

MOLECULAR PARTITION FUNCTIONS

Introduction

In the last chapter, we have been introduced to the three main ensembles used in statistical mechanics and some examples of calculations of partition functions were also given. In chemistry, we are concerned with a collection of molecules. If the molecules are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. The next chapters will include detailed consideration of intermolecular forces. In ensemble theory, we are concerned with the ensemble probability density, i.e., the fraction of members of the ensemble possessing certain characteristics such as a total energy E , volume V , number of particles N or a given chemical potential μ and so on. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system. The equivalence of the ensemble approach and a molecular approach may be easily realized if we treat part of the molecular system to be in equilibrium with the rest of it and consider the probability distribution of molecules in this subsystem (which is actually quite large compared to systems containing a small number of molecules of the order of tens or hundreds). Since we are dealing with number of particles of the order of Avogadro number, the ensemble description and the molecular descriptions are equivalent. The energies of atoms and molecules are quantized. While atoms have only electronic energy levels, molecules have quantized energy levels arising from electronic, vibrational and rotational motion. A schematic energy level diagram is shown in Fig. 3.1.

We have already seen that in the canonical ensemble, the probability of a system having energy E_i is proportional to the Boltzmann factor and is given in terms of the canonical partition function q by

$$P(E_i) = e^{-E_i/kT} / \sum_i e^{-E_i/kT} = e^{-E_i/kT} / q \quad (3.1)$$

Where q is defined by

$$q = \sum_i e^{-\beta E_i} \quad (3.2)$$

Here, $\beta = 1/kT$ and $e^{-\beta E_i}$ is called the Boltzmann factor. Often the Boltzmann constant is written as k_B . But when there is no ambiguity, we will simply write k .

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities. To calculate $P(E_i)$ s we need the energy levels of a system. The energy ("levels") of a system can be built up from the molecular energy levels. We will consider the simpler problem of molecular energy levels which are pictorially shown in the Fig 3.1.

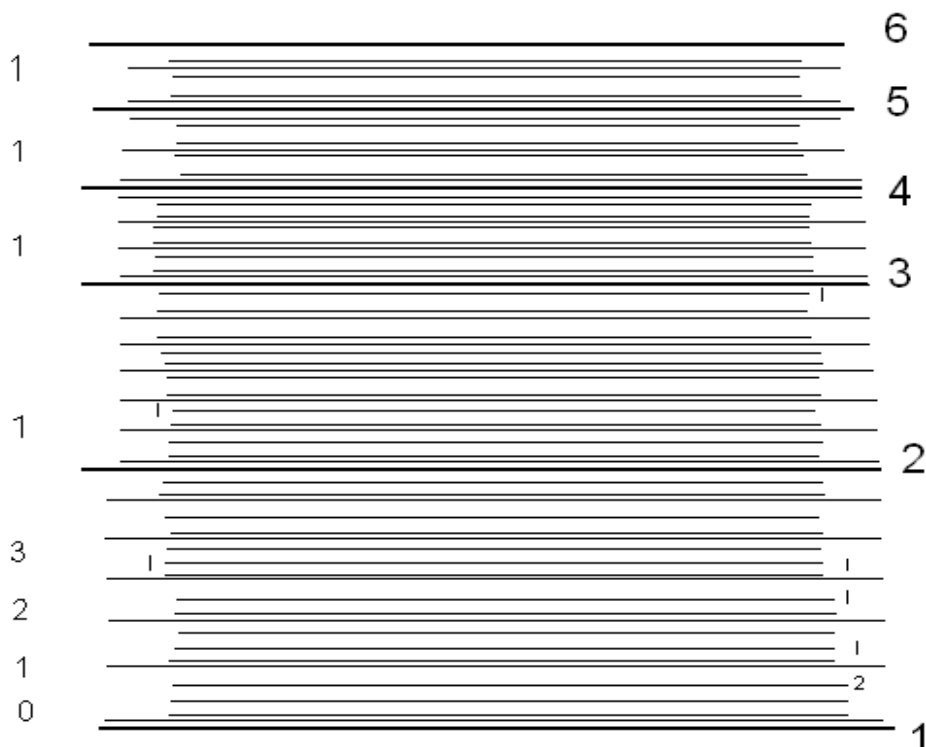


Figure 3.1 A schematic diagram showing electronic (bold lines), vibrational and rotational energy levels. The electronic quantum numbers are shown to the extreme right. Vibrational quantum numbers are shown to the extreme left. The rotational quantum numbers are shown between the vibrational levels.

