

## 18.4: Most Molecules are in the Ground Vibrational State

The vibrational energy levels of a diatomic are given by:

$$E_v = (v + 1/2)h\nu$$

where  $\nu$  is the vibrational frequency and  $v$  is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT} \left( 1 + e^{-h\nu/2kT} + e^{-2h\nu/2kT} + \dots \right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT} (1 + x + x^2 + x^3 + \dots) \quad (18.4.1)$$

where  $x = e^{-h\nu/kT}$ . Given the following power series expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \dots$$

Equation 18.4.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT} \left( \frac{1}{1-x} \right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \quad (18.4.2)$$

If the zero of energy scale is at  $h\nu/2kT$ , then Equation 18.4.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1 - e^{-h\nu/kT}} \quad (18.4.3)$$

A vibrational temperature  $\Theta_{\text{vib}}$  may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where  $\tilde{\nu}$  is the vibrational frequency in  $\text{cm}^{-1}$ .  $\Theta_{\text{vib}}$  is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond you are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table 18.4.1 : Representative molecular data for a few diatomics

Molecule	g	Bond Length (pm)	$\omega$ ( $\text{cm}^{-1}$ )	$\Theta_{\text{vib}}$ (K)	$\tilde{B}$ ( $\text{cm}^{-1}$ )	$\Theta_{\text{rot}}$ (K)	Force constant $k$ (dynes/cm)	$D_0$ (kcal/mol)
$\text{H}_2$	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
$\text{D}_2$	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
$\text{N}_2$	1	1.097	2358	3393	2.001	2.99	22.94	225.1
$\text{O}_2$	3	1.207	1580	2274	1.446	2.08	11.76	118.0
$\text{Cl}_2$	1	1.987	560	805	0.244	0.351	3.2	57.0
$\text{CO}$	1	1.128	2170	3122	1.931	2.78	19.03	255.8

Molecule	g	Bond Length (pm)	$\omega$ ( $\text{cm}^{-1}$ )	$\Theta_{\text{vib}}$ (K)	$\tilde{B}$ ( $\text{cm}^{-1}$ )	$\Theta_{\text{rot}}$ (K)	Force constant $k$ (dynes/cm)	$D_0$ (kcal/mol)
<i>NO</i>	2	1.15	190	2719	1.695	2.45	15.7	150.0
<i>HCl</i>	1	1.275	2938	4227	10.44	15.02	4.9	102.2
<i>HI</i>	1	1.609	2270	3266	6.46	9.06	3.0	70.5
<i>Na<sub>2</sub></i>	1	3.096	159	229	0.154	0.221	0.17	17.3
<i>K<sub>2</sub></i>	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

### ✓ Example 18.4.1

The vibrational frequency of *I<sub>2</sub>* is  $214.57 \text{ cm}^{-1}$ . Calculate the vibrational partition function of *I<sub>2</sub>* at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{\text{vib}} = \frac{1}{1 - 0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

## Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume,  $\bar{C}_V$  is given by:

$$\bar{C}_V = \left( \frac{\partial E}{\partial T} \right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \quad (18.4.4)$$

$$= \frac{-1}{kT^2} \frac{\partial}{\partial \beta} \quad (18.4.5)$$

$$= (-k\beta^2) \left( \frac{\partial}{\partial \beta} \right) \quad (18.4.6)$$

Therefore:

$$\bar{C}_V = (-k\beta^2) \left( \frac{\partial \epsilon_{\text{vib}}}{\partial \beta} \right)$$

and when the vibrational partition function (Equation 18.4.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{[(1 - e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})] e^{-hc\nu/kT}}{(1 - e^{-hc\nu/kT})^2} hc\tilde{\nu} \quad (18.4.7)$$

$$= k \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2} \quad (18.4.8)$$

For large  $T$ , the  $\bar{C}_V$  becomes:

$$N_A k = R$$

and for small  $T$ ,  $\bar{C}_V$  goes to zero as demonstrated in Figure 18.4.1.

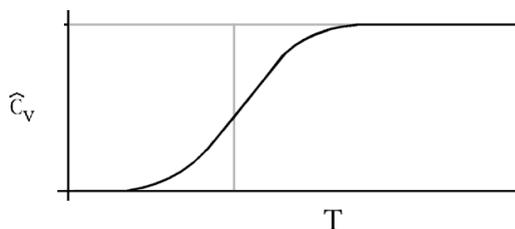


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature  $T/\Theta$  to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of  $\Theta_{\text{vib}}$  is determined mostly by

1. the strength of a bond (the stronger the higher  $\Theta_{\text{vib}}$ )
2. the (effective) mass of the molecule (the lighter the higher  $\Theta_{\text{vib}}$ )

Molecules with low  $\Theta_{\text{vib}}$  often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

## Vibrational Populations

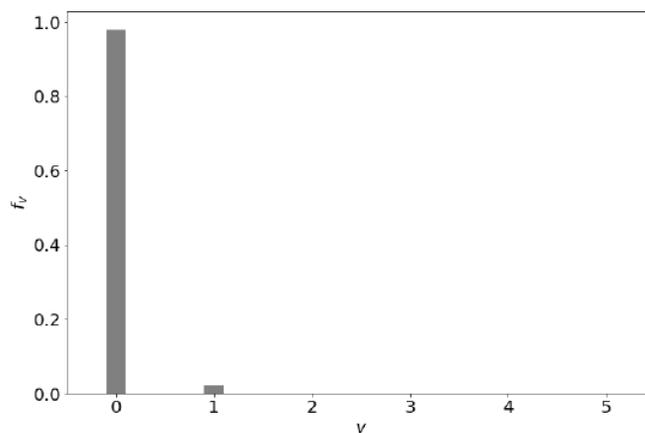
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the  $v$ th vibrational state is given by:

$$f_v = \frac{e^{-hv(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 18.4.2, we get:

$$\begin{aligned} f_v &= (1 - e^{-hv/kT}) e^{-hv/kT} \\ &= (1 - e^{-\Theta_{\text{vib}}/T}) e^{-\Theta_{\text{vib}}v/T} \end{aligned}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl<sub>2</sub> at 300 K. Most of the molecules are in the ground vibrational state,  $v = 0$ .

From the figure, we can see that most of the Cl<sub>2</sub> molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

### Contributors and Attributions

- [www.chem.iitb.ac.in/~bltembe/pdfs/ch\\_3.pdf](http://www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf)

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