University of Washington
Department of Chemistry
Chemistry 453
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Lecture 20 2/4/15

A. Summary of Partition Functions

- The translational partition function is:

$$q_{trans} = \left(\int_0^\infty e^{-n^2h^2/8ma^2} dn \right)^3 = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} = \frac{V}{\Lambda^3}$$

(20.1)

  where particle-in-the-box energies $E_n = \frac{n^2h^2}{8ma^2} << k_B T$ are used to model translations and V=abc. Note $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is called the thermal wavelength. It is the thermally averaged wavelength of the particle.

- The vibrational partition function is:

$$q_{vib} = \sum_{n=0}^{\infty} e^{-h\nu(n+1/2)/k_BT} = \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}} = \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \qquad (20.2)$$

  where quantized harmonic oscillator energies $E_n = h\nu\left(n+\frac{1}{2}\right)$ are used to model vibrations. Note $\theta_{vib} = \frac{h\nu}{k_B}$ is the vibrational temperature. If $T \gg \theta_{vib}$ the LHO behaves classically. The heat capacity C_v for a 1D oscillation approaches R, and the internal vibrational energy U_{vib} approaches RT. If $T \ll \theta_{vib}$ C_v and U_{vib} will depart from these values and must be calculated using equation 20.2.

- The rotational partition function is:

$$q_{rot} = \frac{1}{\sigma}\int_0^\infty \left(2J+1\right) e^{-\hbar^2 J(J+1)/2Ik_BT} dJ = \frac{8\pi^2 I k_B T}{\sigma h^2} = \frac{2Ik_BT}{\sigma \hbar^2} = \frac{T}{\sigma\theta_{rot}} \qquad (20.3)$$

where the quantized rotational energy is $E_J = \frac{\hbar^2}{2I} J\left(J+1\right)$ and $\theta_{rot} = \frac{\hbar^2}{2Ik_B}$.

- Finally , because $\Delta E >> k_B T$ for electronic transitions, only the ground state is populated for most atoms and molecules. There are two conventions for referencing electronic ground state energies:
  - In isolated atoms we reference to the energy of the ground state and set E_1=0. Then the electronic partition function for atoms is generally

equal to the degeneracy of the electronic ground state:

$$q_{elec} = \sum_{n=1}^{\infty} g_n e^{-E_n/k_BT} \approx g_1 e^{-E_1/k_BT} = g_1 \quad (20.4)$$

- As we will explain below, the ground state of molecules is referenced differently than atoms. As we will explain below the ground state E_1 is NOT set to zero in molecules so the partition function for molecules is

$$q_{elec} = \sum_{n=1}^{\infty} g_n e^{-E_n/k_BT} \approx g_1 e^{-E_1/k_BT} \qquad (20.5)$$

B. Molecular Partition Functions for Diatomics

- The molecular partition function is a product of the partition functions for motions 20.1-20.4.

$$\begin{aligned} q &= q_{trans} q_{vib} q_{rot} q_{elec} \\ &= \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \times \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}} \times \frac{8\pi^2 I k_B T}{\sigma h^2} \times g_1 e^{-E_1/k_BT} \qquad (20.6) \\ &= \frac{V}{\Lambda^3} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times \frac{T}{\sigma \theta_{rot}} \times g_1 e^{-E_1/k_BT} \end{aligned}$$

- Equation 20.5 is used to define all thermodynamic properties of a molecular substance and is also used to calculate equilibrium constants.
- A great deal of information is required to calculate the molecular partition function: including: the vibration frequency ν, the moment of inertia I, the electronic ground state g_1, and the molecular electronic ground state energy E_1.
- To calculate these quantities efficiently, we should be familiar with some of the order of magnitude values.
- The thermal wavelength Λ can be thought of as the particle averaged over all the particle in the box energy levels occupied at a given temperature. Therefore Λ^3 is the thermally averaged volume occupied by this particle wave and the translational partition function can be thought of as the number thermally averaged particle volumes that can be accommodated in a volume V: $q_{trans} = \frac{V}{\Lambda^3}$. For hydrogen this wavelength is:

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi m k_B T}} = \frac{6.62\times10^{-34}\,Js}{\left[(6.28)\left(1.66\times10^{-27}\,kg\right)\left(1.38\times10^{-23}\,JK^{-1}\right)(1000K)\right]^{1/2}} \\ &= \frac{6.62\times10^{-34}\,Js}{\left(1.44\times10^{-46}\,kgJ\right)^{1/2}} = \frac{6.62\times10^{-34}\,Js}{1.20\times10^{-23}\,kgms^{-1}} = 5.52\times10^{-11}\,m \end{aligned} \qquad (20.7)$$

- Note the thermal wavelength gets smaller the higher the temperature (why?) or the heavier the particle.