3.1 Electronic, Vibrational, Rotational and Translational Partition Functions

The electronic energy levels are generally very widely separated in energy compared to the thermal energy kT at room temperature. In each electronic level, there are several vibrational levels and for each vibrational level, there are several rotational states. This is a simplified and useful model to start with. The total energy is a sum of all these energies and is given by

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} + E_{\text{others}} \quad (3.3)$$

The term E_{others} includes nuclear spin energy levels and may also be used later to include the interactions between the first four. Assuming the first three to be independent and neglecting the last term, the molecular partition function (ie, a sum over the molecular energy states) is given by

$$q = \sum e^{-(E_{el} + E_{vib} + E_{rot} + E_{trans}) / kT} = \sum_{el} e^{-\beta E_{el}} \sum_{vib} e^{-\beta E_{vib}} \sum_{rot} e^{-\beta E_{rot}} \sum_{trans} e^{-\beta E_{trans}} \quad (3.4)$$

Here, the summation is over the electronic, vibrational and rotational states can be done separately since they are assumed to be independent. Therefore,

$$q = q_{el} q_{vib} q_{rot} q_{trans} \quad (3.5)$$

The molecular partition q function is written as the product of electronic, vibrational, rotational and partition functions.

The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q , larger the number of states which are available for the molecular system to occupy. Since $E_{el} > E_{vib} > E_{rot} > E_{trans}$, there are far too many translational states available compared to the rotational, vibrational and electronic states. q_{el} is very nearly unity, q_{vib} and q_{rot} are in the range of 1 to 100 while q_{trans} can be much in excess of 10^{20} . We shall calculate the values of these q s and indicate how these q s are useful in calculating the equilibrium constants and also in certain cases, the rate constants.

Using the standard formulae for the translational, rotational and vibrational energy levels, we will now calculate the molecular translational, vibrational and rotational partition functions for diatomic molecules first.

3.1.1 The Translational Partition Function, q_{tr} .

Consider a molecule confined to a cubic box. A molecule inside a cubic box of length L has the translational energy levels given by $E_{tr} = h^2 (n_x^2 + n_y^2 + n_z^2) / 8mL^2$ where n_x , n_y and n_z are the quantum numbers in the three directions (See Chapter 1 for details). The translational partition function is given by

$$\sum_{tr} e^{-\beta E_{tr}} = \sum_{n_x} e^{-\beta E_x} \sum_{n_y} e^{-\beta E_y} \sum_{n_z} e^{-\beta E_z} \quad (3.6)$$

$$\therefore q_{tr} = q_x q_y q_z, \quad (3.7)$$

Which is the product of translational partition functions in the three directions. Since the levels are very closely spaced, we can replace the sum by an integral

$$q_x = \int_1^{\infty} e^{-n_x^2 h^2 / (8mL^2 k_B T)} dn_x \approx \int_0^{\infty} e^{-a n_x^2} dn_x, \quad a = \frac{h^2}{8mL^2 k_B T} \quad (3.8)$$

using $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\pi/a}$ we get,

$$q_x = 1/2 (\pi/a)^{1/2} = \frac{1}{2} \frac{\sqrt{8\pi m k_B T}}{h} L = \frac{\sqrt{2\pi m k_B T}}{h} L = L/\Lambda \quad (3.9)$$

where, Λ is the de Broglie thermal wavelength given by $\frac{h}{\sqrt{2\pi m k_B T}}$.

Multiplying q_x , q_y and q_z , and using $V =$ volume of the box $= L^3$, we have,

$$q_{tr} = [2\pi m k_B T / h^2]^{3/2} V = V / \Lambda^3 \quad (3.10)$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for a typical small molecular mass. This means that such a large number of translational states are accessible or available for occupation by the molecules of a gas.

Example 3.1 Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution: Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} \text{ kg}$

$$2\pi m k_B T = 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27} \text{ kg}) \times 1.3807 \times 10^{-23} \text{ J/K} \times 300 \text{ K} \\ = 1.0969 \times 10^{-44} \text{ J kg}$$

$$\Lambda = h / (2 \pi m k_B T)^{1/2} = 6.6262 \times 10^{-34} \text{ J s} / (1.0969 \times 10^{-44} \text{ J kg})^{1/2} = 6.326 \times 10^{-12} \text{ m}$$

$q_{tr} = V / \Lambda^3 = 1000 \times 10^{-6} \text{ m}^3 / (6.326 \times 10^{-12} \text{ m})^3 = 3.95 \times 10^{30}$. This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

3.1.2 The Rotational Partition Function of a Diatomic

The rotational energy levels of a diatomic molecule are given by

$$E_{rot} = \bar{B} J (J + 1) \text{ where } \bar{B} = h / 8 \pi^2 I c \quad (3.11)$$

