.

Two Level Systems

Consider the system outlined below, with an energy level separation of $\Delta\epsilon$ and in equilibrium at a temperature T .

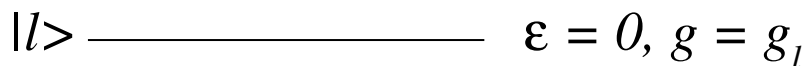
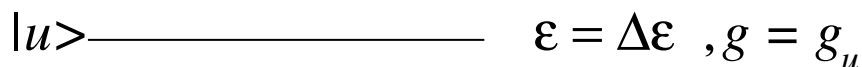


Figure 24.1– A schematic of a two level system whose energy level separation is $\Delta\epsilon$, with lower and upper level degeneracies of g_l and g_u , respectively.

From the Boltzmann equation, the ratio of the upper-to-lower state population is

$$\frac{N_u}{N_l} = \frac{g_u}{g_l} e^{-\Delta\epsilon/kT} = \frac{g_u}{g_l} e^{-\theta/T}, \quad (24.1)$$

where $T/\theta = kT/\Delta\epsilon$ is called the *reduced temperature*. The reduced temperature is clearly dimensionless, and is a concept we will use repeatedly in the remainder of these lecture notes. It will permit us to graph systems universally in terms of the reduced temperature; actual results then flow from the magnitude of T/θ , that is the ratio of $\Delta\epsilon/k$ to the temperature T . For protons in a 10 Tesla magnetic field θ is only 0.02 K, whereas for the vibrational spacing in molecular hydrogen it is nearly 6000 K.

For convenience we have assumed that the lower state energy is at 0; for “real world” problems such as molecular vibration in which properties such as zero-point energy must be included, this non-zero energy offset must be taken into account in the calculation of various thermodynamic state functions.

The partition function flows simply from the equation

$$q = \sum_{i=u,l} g_i e^{-\epsilon_i/kT} = g_l + g_u e^{-\Delta\epsilon/kT} = g_l + g_u e^{-\theta/T} . \quad (24.2)$$

If, for convenience, we ignore the level degeneracies (that is, we treat them as equal to one), the microcanonical partition function is 1 at low temperature ($T/\theta \rightarrow 0$) and 2 at high temperature (where $T/\theta \gg 1$). From the partition function and the constraint $N_l + N_u = N$, where N is the total number of particles, we can use the Boltzmann expression to write

$$\frac{N_l}{g_l} = N \left(g_l + g_u e^{-\theta/T} \right)^{-1}$$

and

$$\frac{N_u}{g_u} = N \left(\frac{e^{-\theta/T}}{g_l + g_u e^{-\theta/T}} \right) . \quad (24.2)$$

The energy of the system follows simply from the expression

$$E = \sum_{i=u,l} N_i \epsilon_i = N_l \times 0 + N_u \times \Delta\epsilon = \left(\frac{g_u N \Delta\epsilon}{g_u + g_l e^{\theta/T}} \right) . \quad (24.4)$$

As $T \rightarrow \infty$, the energy approaches $N\Delta\epsilon/2$. Qualitatively, both the partition function and the energy of the system follow the population in the upper state as the reduced temperature is varied, as is illustrated graphically in Figure 24.2.

