Lecture 17  Chapter 11 – QM energy levels and T-dependence of heat capacity

No seminar today, but things get rolling again next week.

Outline: vibration, electronic, heat capacity, T-dependence

Review:

Translational partition function:

- so \( q_{\text{trans},3D} = \left( \frac{2\pi nkT}{\hbar^2} \right)^{3/2} V \)

- Rotational energy (only molecules – can’t discern atom rotation) Rigid rotator model assumes two masses at a fixed distance. (note that \( L \) should really be \( l \), but I’m using caps for clarity)
  - \( \epsilon_{\text{rotation,L}} = \frac{\hbar^2}{2I} L(L+1) \quad L = 0,1,2… \quad \) degeneracy \( g_L = 2L + 1 \) (note hbar instead of h)
  - Again, we have a rotational temperature: \( \theta_{\text{Rot}} = \frac{\hbar^2}{2k_B} \) (Note error in text on p.204)
  - \( q_{\text{Rot}} = \sum_{L=0}^{\infty} (2L+1)e^{-\epsilon_{\text{Rot}}/kT} = \int_0^\infty dl (2L+1)e^{-L(L+1)\theta_{\text{Rot}}/T} = \frac{T}{\sigma\theta_{\text{Rot}}} = \frac{2kT}{\sigma\hbar^2} \)
    where \( \sigma \) is a symmetry factor that accounts for overcounting rotationally symmetric arrangements.
    - \( \sigma = 1 \) heteronuclear diatomics (HBr)
    - \( \sigma = 2 \) homonuclear diatomics (O\(_2\))
    - \( \sigma = 2 \) water
    - \( \sigma = 12 \) methane
    - \( \sigma = 12 \) benzene

- Vibrational energy (only molecules – vibration requires a bond)
  - assume a bond looks like masses on a spring – Hooke’s law
    - \( f = -kx \) eq. for force, \( k \) is force constant (big = stiff)
    - leads to \( x(t) = A\cos(2\pi\nu t) \) draw and define \( A, \nu, T \)
    - \( V(x) = -\int f(x)dx \) indefinite integral so add constant
    - gives? \( V(x) = \frac{1}{2}kx^2 \) (usually define constant = 0) \( \rightarrow \) draw parabola
  - QM solution is \( \epsilon_{\text{vib,\nu}} = \frac{\hbar}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \left( \nu + \frac{1}{2} \right) = \hbar \nu (\nu + \frac{1}{2}) \quad \nu =? 0,1,2…(\text{add states to parab.}) \)
    (Note stupid use of \( v \) (vee) and \( \nu \) (nu))
  - Reduced mass \( \mu = \frac{m_1m_2}{m_1 + m_2} \)

OK, let’s break into 4 groups. I would like each group to answer the following questions, just a few minutes:
What is \( \nu \); what is vibrational temp; what are the \( \Delta\epsilon \) observed by spectroscopy; what is min \( E_{\text{vib}} \);
\[ \nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{\frac{1}{2}} \]

- Again define vibrational temperature (everything except quantum number): \( \Theta_{\text{vib}} = h/\nu/k \)
- solve for \( \Delta \varepsilon = h/\nu \), how many vibrational lines?, \( \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \), (vib freq. == light freq.)
- also often use wavenumbers for convenience \( \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \)

- minimum vibrational energy is called the zero point energy: \( \frac{1}{2}h/\nu \)

Allright, back to normal.
- 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
- \( D_0 = D_e - \frac{1}{2}h/\nu \) \( D_0 \) is dissociation energy \( D_e \) is ground state electronic energy (where zero is the energy of the atoms infinitely far apart). \( D_e \) is the bottom of the well, \( D_0 \) is the lowest state.
- large force constant (strong bond) or small reduced mass => large spacing

- Looking at the partition function: \( q_{\text{vib}} = \sum_{v=0}^{\infty} e^{-\nu/2h/\nu/kT} = e^{-h/\nu/2kT} \left( 1 + e^{-h/\nu/2kT} + e^{-2h/\nu/2kT} + e^{-3h/\nu/2kT} + \cdots \right) \)

- Can we use our same trick of making this an integral? No spacing is too large.
- But we can use a series approximation to end up with: \( q_{\text{vib}} = \frac{e^{-h/\nu/2kT}}{1 - e^{-h/\nu/2kT}} = \frac{e^{-\nu/2T}}{1 - e^{-\nu/2T}} \)

- Note that it is common to ignore the ground state energy to give \( q_{\text{vib}} = \frac{1}{1 - e^{-h/\nu/2kT}} \)

- Electronic energies (all atoms and molecules) are generally measured by spectroscopy – measures transition energies – differences between two levels (you all know this from GenChem)
  - \( \varepsilon_{\text{elec,hydrogen},n} = -2.17869 \times 10^{-18} / n^2 \) Joules (show H atom levels)
  - \( n \) is? the electronic quantum number 1, 2, 3… (derived through Schrödinger equation)
  - Schrodinger 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, \( g_0 \)

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

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

Now let’s remember that the partition function is what we’re really after and look at this some more:

**HCl:** Let’s consider a volume of 1 mL (a small glass bulb size) at 298K. \( V = 10^{-6} \text{ m}^3 \) and \( m = M/N_A \), where \( M = 0.036 \text{ kg mol}^{-1} \).