Here, \bar{B} is the rotational constant expressed in cm^{-1} . The rotational energy levels are given by $\epsilon_J = J(J+1)h^2/8\pi^2 I$, where I is the moment of inertia of the molecule given by μr^2 where, μ is the reduced mass and r , the bond length. Often, the energies are also expressed in terms of the rotational temperature, Θ_r or Θ_{rot} , which is defined as

$$\Theta_r = \frac{h^2}{8\pi^2 I k} \quad (3.12)$$

In the summation for the expression for q_{rot} , Eq. (3.13), we can do an explicit summation

$$q_{rot} = \sum_j (2J+1) e^{-E_{rot,j}/kT} \quad (3.13)$$

if only a few terms contribute. The factor $(2J+1)$ for each term accounts for the degeneracy of a rotational state J . If energy E_J is degenerate with $(2J+1)$ states corresponding to it, then, the Boltzmann factor $e^{-E_{rot,j}/kT}$ has to be multiplied by $(2J+1)$ to account for all these states. If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} above to get

$$q_{rot} = \int_0^{\infty} (2J+1) e^{-\bar{B}J(J+1)/kT} dJ \quad (3.14)$$

the integration can be easily be done by substituting $x = J(J+1)$ and $dx = (2J+1) dJ$

$$q_{rot} = kT / \bar{B} \quad (3.15)$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is indistinguishable from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ , which is called the symmetry number, which is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes,

$$q_{rot} = \frac{kT}{\sigma \bar{B}} \quad (3.16)$$

Example 3.2 What is the rotational partition function of H_2 at 300K?

Solution: The value of \bar{B} for H_2 is 60.864 cm^{-1} . The value of $k_B T$ in cm^{-1} can be obtained by dividing it by hc , i.e., $(k_B T/hc) = 209.7 \text{ cm}^{-1}$ at 300K . $\sigma = 2$ for a homonuclear molecule. Therefore, $q_{rot} = kT / \sigma \bar{B} = 209.7 / (2 \times 60.864) = 1.723$. Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible to at 300K .

3.1.3 The Vibrational Partition Function of a Diatomic

The vibrational energy levels of a diatomic are given by

$$E_n = (n + 1/2) h\nu \quad (3.17)$$

where ν is the vibrational frequency and n is the vibrational quantum number.

In this case, it is easy to sum the geometric series shown below

$$q_{vib} = \sum_{n=0}^{\infty} e^{-(n+1/2)h\nu/kT} \quad (3.18)$$

$$= e^{-h\nu/(2k_B T)} (1 + e^{-h\nu/k_B T} + e^{-2h\nu/k_B T} + \dots)$$

$$= e^{-h\nu/2kT} (1 + x + x^2 + x^3 + \dots) \quad (3.19)$$

$$= e^{-h\nu/2kT} [1 / (1 - x)] \quad (3.20)$$

where $x = e^{-h\nu/k_B T}$ which is less than 1. Therefore,

$$q_{vib} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \quad (3.21)$$

$$q_{vib} = \frac{1}{1 - e^{-h\nu/kT}} \quad (3.22)$$

if the zero of energy scale is at $h\nu/2kT$. Analogous to Θ_r , a vibrational temperature Θ_v or Θ_{vib} may be defined as $hc\bar{\nu}/k$, where, $\bar{\nu}$ is the vibrational frequency in cm^{-1} .

Example 3.3 Calculate the vibrational partition function of I_2 at 300K .

Solution: The vibrational frequency of I_2 is 214.57 cm^{-1} . $h\nu/kT = 214.57/209.7 = 1.0232$

$e^{-h\nu/kT} = 0.3595 \therefore q_{vib} = 1/(1-0.3595) = 1.561$. This implies, as before, that very few vibrational states are accessible.

3.1.4 The Electronic Partition Function

Writing the electronic energy as E_1, E_2, E_3, \dots with degeneracies g_1, g_2, g_3, \dots the electronic partition function is given by

$$q_{el} = g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} \quad (3.23)$$

Usually, $E_1 \ll E_2$ or E_3 . Treating E_1 to be the reference value of zero of energy, we get,

$$q_{el} = g_1 \quad (3.24)$$

which is the ground state degeneracy of the system.

Example 3.4 Find the electronic partition of H_2 at 300K .

Solution The lowest electronic energy level of H_2 is near -32 eV and the next level is about 5 eV higher. Taking -32 eV as the zero (or reference value of energy),

$$q_{el} = e^0 + e^{-5 \text{ eV} / kT} + \dots$$

At 300 K, $T = 0.02\text{eV}$ and $q_{el} = 1 + e^{-200} + \dots \approx 1.0$

Where all terms other than the first are nearly 0. This implies that $q_{el} = 1$. The physical meaning of this is that only the ground electronic state is generally accessible at room temperature.

Representative data useful for calculating the electronic, vibrational, and rotational partition functions is given in Table 3.1. The electronic degeneracy is represented as g . The vibrational frequency is written as $\bar{\omega}$. The dissociation energy is written as D_0 . It is quite straight forward to calculate the above partition functions for these molecules.

Table 3.1 Representative molecular data for a few diatomics.

