

Chemistry 21b – Spectroscopy & Statistical Thermodynamics

Lecture # 27 – Electronic Partition Functions, Heat Capacities, and Residual Entropy

The final degree of freedom we need to worry about is that of electronic excitation. Even more so than vibrations, the conditions required to excite electronic states are sufficiently extreme that they can be safely neglected; that is, $q_{el} = 1$. For closed shell molecules, even fairly large and conjugated ones, the excited electronic states lie at several eV – so that E/kT only becomes appreciable at temperatures of several thousand to several tens of thousand of Kelvin. At such temperatures, chemical processes such as collisional dissociation or thermal decomposition also become important, and for these reasons the electronic states of closed shell molecules are often ignored.

The Electronic Partition Functions of Radicals

Radicals offer a substantial difference to closed shell molecules in two important respects: (1) The degeneracy of the ground state can be non-zero, and (2) There can be low-lying electronic states whose influence can be felt even near room temperature. It is easiest to see these points by recalling the electronic properties of atoms and molecules outlined in Lecture #13. Recall that the labelling convention for atomic states is $^{2S+1}L_J$, where S is the total electron spin, L is the orbital angular momentum of the electrons, and J is the vector coupling of L and S . For a given configuration, say $1s^22s^22p^4$ for oxygen, a number of terms can arise – in this case 3P , 1D , and 1S (in order of increasing energy). The energy separation between the terms is of order one to a few eV, and so excited terms are unimportant in the current context.

Within a term, however, the spacing of the individual J states is determined by the spin-orbit interaction; which varies as Z^4 , where Z is the nuclear charge. These spin orbit splittings have equivalent temperatures of several tens of Kelvin for first row atoms, and rise to several thousand Kelvin for transition metals and the like. The degeneracy of the lowest state is given by $2J + 1$ thanks to the different m_J levels.

For diatomic molecules, it is the projection of L along the internuclear axis, denoted Λ that is defined. The label for the state becomes $^{2S+1}\Lambda$, where $\Lambda = 0, 1, 2, \dots$ are labelled $\Sigma, \Pi, \Delta, \dots$. The *electronic* degeneracy of the lowest state for a diatomic radical is $g_0 = 2S + 1$ (remember that the Ω degeneracy is taken care of in the *rotational* partition function). Thus, for molecular oxygen, with its $^3\Sigma$ ground state, $g_0 = 3$, while for OH and NO, both $^2\Pi$ ground states, $g_0 = 2$.

The coupling of S (or more precisely, its projection) and Λ is termed Ω ; this serves as the analog for J from the atomic case. Just as for atoms, the Ω states can be split, and for first row atoms the splittings can be of order kT for room temperature (or even less). Thus, many radicals have electronic partition functions that are more complex than outlined above, but very few can be kept in a bottle for measurements!

One of the few is NO, which has as its ground state the $^2\Pi_{1/2}$ level and as a first excited electronic state the $^2\Pi_{3/2}$ level. That is, NO has a so-called ‘regular’ Ω ladder. OH, like the O atom, is inverted, and so has a $^2\Pi_{3/2}$ ground state and a $^2\Pi_{1/2}$ excited

state). If we treat such radicals as a two level system, the partition function is simply

$$q_{el} = g_0 + g_1 e^{-\theta_{el}/T} \quad (27.1)$$

where θ_{el} is the characteristic temperature that defines the energy level separation of the two electronic states. For NO $\theta_{el} = 178$ K, and so

$$q_{el}(\text{NO}) = 2 + 2e^{-178/K} .$$

OH and CH have similar partition functions, but of course are normally very reactive.

From our earlier treatment of two level systems, we know that the *electronic* heat capacity for NO must go to zero at both high and low temperatures; and should peak in between at a value of $T/\theta_{el} \sim 0.42$ (or about 74 K for NO). In reality, of course, the electronic degrees of freedom must be considered along with the translational, rotational, and vibrational degrees of freedom; and as a result the true heat capacity of NO is rather more complex than outlined above. We consider the general behavior of C_V for the simplest molecular system, H_2 , next.

