Lecture 19  Chapters 11 and 12 – Summary of q and heat capacity; negative temperatures and fluctuations

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

Outline:  Vib C_v, Total q, Total C_v, Chapt 12, Equilibrium

Not really any review today as I’ll be reviewing all of last week in just a couple mintues. Remember where we left off:

\[
q_{\text{HCl, vib}} = \frac{1}{1 - e^{-\frac{4227K}{298K}}} = 1.000007
\]

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 \( q_{\text{vib}} = \frac{e^{-hv/2kT}}{1 - e^{-hv/2kT}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \))

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

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

\[
C_{v,\text{vib}} = \frac{d\langle E_{\text{vib}} \rangle}{dT} = nR\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2} \quad \text{(just like Einstein)}
\]

Does anyone see something new?  For the first time we have T-dependence.

This was one of the big early results that helped establish quantum mechanics!
\[ C_{v,\text{vib}} (\text{HCl}, 298 \text{ K}) = 0.0012 \text{ J K}^{-1} \text{ mol}^{-1} \] (very small compared to \( 3/2 \ R \))
\[ C_{v,\text{vib}} (\text{HCl}, 2000 \text{ K}) = 5.81 \text{ J K}^{-1} \text{ mol}^{-1} \] (significant compared to \( 3/2 \ R \))
\[ C_{v,\text{vib}} (\text{HI}, 298 \text{ K}) = 0.0170 \text{ J K}^{-1} \text{ mol}^{-1} \] (smaller theta than HCl due to larger mass)
\[ C_{v,\text{vib}} (\text{HI}, 2000 \text{ K}) = 6.68 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ C_{v,\text{vib}} (\text{HI}, \text{ infinite temp}) = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \] (the maximum contribution to the heat capacity for each vibrational mode is \( R \)).

High temperature limit or classical limit is \( T > \Theta \) (indicate on figure)
(Book misuses this in Katie’s HW)

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

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

It follows then that at any reasonable temperature:
\[
\langle E_{\text{elec}} \rangle = 0 \text{ or } U_{\text{elec}} = 0 \text{ and } C_{v,\text{elec}} = 0
\]

Summary

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

- huge for translational \( (10^{26}) \)
- a handful for rotational \( (20) \)
- just over 1 for vibrational \( (1.0000007) \)
- and exactly 1 for electronic \( (1) \)

I don’t think I said this explicitly, but should be clear that:
\[
E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}
\]
and therefore
\[
q_{\text{tot}} = q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}}
\]
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? **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>(\frac{3}{2} R)</td>
<td>(R)</td>
<td>(R*(0 \rightarrow 3N-5))</td>
<td>0</td>
</tr>
<tr>
<td>polyatomic (nonlinear)</td>
<td>(\frac{3}{2} R)</td>
<td>(\frac{3}{2} R)</td>
<td>(R*(0 \rightarrow 3N-6))</td>
<td>0</td>
</tr>
</tbody>
</table>

**On to Chapt 12**

There are some cool things in chapt 12, but unfortunately these are some of those things that we will barely touch just because of time. You should all write the chair of the department and suggest that PChem be expanded to four semesters in order to help improve things.

We are going to mention four topics in chapt 12… very fast.

1) Density of States:
   Just the fraction of states present at a particular energy. Really just like plotting degeneracy vs. energy. (Sketch plot with #states on X and energy on Y)
   Chris’s HW problem (and the text) do a reasonable job of explaining this.

2) Fluctuations are critical:
   This is dear to my heart and makes me sick to just pass over it. Oh well.
   Note (Eq 12.17) that heat capacity is really a measure of the energy fluctuations in a system.
   \[
   \sqrt{\text{rms}} = T\sqrt{k_bC_v}
   \]
   Thus, a plot of the probability of having a certain energy is narrow if \(C_v\) is small, broad if \(C_v\) big. In other words a high \(C_v\) means that the system can absorb or loose lots of energy without affecting temperature.
3) Negative temp:
I think book’s explanation is very nice, but can also be done more simply by looking at Boltzmann:

Let’s say that we’re looking at a two level system (TLS) (or also the Schottky model used in the book). Let’s label the levels 1 (ground state) and 2 (excited state) and look at the relative probabilities:

\[ p_1 = \frac{e^{-\varepsilon_1/kT}}{q} \quad p_2 = \frac{e^{-\varepsilon_2/kT}}{q} \]

\[ \frac{p_1}{p_2} = e^{\left(\varepsilon_2 - \varepsilon_1\right)/kT} \]

This is a really handy form that you should remember…

Solving for T gives:

\[ T = \frac{\varepsilon_2 - \varepsilon_1}{k_B \left( \ln p_1 - \ln p_2 \right)} \]

By definition \( \varepsilon_2 < \varepsilon_1 \), so if \( p_1 > p_2 \) then \( T > 0 \)

But, what if \( p_2 > p_1 \) then \( T < 0 \)

Note that this is the situation when a laser is running (population inversion)

What does this tell us? That the system must give off energy to increase entropy.