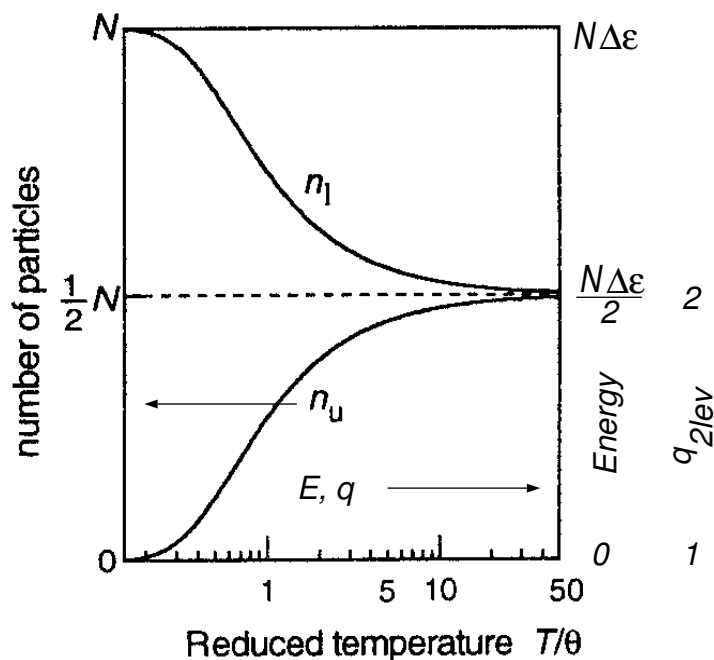


Figure 24.2– A graphical illustration of the energy level populations, system energy, and partition function for the two level system outlined in Figure 24.1 (for $g_l = g_u = 1$).

The same mathematical machinery developed in Lectures #22, 23 can also be used to examine the energy and other thermodynamic state variables. Recall that $U = kT^2(\partial \ln Q / \partial T)|_V$, and that $C_V = (\partial U / \partial T)|_V$. From these expressions and the relation $Q = q^N$, we find

$$U = E = \left[\frac{\left(\frac{g_u}{g_l}\right) N \Delta \epsilon}{\left(\frac{g_u}{g_l} + e^{\theta/T}\right)} \right] \quad (24.5)$$

and

$$\frac{C_V}{Nk} = \left(\frac{\theta}{T}\right)^2 \left[\frac{\left(\frac{g_u}{g_l}\right) e^{\theta/T}}{\left(\frac{g_u}{g_l} + e^{\theta/T}\right)^2} \right] \quad (24.6)$$

By normalizing C_V with Nk , the heat capacity for any two level system can be plotted versus the reduced temperature in a single plot. As $T \rightarrow 0$ the exponential terms in the bracket dominate over T^{-2} and $C_V \rightarrow 0$. Qualitatively, all the population is in the lower state and any small changes in temperature lead to no population transfer since $\Delta \epsilon \gg kT$. At high temperature, the term in brackets goes to a constant and the leading term again drives C_V to zero. Qualitatively, once T/θ becomes large, the populations in the upper and lower state are equal and no further change is possible. Hence, the system can no longer respond to changes in temperature and the heat capacity must go to zero. In between a maximum is obtained, and the value for which it occurs can be derived from setting $(\partial C_V / \partial T) = 0$, which in turn depends on the ratio g_u/g_l . For $g_u/g_l = 1$ the maximum occurs near $T/\theta \sim 0.4$, or where the upper state population begins to change appreciably (c.f. Figure 24.2).

The Helmholtz free energy is $A = A(0) - kT \times \ln(Q)$, or $-kT \times \ln(g_l + g_u e^{-\theta/T})$ assuming the lower state energy is zero. For $g_l = g_u = 1$, $A \rightarrow 0$ as $T \rightarrow 0$ and $A \approx -NkT \ln(2)$ as $T \rightarrow \infty$. For the entropy S the tool kit functions from Lecture #23 may be used, the simplest of which is $S = -(\partial A / \partial T)|_V$, or $S = k \ln Q + kT^2(\partial \ln Q / \partial T)|_V$:

$$S = Nk \ln(g_l + g_u e^{-\theta/T}) + \frac{Nk\theta}{T} e^{-\theta/T} (g_l + g_u e^{-\theta/T})^{-1} . \quad (24.7)$$

As $T \rightarrow \infty$, $S \rightarrow Nk \ln(g_l + g_u)$, and as $T \rightarrow 0$, $S \rightarrow Nk \ln(g_l)$. For $g_u, g_l = 1$, as we expect $S \rightarrow 0$ as $T \rightarrow 0$ (the Third Law); and as $T \rightarrow \infty$, $S \rightarrow Nk \ln(2)$. For one mole, $S(T \rightarrow \infty) = R \ln(2) = 5.8 \text{ J K}^{-1} \text{ mole}^{-1}$. Qualitatively, when $\Delta \epsilon \ll kT$ there are essentially two degenerate states; and each particle can occupy these two states with equal probability. Accordingly, $\Omega = 2^N$, and since $S = k \ln \Omega$, we have $S = Nk \ln(2)$ for $T \rightarrow \infty$, as before.

