Lecture 15 (End of Chapt 11)

Brief Outline:

- QM – energy levels (from small to large)
  - translational – particle in a box (DONE)
  - rotational – rigid rotator
  - vibrational – harmonic oscillator electronic
  - electronic
- Molecular partition functions
- Heat capacities

Review

Depending on whether we are concerned about states or levels:

\[ Q = \sum_i^I e^{-E_i/kt} \]

or

\[ Q = \sum_j^J W_j e^{-E_j/kt} \]

Translational energies given by solving particle in a box

- Applying S.E. to our ‘box’ gives: \( e_{\text{trans},n} = \frac{\hbar^2 n^2}{8ma^2} \) \( n = 1,2,3… \)

- Rotational energy (only molecules – can’t discern atom rotation) Rigid rotator model assumes two masses at a fixed distance

  - \( e_{\text{rotation},L} = \frac{\hbar^2}{2I} L(L+1) \) \( L = 0,1,2… \) degeneracy \( g_L = 2L + 1 \)
  - moment of inertia \( I = \mu R_e^2 \) \( R_e \) is distance (equil. bond length)
    \( \mu \) is reduced mass \( \mu = \frac{m_1 m_2}{m_1 + m_2} \)

  - Usually we use spectroscopy to get a handle on these energies. It measures only energy differences, transitions between levels. So, transition energy
    \[ \Delta e_{\text{rot},L} = e_{L+1} - e_L = \frac{\hbar^2}{I} (L+1) = \frac{\hbar^2}{4\pi^2 I} (L+1) \]

  - \( \Delta e = h\nu \) where \( \nu \) is both the frequency of the light and of the rotational motion.

  - So, for rotation \( \nu = \frac{\hbar}{4\pi^2 I} (L+1) \) where \( L = 0,1,2,… \) the lower level
usually write \( \nu = 2B(L + 1) \), where \( B \) is rotational constant \( B = \frac{h}{8\pi^3 I} \), also \( \bar{B} = \frac{B}{c} \)

- units on \( B \) are \( J*\text{s} / \text{kg*m}^2 = \text{s}^{-1} \) so, divide this by \( \text{m/s} \) and get \( \text{m}^{-1} \) (or \( \text{cm}^{-1} \))
- most large molecules have \( A \), \( B \), and \( C \) (3 axes of rotation)

- **small moment (small mass, small distance) => larger spacing**

- **Vibrational energy (only molecules – vibration requires a bond)**
  - assume a bond looks like masses on a spring – Hooke’s law
  - \( f = -kx \) \( \text{eq. for force, } k \text{ is force constant (big = stiff)} \)
  - leads to \( x(t) = A\cos(2\pi\nu t) \) \( \text{draw and define } A, \nu, T \)
  - \( V(x) = -\int f(x)dx \) \( \text{indefinite integral so add constant} \)
  - **gives?** \( V(x) = \frac{1}{2}kx^2 \) \( \text{(usually define constant = 0) } \Rightarrow \text{draw parabola} \)

- QM solution is \( \varepsilon_{\text{vib,v}} = \frac{\hbar}{2\pi} \left( \frac{k}{\mu} \right)^{\frac{1}{2}} (\nu + \frac{1}{2}) = h\nu(\nu + \frac{1}{2}) \) \( \nu = 0, 1, 2 \ldots \text{(add states to parab.)} \)

- solve for \( \Delta \varepsilon = \hbar\nu \), **how many vibrational lines?**, \( \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \), \( \text{(vib freq. === light freq.)} \)

- also often use wavenumbers for convenience \( \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \)

- harmonic oscillator has equal level spacing, real molecules do not (sketch Morse vs. parabola)

- Show harmonic oscillator levels and zero point energy – always some vib energy

- \( D_0 = D_e - \frac{1}{2}\hbar\nu \) \( \text{\( D_0 \) is dissociation energy } \text{\( D_e \) is ground state electronic energy (where zero is the energy of the atoms infinitely far apart).} \text{\( D_e \) is the bottom of the well, } \text{\( D_0 \) is the lowest state.} \)

- **large force constant (strong bond) or small reduced mass => large spacing**

- **Electronic energies (all atoms and molecules) are generally measured by spectroscopy – measures transition energies – differences between two levels**
  - \( \varepsilon_{\text{elec.hydrogen,n}} = -2.17869 \times 10^{-18} / n^2 \) Joules \( \text{(show H atom levels)} \)
  - \( n \text{ is? } \text{the electronic quantum number } 1, 2, 3 \ldots \text{(derived through Schrödinger equation)} \)
  - Schrödinger equation can only be solved exactly for hydrogen… other atoms and molecules require extensive approximation, use experiments
  - electronic energies not a big concern for thermo – usually only ground state
  - So, we won’t really get into. Be sure to note the degeneracy, \( g_n \)