Putting it all Together – $C_V(\text{H}_2)$

Molecular hydrogen is a particularly good system to examine the overall behavior of C_V because the degrees of freedom are so well separated. Here, $\theta_B(\text{H}_2) = 64.1$ K and $\theta_{vib}(\text{H}_2) = 5300$ K. Figure 27.1 presents the measured molar heat capacity of HD divided by R on a logarithmic temperature scale.

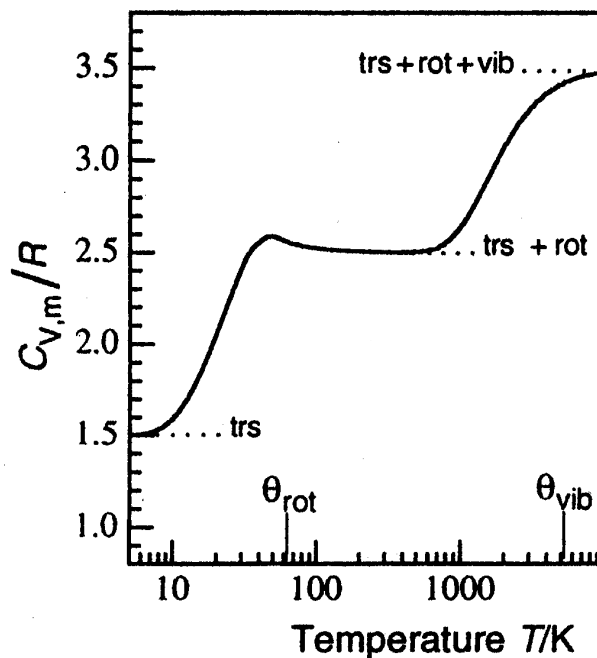


Figure 27.1– The heat capacity of hydrogen deuteride, where the maximum near 30 K arises because the rotational degrees of freedom can be roughly approximated as a two level system near these temperatures.

At sufficiently low temperatures, both the rotations and vibrations can be treated as two level systems; hence their contribution to the heat capacity must be close to zero and only the translational degrees of freedom are active. For H₂ this occurs below 10-20 K. From the equipartition principle, we expect the three degrees of freedom to contribute $RT/2$ each to the energy, and so the value of $C_{V,m}/R$ of 1.5 at low T is readily explained.

As the temperature is gradually increased, the rotational states can begin to respond, but we are still well into the two state limit for vibrations. A simple two state model for the rotations would predict the heat capacity would rise at first, and then fall as the reduced temperature became large compared to one. This is responsible for the maximum seen in the heat capacity curve for H₂ observed near 40-50 K. In reality, of course, there are many additional rotational states that can be populated, and so at temperatures large compared to 64.1 K the rotational contribution to the heat capacity saturates at $C_{V,m}/R=1$ to yield a total heat capacity including translation and rotation of $C_{V,m}(\text{H}_2, \text{trans} + \text{rot})/R=2.5$. The slight bump in the heat capacity curve arises because the degeneracy of the $J = 2$ (para) state only has a nuclear spin weight of 1 compared to the $J = 1$ (ortho) state nuclear spin weight of 3. Hence, the system behaves approximately as a two-level system until substantial excitation of $J = 2$ and higher states occurs.

There is then a lengthy plateau because θ_{vib} is so much larger than θ_B . Two level-like behavior is again observed, but now in the region of $0.4\theta_{vib}$, or temperatures well over 1000 K. At sufficiently high temperatures the full vibrational manifold becomes active and complete equipartition is achieved for translation+rotation+vibration to give an overall heat capacity of $C_{V,m}/R=3.5$. In molecules other than H₂, similar behavior is predicted but since the rotational and vibrational characteristic temperatures are much more similar the ‘steps’, or contrast, in the heat capacity curve versus temperature are not nearly as clear; and the full heat capacity predicted by equipartition occurs at much lower temperatures.