Translational Degrees of Freedom in a Perfect Gas

If we think about a perfect gas with no internal degrees of freedom, the problem may be treated quantum mechanically as a particle-in-a-box. This will work well for atoms in which the first excited state has $E \gg kT$, or $\theta/T \gg 1$; as is certainly the case for the rare

gases (He, Ne, Ar, ...) where the excited states lie well into the vacuum-ultraviolet. He, for example, has a first excited state nearly 20 eV above ground. Since $1 \text{ eV} = 11,600 \text{ K}$, $\theta/T(\text{He}) \approx 800$ near room temperature! Any excited state contribution to the partition function therefore goes as e^{-800} in He, and can be safely neglected.

For a box with sides L_x , L_y , and L_z , there are three quantum numbers n_x , n_y , $n_z = 1, 2, 3, \dots$, and the particle-in-a-box energies for a particle of mass m are

$$\epsilon = \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2} + \frac{n_z^2 h^2}{8mL_z^2} . \quad (24.8)$$

Since the energies are additive, this means that the full microcanonical partition function is simply the product of the 1D partition functions, or $q_{trans} = q_{trans,x} \times q_{trans,y} \times q_{trans,z}$, where the individual partition functions are given by

$$q_{trans,x} = \sum_{n=1}^{\infty} e^{-n^2 h^2 / 8mL_x^2 kT} . \quad (24.9)$$

The full canonical partition function is given by $Q_{trans} = q_{trans}^N / N!$ since the particles are indistinguishable.

Remember we are concerned here about the statistical mechanics of a weakly interacting system in what is called the dilute limit. That is, we assume a given quantum state is occupied by at most one particle. Is this true? If you plug in a given set of quantum numbers into the energy expression and compare the difference between adjacent quantum states to the average kinetic energy of the particles, you find that the ratio $\Delta\epsilon/kT$ is of order 10^{-20} . This is a good start for our approximation, and from it we can safely turn the summation in eq. (24.9) into an integral, and a definite one at that since the sum is so large that we can safely replace the lower limit $n = 1$ with $n = 0$; or

$$q_{trans,x} \approx \int_{n=0}^{\infty} e^{-n^2 h^2 / 8mL_x^2 kT} dn_x , \quad (24.10)$$

and since $\int_{n=0}^{\infty} e^{-a^2 x^2} dx = \sqrt{\pi}/2a$ we have

$$q_{trans,x} = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} L_x . \quad (24.11)$$

Putting it all together and recognizing that $L_x L_y L_z = V$, where V is the volume of the container, we find

$$Q_{trans} = \frac{1}{N!} \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right]^N \quad (24.12)$$

for the canonical partition function for the translation of a perfect gas.

It's instructive at this stage to consider the size of q_{trans} (and by extension Q_{trans}) under "reasonable" conditions. For He at very low temperatures, near the boiling point of 4.2 K, with a molar volume of $3.5 \times 10^{-4} \text{ m}^3 \text{ mole}^{-1}$, it is found that $q_{trans} = 4.5 \times 10^{24}$; which is larger than Avogadro's number (but not by all that much!). For CO_2 at room temperature, $q_{trans} \sim 10^{30}$ in vessels close to a liter in volume, and so $q_{trans}/N_A \gg 1$. This plus the considerations above concerning the energy level differences demonstrates that both the diluteness and virtual continuum approximations used are easily satisfied for the rare gases at any temperature reasonably above their boiling points.

As before, the derivation of the thermodynamic state functions involves $\ln(Q_{trans})$ and its derivatives, especially with respect to temperature. These are particularly simple in this case, and an examination of eq. (24.12) yields

$$\left(\frac{\partial \ln Q_{trans}}{\partial T}\right)_V = \frac{3N}{2T} \quad \left(\frac{\partial^2 \ln Q_{trans}}{\partial T^2}\right)_V = -\frac{3N}{2T^2} \quad \left(\frac{\partial \ln Q_{trans}}{\partial V}\right)_T = \frac{N}{V} .$$