- **Degrees of freedom**
  - **always total must be** \( 3*N \). DOF are not lost or gained by bonds
  - always 3 translational DOF total for molecule
  - either 2 or 3 rotational DOF depending on shape
  - remainder are vibrational

- Several common units for transition energy from spectroscopists – relate to light
- Frequency $\varepsilon = h\nu$ units of $s^{-1}$ also called Hz
- Wavenumbers $cm^{-1}$ $\tilde{\nu}c = \nu$ (clear from dimensional analysis)
- Wavelength (length $\sim 1/\text{energy}$) $c = \lambda\nu$ so $\lambda = c/\nu$, note that $\lambda = 1/\tilde{\nu}$

Of course we began this whole enterprise by saying we were going to learn something about thermodynamics. We need to connect these energy levels to energy and entropy and stuff. **How do we make this connection?** PARTITION FUNCTION!!

Think back to translation…

$$\varepsilon_{\text{trans},n} = \frac{h^2n^2}{8ma^2} \quad \text{or} \quad \varepsilon_{\text{trans},n} = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

If we just think about 1-D case, what is molecular partition function?

$$q_{\text{trans}} = \sum_{n=1}^{\infty} e^{-\varepsilon_{\nu}/kT} = \sum_{n=1}^{\infty} e^{-n^2h^2/(8ml^2kT)}$$

This is often simplified a bit

$$q_{\text{trans}} = \sum_{n=1}^{\infty} e^{-n^2\theta_{\text{trans}}/T} \quad \text{where} \quad \theta = \frac{h^2}{8ml^2} \quad \text{is the translational temp.}$$

If $\theta/T << 1$ then the level spacing is tiny and we can approximate as an integral

$$q_{\text{trans}} = \int \sum_{n=1}^{\infty} e^{-n^2h^2/(8ml^2kT)} dn = \left( \frac{2\pi mkT}{h^2} \right)^{1/2} L$$

remember this is one dimension… what should 3D look like?

$$q_{\text{trans}} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3} \quad (L \text{ has units of length, } \sim \text{ size of molecule})$$

$q$ depends on? mass, volume, and temp

HCl: Let’s consider a volume of 1 L (a typical glass bulb size) at 298K. $V = 0.001$ m$^3$ and $m = M/\text{N}_A$, where $M = 0.036$ kg mol$^{-1}$.

$$q_{\text{trans}}^{\text{HCl}} = \left( \frac{2\pi \times 6.0 \times 10^{-26} \text{ kg} \times (1.38 \times 10^{-23} \text{ JK}^{-1} \times 298K)}{(6.626 \times 10^{-34} \text{ J s})^3} \right) \times 0.001 \text{ m}^3 = 2.2 \times 10^{39}$$

At room temperature, the translational energy is spread out over an incredible number of energy levels!
\[ \langle E_{\text{trans}} \rangle = U_{\text{trans}} = NkT^2 \left( \frac{\partial \ln q}{\partial T} \right) = \frac{3}{2} NkT \quad \text{or} \quad 3/2 \text{ RT per mole} \]

\[ C_{v,\text{trans}} = \langle \delta U/\delta T \rangle_V = 3/2 \text{ R (on a molar basis)} \]

For rotation we play a similar trick by integrating to get

\[ q_{\text{rot}} = \frac{8\pi^2 kT}{\sigma \hbar^2} = \frac{T}{\sigma \Theta_{\text{rot}}} \]

where \( \sigma \) is the **symmetry number**

- \( \sigma = 1 \) for heteronuclear diatomic molecules (i.e., H-Cl)
- \( \sigma = 2 \) for homonuclear diatomic molecules (i.e., N-N)

and \( \Theta_{\text{rot}} \) is the more convenient notation, rotational temperature (\( h^2/8\pi^2 kT \)).

The rotational partition function depends on the moment of inertia (which is related to the structure of the molecule and the mass of the associated atoms) and the temperature.