Molecule	g	Bond Length (Å)	$\bar{\omega}$, cm^{-1}	Θ_{vib} , K	\bar{B} , cm^{-1}	Θ_{rot} , K	Force constant k (dynes/cm)	D_0 (kcal/mol)
H ₂	1	0.7414	4400	6332	60.9	87.6	5.749	103.2
D ₂	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
N ₂	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O ₂	3	1.207	1580	2274	1.446	2.08	11.76	118.0
Cl ₂	1	1.987	560	805	0.244	0.351	3.2	57.1
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8
NO	2	1.15	1890	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na ₂	1	3.096	159	229	0.154	0.221	0.17	17.3
K ₂	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 3.5 Express the partition function of a collection of N molecules Q in terms of the molecular partition function q .

Solution: Assuming the N molecules to be independent, the total energy E of molecules is a sum of individual molecular energies E_s and

$$Q = \sum_{\text{all possible } E_s} e^{-\beta E} = \sum_i e^{-\beta \epsilon_i^{(1)}} \sum_i e^{-\beta \epsilon_i^{(2)}} \dots \sum_i e^{-\beta \epsilon_i^{(N)}} \quad (3.25)$$

$$= q \cdot q \dots q = q^N \quad (3.26)$$

Here $\epsilon_i^{(1)}, \epsilon_i^{(2)}, \dots, \epsilon_i^{(N)}$ are energies of individual molecules and a sum of all E_s can only come from summing over all ϵ_i s. Gibbs postulated that

$$Q = q^N / N! \quad (3.27)$$

The $N!$ in the denominator is due to the indistinguishability of the tiny molecules (or other quantum particles in a collection).

Example 3.6 Derive the Maxwell Boltzmann distribution of molecular speeds.

Solution: If we represent a molecular velocity by v , it has three independent components v_x , v_y and v_z in the three directions x , y and z . Let us consider monatomic gas of mass m . The probability $F(x, y, z)$ that given molecule will have velocity components lying between x and $x + dx$, y and $y + dy$ and z and $z + dz$ can be written as

$$F(x, y, z) dx dy dz = f(x) f(y) f(z) dx dy dz.$$

F is written as a product of three functions f because x , y and z are independent and since nature does not distinguish between x , y and z (unless directional fields like gravitational or electromagnetic are present), the form of f is the same in the three directions. Again, since there is no distinction between positive and negative x , f depends on $|x|$ or x^2 . We can rephrase the above equation as

$$F() = f() f() f() \quad (3.28)$$

The only function that satisfies the above equation is an exponential function since

$$e^{x^2+y^2+z^2} = e^{x^2} e^{y^2} e^{z^2} \text{ and so we conclude that } f() \text{ may be written as}$$

$$f() = C e^{\pm b v_x^2} \rightarrow C e^{-b v_x^2} \quad (3.29)$$

We take only the negative exponent (C and b are positive) because a positive exponent implies that very large velocities have very high probabilities which is highly unlikely. To evaluate C , We invoke the physical argument that the velocity has to lie somewhere between $-\infty$ to $+\infty$ and that the total probability is 1 i.e.,

$$\int_{-\infty}^{\infty} f(v_x^2) dv_x = C \int_{-\infty}^{\infty} e^{-b v_x^2} dv_x = 1$$

The above integral is a standard integral $\int_0^{\infty} e^{-a x^2} dx = \pi^{1/2}/2$

$$\text{Thus, } C \int_{-\infty}^{\infty} e^{-b v_x^2} dv_x = C (\pi / b)^{1/2} \quad (3.30)$$

But since we want the right side to be unity, $C (\pi / b)^{1/2} = 1$ or $C = (b / \pi)^{1/2}$ and

$$f(x) = (b / \pi)^{1/2} e^{-b v_x^2}$$

From a probability distribution such as $f(x)$, average quantities can be determined. The averages of x and x^2 are given by

$$\langle x \rangle = \int_{-\infty}^{\infty} (b / \pi)^{1/2} x e^{-b v_x^2} dx = 0 \quad (3.31)$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 (b / \pi)^{1/2} e^{-b v_x^2} dx = 1/2b \quad (3.32)$$

The averages have been denoted by $\langle \rangle$. We have also used another standard integral,

$$\int_0^{\infty} x^2 e^{-a x^2} dx = 1/4 (\pi/a^3)^{1/2} \quad (3.33)$$

The integral for $\langle x \rangle$ is zero because the value of the integrand for positive x is equal and opposite to its value at $-x$. Thus the area on the left of $x = 0$ is equal and opposite in sign to the area on the right. This is a special case of a general result that the integral of

the product of an even function and an odd function of x is zero over a symmetric interval around zero.

To evaluate b , we take the help of the kinetic theory of gases. Do look up the details.