What about if \( p_2 = p_1 \) then \( T = \infty \)

This is the point of maximum entropy

So, to get to a situation where \( T < 0 \), one must heat the system past infinity!

4) Graphical connection between energy functions. Check out p.226 carefully.

All right then on to Chapt 13.

We have done a lot recently figuring out how to relate microscopic information (energy levels and such) to macroscopic quantities (H, T, S, U...) through the partition function. Today we are going to start really applying this to find out some useful chemical information. We are getting into some real freshman chemistry – equilibrium constants. Of course, we’ll do it in just a bit more detail than you saw in CHEM111.

Let’s define the simplest possible reaction:

\[ aA \rightarrow zZ \]

If we started with \( n_{A0} \) and \( n_{Z0} \) moles of A and Z then let’s define the amounts of A and Z at any time…

\[ n_A = n_{A0} - a\xi \]
\[ n_Z = n_{Z0} + z\xi \]

\( \xi \) (xi or squiggle) is the extent of reaction. It measures the progress of the reaction and has units of moles. Subtraction is because A is a reactant.
For instance: \( \text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O} \)

At start: \( n_{\text{H}_2} \quad n_{\text{O}_2} \quad n_{\text{H}_2\text{O}} \)
Later: \( n_{\text{H}_2} - \xi \quad n_{\text{O}_2} - \frac{1}{2}\xi \quad n_{\text{H}_2\text{O}} + \xi \)

Of course, we are really interested in the change in the amount of the substances:
\( \text{dn}_j = j \text{d}\xi \) (negative if reactant)

We can substitute this expression into what is called the Gibbs-Duhem equation:
Gibbs-Duhem is for constant \( T \) and \( p \) (recall \( dG = -SdT + Vdp + \mu_AdN_A + \mu_ZdN_Z \))

\[
dG = \sum_j \mu_j \text{dn}_j
\]

So, rewriting Gibbs-Duhem in terms of \( \xi \) gives:
\[
dG = \sum_j j\mu_j \text{d}\xi
\]

(where products have positive and reactants negative coefficients)

This can be rewritten as:
\[
\left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_j j\mu_j(\xi) = \Delta_r G
\]

where \( \Delta_r G \) is the reaction Gibbs energy. This is defined for a balanced chemical equation and the reactants and products at their standard states. (add products, subtract reactants)

Let’s look at a simple case:
**Isomerization Reaction:** 11-cis retinal \( \leftrightarrow \) all trans retinal

**Everyone know what this does?** vision

\[
\left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_{\text{trans}}(\xi) - \mu_{\text{cis}}(\xi)
\]

Both of these chemical potentials change as the rxn proceeds, so this differential depends on the extent of reaction.
When $\mu_A > \mu_Z$, or $\left( \frac{\partial G}{\partial \xi} \right)_{p,T} < 0$ the reaction $A \rightarrow Z$ is spontaneous ($\xi$ must increase to minimize $G$)

When $\mu_A < \mu_Z$, or $\left( \frac{\partial G}{\partial \xi} \right)_{p,T} > 0$ the reaction $Z \rightarrow A$ is spontaneous ($\xi$ must decrease to minimize $G$)

The minimum in $\left( \frac{\partial G}{\partial \xi} \right)_{p,T}$ occurs when its value is zero, or $\mu_A = \mu_Z$. (really $a\mu_A = z\mu_Z$. This is when the reaction is at equilibrium! The reaction “stops.”)

All right then, we can see that equilibrium is determined by the chemical potential. Another way of saying this is that the chemical potential is the molar $G$ for each product/reactant. (Note that chemical potential depends on concentration, $p$, $T$, etc.)

Note that the standard molar reaction Gibbs energy is different than the reaction Gibbs energy because for the standard energy, the composition of reactants and products are fixed at their standards states (1 M or 1 atm), rather than an arbitrary composition:

$$\Delta_r G^0 = z\mu_Z^0 - a\mu_A^0$$