From these derivatives the expected relationships for a perfect gas can be easily derived. Since there are no internal degrees of freedom, the translational energy is the system energy, and

$$E_{trans} = U = kT^2 \left(\frac{\partial \ln Q_{trans}}{\partial T}\right)_V = \frac{3}{2}NkT = \frac{3}{2}RT$$

for one mole of perfect gas. This is the result predicted by the *equipartition principle*, which states that for each degree of freedom in the system (quantum mechanically, for each *quadratic* operator term in the Hamiltonian) there is an associated energy $kT/2$ per particle. Thus, in three dimensions and for translation alone, $U = \frac{3}{2}RT$ for one mole. We will revisit the equipartition principle in our treatment of the rotations and vibrations of polyatomic molecules.

The heat capacity at constant volume is simply $C_V = (\partial U/\partial T)_V = \frac{3}{2}R$, again as expected from the equipartition of energy. Notice there is no temperature dependence. Why? Even at low temperatures the spacing between levels is $\ll kT$, hence the system remains in an extremely large number of states. Similarly, we have assumed the potential to be infinite outside the box, and so there are an infinite number of states that can be accessed at high temperatures. Thus, the ability of the system to respond to heating or cooling is insensitive to the actual value of the temperature. The equation of state is similarly straightforward to derive since $P = kT \left(\frac{\partial \ln Q_{trans}}{\partial V}\right)_T = \frac{NkT}{V}$, as expected.

What about the molar entropy of a perfect gas? This is not so easy to derive from classical considerations, but straightforward with statistical thermodynamics since

$$S = k \ln Q_{trans} + kT \left(\frac{\partial \ln Q_{trans}}{\partial T}\right)_V ,$$

from which we derive

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V}{N} \right] + Nk + \frac{3}{2}Nk , \quad (24.14)$$

where we have used $Q_{trans} = q_{trans}^N/N!$ and Stirling's approximation for $\ln N!$. Equation (24.14) can be rearranged to yield

$$S = Nk \times \left\{ \ln T^{3/2} + \ln \frac{V}{N} + \ln \left[\left(\frac{2\pi mk}{h^2} \right)^{3/2} e^{5/2} \right] \right\} , \quad (24.15)$$

which is one form of the *Sackur-Tetrode* equation. From it we see there is a volume and temperature dependence, which could have been predicted from classical thermodynamics; as well as a constant that depends on the mass of the gas and whose value can only be calculated via quantum theory.

The Sackur-Tetrode equation is linearly dependent on the particle number N , and if we consider one mole of a perfect gas, $N = N_A$ and $N_A k = R$. By inserting these values and using the perfect gas equation of state, the Sackur-Tetrode equation may be recast in terms of pressure. Strictly speaking, the conversion to pressure as a variable is only valid for sufficiently high temperatures, but does not cause large errors in practice. Doing this and evaluating the constant term yields an expression for the molar entropy of

$$S_m/R = \ln \left\{ M^{3/2} T^{5/2} P^{-1} \right\} + 20.723 , \quad (24.16)$$

where the mass M is in kg mole^{-1} , the temperature T is in K, and the pressure P is in pascal (abbreviated Pa, 101.325 kiloPa or kPa equals one atmosphere). The value of R is $8.314 \text{ J mole}^{-1} \text{ K}^{-1}$. The advantage of this expression is that the term in brackets is small and slightly negative near STP. Consider Ar, for example. The mass is $40 \times 10^{-3} \text{ kg mole}^{-1}$, and at 273 K and 1 atmosphere (101325 Pa), the calculated value of S_m/R is 15.54 (as compared to a calorimetric value of 15.60), while at 300 K the value for Ar is 18.63. The value of S_m/R for Kr at STP is 17.45, versus an experimental value of 17.43. Multiplying through by R yields an entropy of $155 \text{ J K}^{-1} \text{ mole}^{-1}$ for Ar at 1 atm and 300 K, or $37.05 \text{ cal K}^{-1} \text{ mole}^{-1}$ since $1 \text{ cal mole}^{-1} = 4.184 \text{ J mole}^{-1}$. Recall that $S = k \ln \Omega$, this reveals that $\Omega(\text{Ar}, 300 \text{ K}) = 1.1 \times 10^{25}$.