The pressure of a gas is given in terms of the mean square velocity (speed) as

$$p = 1/3 (N/V) m \langle v^2 \rangle$$

Where N/V = (number of molecules of the gas / volume) = the density of the gas. But $N = nN_A$ where n = number of moles and N_A , the Avogadro number; and since $pV = nRT$, we have

$$pV = 1/3 Nm \langle v^2 \rangle = 1/3 n N_A m \langle v^2 \rangle = nRT \quad (3.34)$$

$$\langle v^2 \rangle = 3 RT / mN_A = 3 k_B T / m \quad (3.35)$$

Where $k_B = R / N_A$ is the Boltzmann constant, 1.3806×10^{-23} J / K. Since

$\langle v^2 \rangle = 3 k_B T / m$, we have $\langle v_x^2 \rangle = k_B T / m$ and substituting, we get $b = m / 2 k_B T$.

Equations for f and F now become

$$f(v_x) = (m / 2 k_B T)^{1/2} e^{-m v_x^2 / 2 k_B T} \quad (3.36)$$

$$F(v_x, v_y, v_z) = (m / 2 k_B T)^{3/2} e^{-m (v_x^2 + v_y^2 + v_z^2) / 2 k_B T} \quad (3.37)$$

This is the Maxwell - Boltzmann distribution of molecular speeds. $F(v_x, v_y, v_z) dv_x dv_y dv_z$ gives the probability of finding an arbitrary molecule with a velocity (v_x, v_y, v_z) in the volume element $dv_x dv_y dv_z$. A more appealing interpretation of the same is that it is the fraction (of the total molecules) of molecules having velocities (v_x, v_y, v_z) . Analogous to the radial probability distribution in coordinate space, we can now estimate the probability of finding a particle in a spherical shell of volume $4\pi v^2 dv$. This probability in such a spherical shell of radius v and thickness dv is given by

$$4\pi v^2 dv (m / 2 k_B T)^{3/2} e^{-m (v_x^2 + v_y^2 + v_z^2) / 2 k_B T} \quad (3.38)$$

3.2 Thermodynamic Functions

We will be restricting ourselves to the canonical ensemble here. Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i .

In the collection of N molecules, how many molecules (n_i) have the energy E_i ? This has to be $N \exp^{-\beta E_i} / Q$. This is because the fraction of molecules n_i / N having the energy E_i is $e^{-\beta E_i} / Q$ which is the same as the probability of finding a molecule with energy E_i in the collection. The average energy is obtained by multiplying E_i with its probability and summing over all i . ie,

$$\begin{aligned} \langle E \rangle &= \sum_i E_i P_i = \sum_i E_i e^{-\beta E_i} / Q = - \sum_i \frac{1}{Q} \frac{\partial}{\partial \beta} e^{-\beta E_i} = - \frac{1}{Q} \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} \\ &= - \frac{1}{Q} \frac{\partial Q}{\partial \beta} = - \frac{\partial \ln Q}{\partial \beta} \end{aligned} \quad (3.39)$$

Detailed connection between partition functions and thermodynamic functions has been derived in Chapter 2, Section 2.4.2. The relations between Q and pressure and entropy are given by Eqns. (2.168) and (2.171) respectively. The pressure p can also be obtained as the ensemble average of $(-\partial E/\partial V)_T = (-\overline{d w/dV})_T$ giving,

$$p = \sum_i -\frac{\partial E_i}{\partial V} P_i = \sum_i -\frac{\partial E_i}{\partial V} \frac{e^{-\beta E_i}}{Q} = \frac{1}{\beta Q} \frac{\partial Q}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V} \quad (3.40)$$

The entropy is given by

$$S = k \ln (Q + \beta \langle E \rangle) \quad (3.41)$$

The notation change is that Z is written as Q here and \bar{E} is written as $\langle E \rangle$.

Let us recall the four fundamental thermodynamic relations.

$$dE = TdS - pdV \quad (3.42)$$

$$dH = TdS + Vdp \quad (3.43)$$

$$dA = -SdT - pdV \quad (3.44)$$

$$dG = -SdT + Vdp \quad (3.45)$$

Here, E is the internal energy, $H = E + pV$, the enthalpy, $A = E - TS$, the Helmholtz free energy and $G = H - TS$, the Gibbs free energy. Let us now replace $\langle E \rangle$ by simply E or more correctly by $E - E(0)$, where $E(0)$ is the reference value of E at $T = 0$. This is necessary because, the absolute value of E is not measurable and only differences can be measured. The same idea holds for H , A as well as G . Therefore, we rewrite the equation for energy as

$$E - E(0) = -(\partial \ln Q / \partial \beta)_V \quad (3.46)$$

From the equation for enthalpy, $H = E + pV$, we get,

$$H - H(0) = -(\partial \ln Q / \partial \beta)_V + kTV (\partial \ln Q / \partial V)_\beta \quad (3.47)$$