- The vibrational frequency is defined in terms of the vibrational temperature defined as $\theta_{vib} = \frac{h\nu}{k_B}$. For a typical vibrational frequency of $\nu = 10^{14} s^{-1}$ the vibration frequency is

$$\theta_{vib} = \frac{h\nu}{k_B} = \frac{\left(6.62\times10^{-34} Js\right)\left(10^{14} s^{-1}\right)}{1.38\times10^{-23} JK^{=1}} = 4.80\times10^{3} K \qquad (20.8)$$

- Vibrational frequencies are typically at least 10 times room temperature for light molecules like H_2, HF, HCl etc. For heavier molecules like I_2 the vibrational temperature is a lot lower and can be close to room temperature. The physical significance of the value of a vibrational temperature it is the temperature that must be reached before the vibrations of the system behave classically. As shown in Figure 20.1, when the vibrational temperature is exceeded, the vibrational heat capacity approaches its classical value which for a diatomic molecule is Nk_B.

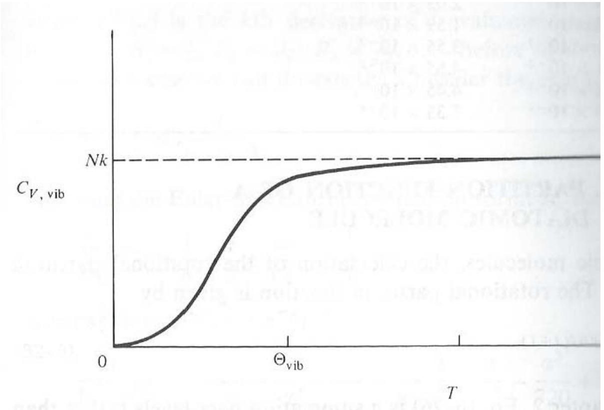


Figure 20.1: When T exceeds θ_{vib} the heat capacity for a one dimensional vibration approaches $Nk_B=R$, which is the classical limit...

- The rotational temperature is similarly defined as $\theta_{rot} = \frac{\hbar^2}{2Ik_B}$. A typical value for the moment of inertia I is 10^{-46} kg m^2. Using this value a typical rotational temperature is

$$\theta_{rot} = \frac{\hbar^2}{2Ik_B} = \frac{\left(1.05\times10^{-34} Js\right)^2}{2\left(10^{-46} kgm^2\right)\left(1.38\times10^{-23} JK^{-1}\right)} \approx 4.06K \qquad (20.9)$$

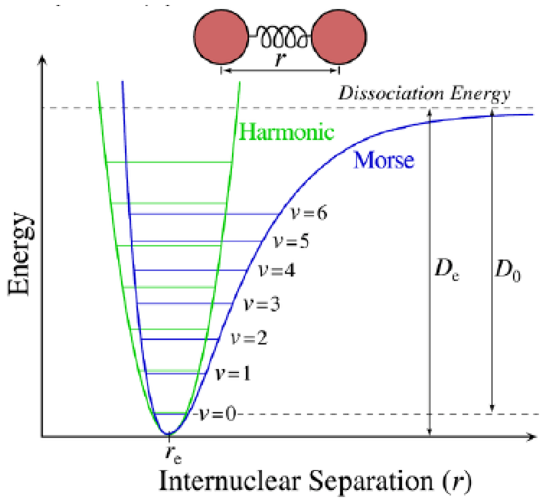
- This means that for a diatomic molecule the rotational properties approaches classical values when temperature exceeds its rotational temperature. Rotational temperatures are typically lower than room temperature.
- The electronic ground state energy E_1 is defined as follows. The vibrational potential energy for a real molecular bond is not the simple harmonic expression $V(x) = \frac{1}{2}\kappa x^2$. This is because as the bond stretches to greater lengths, eventually the molecule will dissociated into individual atoms. An empirically derived potential that is more realistic than the simple harmonic potential is the Morse potential, shown in Figure 20.2. The Morse potential has the equation

$$V(x) = D_e\left(1-e^{\alpha(x-x_e)}\right)^2 \ldots \alpha = \sqrt{\frac{\kappa}{2D_e}} \quad (20.10)$$

Where De is the dissociation energy measured from the classical bottom of the well. Unlike the harmonic potential, the quantized energies for the Morse potential are not equally spaced:

$$E_n = h\nu\left(n+\tfrac{1}{2}\right) - \frac{(h\nu)^2}{4D_e}\left(n+\tfrac{1}{2}\right)^2 \tag{20.11}$$

Figure 20.2: Comparison of the harmonic potential and the Morse Potential



- By convention the energies of the individual atoms are zero, as shown in Figure 20.2.
- The ground state electronic energy E_1 is by conventional assigned as the bottom of the classical vibrational well. This energy is defined as the classical dissociation energy and is $-D_e$ relative to the dissociated atomic states, as shown in Figure 18.3.