Spectroscopic and Residual Entropy

The approach we have outlined above and in the last few lectures permits us to define a *spectroscopic entropy*, or S_{spec} , as calculated by the eigenstates of molecules in the weakly interacting limit. Mathematically,

$$S_{spec} = \sum_i S_i \quad , \quad (27.1)$$

where

$$S_i = k \ln Q_i + kT \left(\frac{\partial \ln Q_i}{\partial T} \right)_V \quad (27.2)$$

and i runs over the translational, rotational, vibrational, and electronic degrees of freedom. Typically we ignore electronic excitation, and have used rigid rotor and harmonic oscillator models to describe the rotational and vibrational degrees of freedom of a perfect gas. We should expect some small differences between the values predicted theoretically and those observed experimentally through the use of calorimetry, which define S_{cal} .

The difference is called the residual entropy, or $S_{resid} = S_{spec} - S_{cal}$, and is small for most gases. Below we will consider *molecular* solids, that is solids composed of fairly

weakly interacting molecules such as CO or CH₄. Of course, these solids are only stable at low temperatures, but they reveal some interesting thermodynamic properties and fairly large residual entropies. Why?

From our studies to date, you might expect we could write

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT = \int_{\ln T_1}^{\ln T_2} C_P d \ln T \quad (27.3)$$

for the change in entropy as a substance is heated over the $T_1 \rightarrow T_2$ interval. However, if the substance in question undergoes any sort of phase transitions we have neglected the change in entropy, or order, that can result. Such phase transitions do not, of course, occur in gases, but in weakly bound solids changes often manifest themselves at low- to moderate temperatures. Think about water ice formed in vacuum by spraying water onto a cryogenic surface. As the molecules strike the surface they stick together and form an ice layer, but there is little or no chance for the molecules to reorient themselves. The ice so formed is termed *amorphous* because it does not have long range order. As the amorphous ice is warmed however, at some point well before the ice sublimates it becomes possible for the individual water molecules to reorient themselves and find the more stable energy form that is crystalline water ice. In this case, the entropy *decreases* as disorder becomes order, and heat must be supplied to drive this transition. That is, there is an enthalpy associated with the phase change that eq. (27.3) does not account for.

To account for the possibility of such phase changes in the more general case, the correct form of eq. (27.3) is

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT + \sum_i \left(\frac{\Delta H_{tr}}{T_{tr}} \right)_i, \quad (27.4)$$

where ΔH_{tr} is the enthalpy change upon a phase transition at temperature T_{tr} . Equation (27.4) needs to be consistent with the Third Law of Thermodynamics, which we will restate here (see Maczek p. 74):

Third Law: *There is no contribution to the entropy at absolute zero from any substance in internal equilibrium.*

Thus, for the calorimetric entropy the integral needs to be started at absolute zero. We may therefore write

$$S_{cal} = \int_0^{T_2} \frac{C_P}{T} dT + \sum_i \left(\frac{\Delta H_{tr}}{T_{tr}} \right)_i = \int_{-\infty}^{\ln T_2} C_P d \ln T + \sum_i \left(\frac{\Delta H_{tr}}{T_{tr}} \right)_i, \quad (27.5)$$

and can now proceed to examine realistic systems in order to compare the predicted and experimental entropies. For OCS at 298 K, for example, $S_{spec} = 55.268 \text{ cal K}^{-1} \text{ mole}^{-1}$, while $S_{cal} = 55.339 \text{ cal K}^{-1} \text{ mole}^{-1}$. This small difference can easily be accounted for by a more accurate spectroscopic model of the rotational and vibrational eigenstates of OCS in the gas phase.

What about more complex systems? This discussion follows that in Maczek.