Since $p = -(\partial A / \partial V)_T$, we get from (3.47),

$$A - A(0) = -kT \ln Q \quad (3.48)$$

And finally we have for G

$$G - G(0) = -kT \ln Q + kTV (\partial \ln Q / \partial V)_\beta \quad (3.49)$$

For an ideal gas, $pV = nRT$ where, n = number of moles of the gas and $R = N_A k$ = the gas constant and N_A is the Avogadro number. Substituting this and $Q = q^N / N!$ in the above equation, we get,

$$G - G(0) = -NkT \ln q + kT \ln N! + nRT$$

Noting that $N = nN_A$ and using Stirling's approximation,

$$G - G(0) = -nRT \ln q + kT(N \ln N - N) + nRT$$

$$G - G(0) = -nRT \ln q + nRT \ln n N_A = -nRT \ln \frac{q}{N} = -nRT \ln \frac{q_m}{N_A} \quad (3.50)$$

Where, $q_m = q / n$, the molar partition function in units of mol^{-1} . The function $[G(T) - G(0)] / T$ is referred to as the Giauque function.

Example 3.6 The equipartition principle states that each quadratic degree of freedom contributes $\frac{1}{2} kT$ to the energy at high temperature. Verify this assertion for the rotational, translational and vibrational motions of a diatomic molecule.

Solution

Consider the molecular partition functions. The rotational energy is given by

$$\langle \epsilon^{rot} \rangle = -\frac{1}{q_{rot}} \frac{\partial q_{rot}}{\partial \beta} = -\sigma \beta \bar{B} \frac{1}{\sigma \bar{B}} \frac{\partial}{\partial \beta} \frac{1}{\beta} = \frac{1}{\beta} = kT \quad (3.51)$$

The classical expression for the rotational energy is $\frac{1}{2} I (\omega_x^2 + \omega_y^2)$, where I is the moment of inertia and ω_x and ω_y are the angular velocities in the x and y directions. The rotation along the molecular axis (the z axis here) has no meaning in quantum mechanics because the rotations along the molecular axis lead to configurations which are indistinguishable from the original configuration. The two degrees of freedom have thus given a value of kT. The translational contribution gives,

$$\langle \epsilon^{tr} \rangle = -\frac{1}{q_{tr}} \frac{\partial q_{tr}}{\partial \beta} = -\frac{\Lambda^3}{V} \frac{\partial}{\partial \beta} \frac{V}{\Lambda^3} = \frac{3}{\Lambda} \frac{\partial \Lambda}{\partial \beta} = \frac{3}{2\beta} = \frac{3}{2} kT \quad (3.52)$$

Thus, the three translational degrees of freedom in three dimensions satisfy the equipartition theorem. Turning to the vibrational contribution, we get,

$$\langle \epsilon_{vib} \rangle = -\frac{1}{q_{vib}} \frac{\partial q_{vib}}{\partial \beta} = \frac{1}{q_{vib}} \frac{hc\bar{\nu} e^{-hc\bar{\nu}\beta}}{(1 - e^{-hc\bar{\nu}\beta})^2} = hc\bar{\nu} \frac{e^{-hc\bar{\nu}\beta}}{(1 - e^{-hc\bar{\nu}\beta})} \rightarrow kT \text{ if } hc\bar{\nu}\beta \ll 1 \quad (3.53)$$

The classical expression for the vibrational energy is $\frac{1}{2} kx^2 + \frac{1}{2} \mu v_x^2$. At high temperature the equipartition theorem is valid but at low temperature, only a few vibrational states are occupied and the equipartition principle is not valid.

Example 3.7 Calculate the vibrational heat capacity for diatomic and sketch its temperature dependence.

Solution The vibrational energy is given by the above expression and the heat capacity at constant volume, C_V , is given by $\partial E / \partial T$.

$$\text{We have, } \partial / \partial T = (\partial \beta / \partial T) (\partial / \partial \beta) = (-1/kT^2) (\partial / \partial \beta) = (-k \beta^2) (\partial / \partial \beta) \quad (3.54)$$

Therefore, $C_V = (-k \beta^2) (\partial \epsilon_{vib} / \partial \beta) =$

$$-k\beta^2 \frac{\left\{ (1 - e^{-hc\bar{\nu}\beta}) (-hc\bar{\nu}) - e^{-hc\bar{\nu}\beta} (+hc\bar{\nu}) \right\} e^{-hc\bar{\nu}\beta}}{(1 - e^{-hc\bar{\nu}\beta})^2} hc\bar{\nu} = k \left\{ \frac{\Theta_V}{T} e^{-\frac{\Theta_V}{2T}} \right\}^2 \left\{ \frac{1}{1 - e^{-\frac{\Theta_V}{T}}} \right\} \quad (3.55)$$

For large T, the molar C_V becomes $N_A k = R$ and for small T, C_V goes to zero as shown in the sketch below. The vibrational temperature Θ_V is defined as $\Theta_V = hc\bar{\nu} / k$. For H_2 , it has a value of 6323 K and for I_2 it is 309 K.