HCl: 298 K (\( \Theta_{\text{rot}} = 15.02 \text{ K} \))

\[ q_{\text{HCl}}^{\text{rot}} = \frac{298K}{1 \times 15.02 \text{K}} = 20 \]

We can similarly calculate \( \langle E_{\text{rot}} \rangle \):

\[ \langle E_{\text{rot}} \rangle = NkT^2 \left( \frac{\partial \ln q_{\text{rot}}}{\partial T} \right)_V \]

\[ \langle E_{\text{rot}} \rangle = NkT^2 \left( \frac{\partial \ln \left( \frac{T}{\Theta_{\text{rot}}} \right)}{\partial T} \right)_V = NkT^2 \left( \frac{\Theta_{\text{rot}}}{T} \right) \left( \frac{\partial \left( \frac{T}{\Theta_{\text{rot}}} \right)}{\partial T} \right) = NkT^2 \times \frac{\Theta_{\text{rot}}}{T} \times \frac{1}{\Theta_{\text{rot}}} = NkT \]

On a molar basis \( U_{\text{rot}} = RT \)

\( C_{v,\text{rot}} \) is a trivial result. \( C_{v,\text{rot}} = R \)
For vibration, the partition function can’t be integrated because the spacings are too large – not nearly continuous. But, it works out to be a standard series approximation.

\[ q_{\text{vib}} = \frac{e^{-\hbar \nu / 2kT}}{1 - e^{-\hbar \nu / kT}} \]

The vibrational partition function depends on the vibrational frequency (which depends on the strength of the chemical bond and the mass of the constituent atoms) and the temperature.

It is common to define a vibrational temperature to make the expression more compact, \( \theta_{\text{vib}} = \frac{\hbar \nu}{k} \) so that the partition function is

\[ q_{\text{vib}} = \frac{e^{-\theta_{\text{vib}} / 2T}}{1 - e^{-\theta_{\text{vib}} / T}} \text{ or } q_{\text{vib}} = \frac{1}{1 - e^{-\theta_{\text{vib}} / T}} \text{ if the zero point energy is neglected} \]

HCl: 298 K \( (\Theta_{\text{vib}} = 4227 \text{ K}) \). If \( \theta / T \) is >> 1, then what is \( q \) ~ 1.

\[ q_{\text{HCl}}^{\text{vib}} = \frac{1}{1 - e^{\frac{4227 \text{ K}}{298 \text{ K}}}} = 1.0000007 \]

At room temperature, the vibrational energy for HCl is almost solely distributed in its ground state.

MT gives the results for the evaluation of the vibrational contribution to the energy and heat capacity as

\[ \langle E_{\text{vib}} \rangle = NkT \sum \frac{d \ln q_{\text{vib}}}{dT} = Nk \left( \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\theta_{\text{vib}} / T} - 1} \right) \]

\[ U_{\text{vib}} = R \left( \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\theta_{\text{vib}} / T} - 1} \right) \text{ (molar basis)} \]

\[ C_{\text{vib}} = \frac{d \langle E_{\text{vib}} \rangle}{dT} = R \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\theta_{\text{vib}} / T} / (1 - e^{-\theta_{\text{vib}} / T})^2}{(1 - e^{-\theta_{\text{vib}} / T})^2} \text{ (molar basis)} \]

Finally for electronic the energy spacings are huge, so the ground state is the only one that contributes, even at very high temperatures.

\[ q_{\text{elec}} = \sum_{\text{levels}} g_j e^{-\beta \epsilon_j} \]
HCl: 298 K

\[ q_{\text{elec}}^{\text{HCl}} = 1 \] (energy of lowest excited state is much higher than kT at 298 K)

For most atoms and molecules, the electronic degree of freedom does not significantly contribute to the average energy or to the heat capacity

\[ <E_{\text{elec}}> = 0 \text{ or } U_{\text{elec}} = 0 \text{ and } C_{V,\text{elec}} = 0 \]

**Summary**

So for HCl, we have found that the translational energy was widely distributed, the rotational energy was distributed among a handful of states, and the vibrational and electronic energy distributions were confined to the ground state. **Show diagram.**

We can now sum up the total heat capacity for a molecule like HCl at 298 K

\[
C_{V,298 \text{ K}} = C_{V,\text{trans}} + C_{V,\text{rot}} + C_{V,\text{vib}} + C_{V,\text{elec}} = \frac{3}{2} R + R + C_{V,\text{vib}} + C_{V,\text{elec}}
\]

\[
= 12.46 + 8.31 + 0.0012 + 0 \text{ J K}^{-1} \text{ mol}^{-1} = 20.78 \text{ J K}^{-1} \text{ mol}^{-1}
\]

The experimental value at 298 K is 20.81 J K\(^{-1}\)mol\(^{-1}\).

At 2000 K, HCl has a higher heat capacity because of the ability of its vibrational modes to store energy:

\[
C_{V,2000 \text{ K}} = 26.59 \text{ J K}^{-1} \text{ mol}^{-1}
\]