CO Ice. For a perfect CO crystal at low temperatures, for example, all of the CO molecules should be lined up with the same orientation; but if we make an amorphous solid along the lines we noted above for water then disorder should be introduced. For a CO lattice, there are two possible orientations for each molecule (CO versus OC) that lie very close in energy because the dipole moment of CO is so small (~ 0.1 Debye). At sufficiently high temperatures in the solid the molecules can still reorient themselves, and if the temperature is extremely low the interconversion time scale becomes quite long (solid CO sublimates at ~ 25 K under ultra-high vacuum conditions). From our discussion of two level systems at high T/θ , we know that the number of possible combinations for a doubly degenerate system is $\Omega = 2^N$ for N particles. With a mole of CO in a lattice at low T , a perfectly disordered system would therefore have $S_{resid}(\text{CO, disordered}) \leq k \ln 2^N = R \ln 2$. As we have seen before, $R \ln 2 = 5.8 \text{ J K}^{-1} \text{ mole}^{-1}$ or $1.39 \text{ cal K}^{-1} \text{ mole}^{-1}$. The actual value of $S_{resid} = S_{spec} - S_{cal}$ is $4.6 \text{ J K}^{-1} \text{ mole}^{-1}$, and so actual CO solids at low temperature are not completely randomized (but are close!).

This is an example of the Third Law becoming invalid because the system *cannot* achieve internal equilibrium at very low temperatures, and so $S_0 > 0$ as $T \rightarrow 0$. The $T \rightarrow 0$ value of the entropy can also be non-zero if the ground state degeneracy is larger than one (radicals for example), or if there are extremely low temperature phase transitions that can be accessed (this would result in associated entropy changes of $\Delta S = \Delta H/T$). Let's look at a few other examples of low temperature molecular solids to round things out:

NO Ice. If NO remained intact in the molecular solid, we have already seen that the low temperature degeneracy would be 2, not 1. However, it can dimerize to make N_2O_2 at low temperatures and in the high density solid environment. There are two possible ways to make this rectangular molecule, which leads us to the same situation as above – except for the fact that we have converted the original N molecules into $N/2$ dimers. We thus expect $S_{resid}(\text{NO, equivalence}) = S_{resid}(\text{CO, disordered})/2$, or $2.88 \text{ J K}^{-1} \text{ mole}^{-1}$. The measured value of the residual entropy is $2.89 \text{ J K}^{-1} \text{ mole}^{-1}$, and so in this case the assumption of complete randomization is in fact a very good one. Why? In this case the dimer is symmetric, with no dipole moment. Thus the orientations in this case are *equivalent* to the system, there are no energetic penalties to be paid as there are in a CO crystal.

CH₃D Ice. Since we've now 'labelled' one of the C–H bonds, there are now four equivalent orientations that CH₃D can occupy in a matrix. Thus, $\Omega = 4^N$, and for a mole of deuterated methane $S_{resid}(\text{CH}_3\text{D, equivalence}) = R \ln 4 = 11.52 \text{ J K}^{-1} \text{ mole}^{-1}$. The measured value is $11.56 \text{ J K}^{-1} \text{ mole}^{-1}$, again excellent agreement. There is, in fact, a very weak dipole moment for CH₃D, but it is so small (~ 0.007 Debye) as to be energetically unimportant and the four possible positions for the D atom can be treated as equivalent.

H₂O Ice-I. Ice-I is the STP phase of water ice. In a perfect Ice I crystal, the water molecules are arranged in tetrahedral bonding patterns. However, not all of the possible hydrogen bonded geometries are occupied by a given suite of water molecules. There are in fact $6/4 = 3/2$ choices/water molecules (see Maczek), and so $(3/2)^N$ possible equivalent orientational rearrangements in water ice. The molar residual entropy is thus $S_{resid}(\text{H}_2\text{O, equivalence}) = R \ln(1.5) = 3.37 \text{ J K}^{-1} \text{ mole}^{-1}$ as compared to the experimental residual entropy of $3.4 \text{ J K}^{-1} \text{ mole}^{-1}$.