Recall that \( q_{trans,3D} = \left( \frac{2\pi nkT}{h^2} \right)^{3/2} V \)

\[
q_{trans}^{HCl} = \left( \frac{2\pi \times 6.0 \times 10^{-26} \text{ kg} \times (1.38 \times 10^{-23} \text{ JK}^{-1} \times 298 \text{ K})}{(6.626 \times 10^{-34} \text{ Js})^2} \right)^{3/2} \times 10^{-6} \text{ m}^3 = 2.2 \times 10^{26}
\]

At room temperature, the translational energy is spread out over an incredible number of energy levels!

\[
\langle E_{trans} \rangle = U_{trans} = NkT^2 \left( \frac{\partial \ln q}{\partial T} \right) = \frac{3}{2} NkT \text{ or } 3/2 \text{ RT per mole}
\]

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

Remember my question about # of DOF in monatomic ideal gas?
  so \( \frac{1}{2} \text{ R of heat capacity per DOF (in this case)} \)

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 (\( \Theta_{rot} = 15.02 \text{ K} \))

recall \( q_{rot} = \frac{T}{\Theta_{rot} \sigma} \)

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

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

\[
\langle E_{rot} \rangle = NkT^2 \left( \frac{\partial \ln q_{rot}}{\partial T} \right)_V = NkT^2 \times \left( \frac{\Theta_{rot}}{T} \right) \times \left( \frac{\partial \left( \frac{T}{\Theta_{rot}} \right)}{\partial T} \right)_V = NkT^2 \times \frac{\Theta_{rot}}{T} \times \frac{1}{\Theta_{rot}} = NkT
\]
On a molar basis $U_{\text{rot}} = RT$

$C_{v,\text{rot}}$ is a trivial result. $C_{v,\text{rot}} = R$

Keep in mind that this is for HCl – 2 rotational DOF. Something that is nonlinear would have 3 rotational DOF so $C_{v,\text{rot}}$ would be $3/2R$

**Vibrational**

If we use $q_{\text{vib}} = \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}}$

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

$$q_{\text{vib}}^{\text{HCl}} = \frac{1}{1 - e^{-(4227\text{K})/(298\text{K})}} = 1.000007$$

What does this mean? At room temperature, HCl, like most molecules, is almost solely in its ground vibrational state.

How does this translate to energy and heat capacity? (using $q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/2kT}} = \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}$)

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

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

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

Does anyone see something new? **For the first time we have T-dependence.**
\( C_{v,vib} \) (HCl, 298 K) = 0.0012 J K\(^{-1}\) mol\(^{-1}\) (very small compared to 3/2 R)
\( C_{v,vib} \) (HCl, 2000 K) = 5.81 J K\(^{-1}\) mol\(^{-1}\) (significant compared to 3/2 R)
\( C_{v,vib} \) (HI, 298 K) = 0.0170 J K\(^{-1}\) mol\(^{-1}\)
\( C_{v,vib} \) (HI, 2000 K) = 6.68 J K\(^{-1}\) mol\(^{-1}\)
\( C_{v,vib} \) (HI, infinite temp) = 8.31 J K\(^{-1}\) mol\(^{-1}\) (the maximum contribution to the heat capacity for each vibrational mode is R) High temperature limit is \( T > \Theta \) (indicate on figure)

We can see here that the vibrational contribution to the heat capacity depends on the temperature and bond strength of the molecule (frequencies of its vibrational modes). This vibrational contribution is the primary reason why heat capacity does, in general, depend on temperature for polyatomic molecules.

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

\[
q_{elec} = \sum_{\text{levels}} g_j e^{-\beta \varepsilon_j}
\]

HCl: 298 K

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

(indegeneracy of ground state is typically 1)

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**

OK, so let’s go back and summarize. For HCl the partition function is (ask for values?)

- huge for translational \( 10^{29} \)
- a handful for rotational (20)
- just over 1 for vibrational (1.0000007)
- and exactly 1 for electronic (1)

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

\[
C_{v,298 \text{ K}} = C_{v,\text{trans}} + C_{v,\text{rot}} + C_{v,vib} + C_{v,\text{elec}} = 3/2 R + R + C_{v,vib} + C_{v,\text{elec}} = 12.46 + 8.31 + 0.0012 + 0 \text{ J K}^{-1} \text{ mol}^{-1} = 20.78 \text{ J K}^{-1} \text{ mol}^{-1}
\]

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 **it has more vibrational modes available** to store energy:

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

Changes for polyatomic molecules?
1) 3 rotational DOF instead of 2
2) many vibrational modes

Total heat capacity is just sum of all component heat capacities

**Individual contributions (have students fill in table):**

<table>
<thead>
<tr>
<th></th>
<th>Translation</th>
<th>Rotation</th>
<th>Vibration</th>
<th>Electronic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomic (linear)</td>
<td>3/2 R</td>
<td>R</td>
<td>R*(0 \rightarrow 3N-5)</td>
<td>0</td>
</tr>
<tr>
<td>polyatomic (nonlinear)</td>
<td>3/2 R</td>
<td>3/2 R</td>
<td>R*(0 \rightarrow 3N-6)</td>
<td>0</td>
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