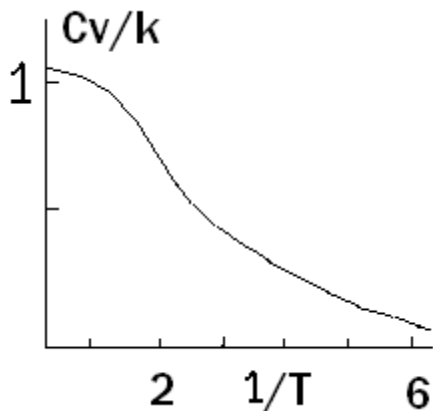


Figure 3.3 Vibrational heat capacity of a diatomic as a function of Θ_V/T .

3.3 Rotational and Vibrational Partition Functions of Polyatomic Molecules

For a polyatomic molecule containing n atoms, the total number of coordinate degrees of freedom is $3n$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. The translational partition function is given by the same formula as Eq. (3.20) with the mass now given by the total mass of the molecule, $\sum m_i$ where m_i is the mass of a constituent atom. We have to consider the three rotational degrees of freedom and the $3n - 6$ vibrational degrees. For a linear molecule, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, for a linear molecule, there are two rotational degrees of freedom and $3n - 5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A , I_B and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold.

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i = 0 \quad (3.56)$$

The inertia products are defined by

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2); \quad I_{xy} = \sum_i m_i x_i y_i \quad (3.57)$$

The other components I_{yy} , I_{zz} ,... are defined analogously. To find the direction cosines $(\alpha_i, \beta_i, \gamma_i)$ of the three principle moments of inertia, we need to solve the following matrix equations.

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0 \quad (3.58)$$

$$\alpha I_{xy} + \beta(I_{yy} - \eta) - \gamma I_{yz} = 0 \quad (3.59)$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0 \quad (3.60)$$

If the off diagonal terms I_{xy} are zero in the above equations then the x , y , z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A , I_B and I_C is given by

$$\varepsilon = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 = \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C} = \quad (3.61)$$

Here, ω_A , ω_B and ω_C are the three angular speeds and L_A , L_B and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K . The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K . The energy levels are given by

$$\varepsilon_{J,K} = \bar{B} J(J+1) + (\bar{A} - \bar{B}) K^2; \quad \bar{B} = \frac{h}{8\pi^2 c I_B}, \quad \bar{A} = \frac{h}{8\pi^2 c I_A} \quad \text{in cm}^{-1} \quad (3.62)$$

Where, J takes on values $0, 1, 2, \dots$ and $K = -J, -J+1, -J+2, \dots, 0, 1, 2, \dots, J$. The rotational partition function is given by

$$q_{\text{rot}} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\bar{B}J(J+1)/kT} \sum_{K=-J}^J e^{(\bar{A}-\bar{B})K^2/kT} \quad (3.63)$$

This can be converted to an integral as in (3.14) and the result is

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 I_B kT}{h^2} \right) \left(\frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \quad (3.64)$$

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A , L_B and L_C as

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(p,q)/kT} dL_A dL_C dL_C = (2\pi I_A kT)^{1/2} (2\pi I_B kT)^{1/2} (2\pi I_C kT)^{1/2} \quad (3.65)$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$ we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π . Integration over all possible orientations of this axis contribute another factor of 4π . The symmetry number σ corrects for overcounting of rotational configurations and the factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space. The final result is

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_B kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_C kT}{h^2} \right)^{1/2} \quad (3.66)$$

We can explicitly obtain the classical rotational partition function of an asymmetric top. by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ , φ and ψ with the ranges of angles 0 to π , 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta

p_θ , p_φ and p_ψ as

$$H = \frac{\sin^2 \psi}{2I_A} \left\{ p_\theta - \frac{\cos \psi}{\sin \theta \sin \psi} (p_\varphi - \cos \theta p_\psi) \right\}^2$$

$$+ \frac{\cos^2 \psi}{2I_B} \left\{ p_\theta + \frac{\sin \psi}{\cos \theta \cos \psi} (p_\phi - \cos \theta p_\psi) \right\}^2 + \frac{1}{2I_C} p_\psi^2 \quad (3.67)$$

The rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \frac{1}{h^3} e^{-H(p,q)/kT} dp_\theta dp_\phi dp_\psi d\theta d\phi d\psi \quad (3.68)$$

The integrations can be simplified by rewriting $H(p,q) / kT$ as

$$H / kT = \frac{1}{2I_A kT} \left(\frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right) \left\{ p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A} \right) \frac{\sin \psi \cos \psi}{\sin \theta \left(\frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right)} (p_\phi - \cos \theta p_\psi) \right\}^2$$

$$+ \frac{1}{2kT I_A I_B \sin^2 \theta} \left\{ \frac{1}{\left(\frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right)} (p_\phi - \cos \theta p_\psi) \right\}^2 + \frac{1}{2kT I_C} p_\psi^2 \quad (3.69)$$