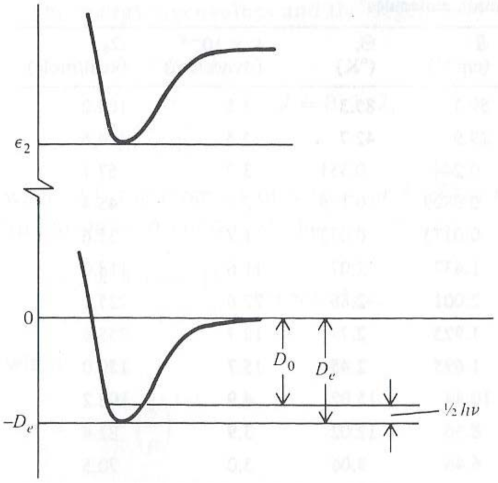


Figure 20.3: The ground electronic state is defined as the bottom of the classical vibrational well or $-D_e$ relative to the dissociated atomic states

- The difference between the dissociated atomic state and the ground vibrational state is defined as D_0

  where $D_e = D_0 + \dfrac{h\nu}{2}$. Using these definitions the electronic partition function is about equal to:

$$q_{elec} \approx g_1 e^{-E_1/k_BT} = g_1 e^{+D_e/k_BT} \tag{20.12}$$

- In practice D_e is usually reported in units of Joules per mole. So if D_e is given in these units the argument of the exponent in 20.12 is D_e/RT. Using equation 20.6 and 20.12 the molecular partition function for a diatomic molecule is defined as:

$$\begin{aligned} q &= q_{trans}q_{vib}q_{rot}q_{elec} \\ &= \frac{V}{\Lambda^3} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times \frac{T}{\sigma\theta_{rot}} \times g_1 e^{D_e/RT} \end{aligned} \tag{20.13}$$

- Useful parameters for calculating molecular partition functions for common diatomic molecules are given in Table 20.1. Again: note the RT in the argument of electronic exponential term. This is because in Table 20.1 D_e is in terms of kJ per mole.

Molecule	$\theta_{vib}\left(K\right)$	$\theta_{rot}\left(K\right)$	ν(x10^{13} s^{-1})	g_1	D_e(kJ mol^{-1})	D_0(kJ mol^{-1})
H_2	6215	85.3	12.960	1	457.6	432.1
Cl_2	808	0.351	1.683	1	242.3	239.2
I_2	308	0.0537	0.642	1	150.3	148.8
CO	3103	2.77	6.471	1	1085	1070
NO	2719	2.45	5.670	2	638.1	626.8
HCl	4227	15.02	8.814	1	445.2	427.8

C. Thermodynamic Properties

- From 20.13 and the data of the type given in Table 20.1 all thermodynamic properties for a diatomic molecule can be determined. For example, the molar internal energy is:

$$
\begin{aligned}
U &= N_A k_B T^2 \frac{\partial \ln q}{\partial T} = N_A k_B T^2 \frac{\partial}{\partial T}\left[\ln q_{trans} + \ln q_{rot} + \ln q_{vib} + \ln q_{elec}\right] \\
&= \frac{3RT}{2} + RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu}{e^{h\nu/k_BT} - 1} - D_e \qquad (20.14) \\
&= \frac{5RT}{2} + \frac{R\theta_{vib}}{2} + \frac{R\theta_{vib}}{e^{\theta_{vib}/T} - 1} - D_e
\end{aligned}
$$

- In the last line of equation 20.14 the first term is the internal energy from translations and rotations, both assumed to be in the classical (i.e. high temperature) limit.
- The second term is the contribution from the ground state vibrational energy...the so-called zero point energy.
- The third term comes from the excited vibrational states.
- Finally, the fourth term is the stabilization of the diatomic molecule arising from the sharing of electrons in a covalent chemical bond between the two nuclei. For this reason the fourth is negative and lowers the energy of the molecule relative to the sum of the energies of the separated atoms. D_e is assumed in units of Joules per mole. It is often tabulated, as above in units of kJoules per mole. So be careful!
- The heat capacity can now be obtained by differentiation of equation 18.14:

$$
C_V = \frac{\partial U}{\partial T} = \frac{5R}{2} + R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{\left(1 - e^{-\theta_{vib}/T}\right)^2} \qquad (20.15)
$$

- Note how the electronic energy makes no contribution to the heat capacity. This is due to the extremely high “electronic temperature” (i.e. >10^5 K) which results in only the ground electronic state being populated at realistic temperatures.