Using the following integral,

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a} \quad (3.70)$$

Integration over p_θ gives using the above expression,,

$$(2\pi kT)^{1/2} \left(\frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right)^{-1/2} \quad (3.71)$$

Integration over p_ϕ gives the factor,

$$(2\pi kT I_A I_B)^{1/2} \sin \theta \left(\frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right)^{1/2} \quad (3.72)$$

This cancels partly the second square root in the earlier expression. Integration over p_ψ gives the factor

$$(2\pi kT I_C)^{1/2} \quad (3.73)$$

Integration over θ , ϕ and ψ gives a factor of $8\pi^2$.

$$\int_0^\pi \sin \theta d\theta = 2; \quad \int_0^{2\pi} d\phi = 2\pi; \quad \int_0^{2\pi} d\psi = 2\pi \quad (3.74)$$

Combining all the integrals, we finally get,

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_B kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_C kT}{h^2} \right)^{1/2} \quad (3.75)$$

Here, we have reintroduced the symmetry number σ as before. And with

$$\Gamma_A = \frac{h^2}{8\pi^2 I_A kT}, \Gamma_B = \frac{h^2}{8\pi^2 I_B kT}, \Gamma_C = \frac{h^2}{8\pi^2 I_C kT} \quad (3.76)$$

The partition function simplifies to

$$\ln q_{rot} = \frac{1}{2} \ln \frac{\pi}{\Gamma_A \Gamma_B \Gamma_C \sigma^2} \quad (3.77)$$

And the molar thermodynamic function can be readily calculated as

$$A_{rot} = -RT \ln q_{rot} = \frac{RT}{2} \ln \frac{\Gamma_A \Gamma_B \Gamma_C \sigma^2}{\pi}; S_{rot} = - \left(\frac{\partial A_{rot}}{\partial T} \right)_V = R \left(\frac{3}{2} + \frac{1}{2} \ln \frac{\pi}{\Gamma_A \Gamma_B \Gamma_C \sigma^2} \right) \quad (3.78)$$

And

$$E_{rot} = \frac{3}{2} RT; C_{V,rot} = \frac{3}{2} R \quad (3.79)$$

Improvements over the classical approximation for the rotational partition function have been obtained and one of the improved version is

$$q_{rot} = q_{rot}^0 \left[1 + \frac{h^2}{96\pi^2 kT} \left(\frac{2}{I_A} + \frac{2}{I_B} + \frac{2}{I_C} - \frac{I_C}{I_A I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C} \right) \right] \quad (3.80)$$

where q_{rot}^0 is the classical approximation.

Let us now consider the vibrational partition function. We have already considered the Lagrangian L for the N oscillators in Eq. (1.43). We saw there that there were cross terms involving x , y and z components of different atoms. This makes the solution of the problem difficult. However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = - \sum_{i=1}^f \frac{h^2}{2\mu_i} \frac{\partial^2}{\partial \xi_i^2} + \sum_{i=1}^f \frac{k_i}{2} \xi_i^2 \quad (3.81)$$

Here, the degrees of freedom f is $3n - 5$ for a linear molecule and $3n - 6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a normal mode. The Eq. (3.81) represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\mathcal{E}_{vib} = \sum_{i=1}^f \left(n_i + \frac{1}{2} \right) h \nu_i \quad (3.82)$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}} \quad (3.83)$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{\text{vib}} = \prod_{i=1}^f \frac{e^{-\Theta_{\text{vib},i}/2T}}{(1 - e^{-\Theta_{\text{vib},i}/T})}, \quad \Theta_{\text{vib},j} = h\nu_j / k \quad (3.84)$$

Where, the $\Theta_{\text{vib},j}$ is called the characteristic vibrational temperature. The molar energies and the heat capacities are given by

$$E_{\text{vib}} = Nk \sum_{i=1}^f \left[\frac{\Theta_{\text{vib},i}}{2} + \frac{\Theta_{\text{vib},i} e^{-\Theta_{\text{vib},i}/T}}{1 - e^{-\Theta_{\text{vib},i}/T}} \right] \quad (3.85)$$

$$C_{V,\text{vib}} = Nk \sum_{i=1}^f \left(\frac{\Theta_{\text{vib},i}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},i}/T}}{(1 - e^{-\Theta_{\text{vib},i}/T})^2} \quad (3.86)$$



Figure 3.3 The three vibrational modes of water, the symmetric stretch (3656.7, 5160), the asymmetric stretch (3755.8, 5360) and the bending mode (1594.8, 2290) are shown. The vibrational frequencies in cm^{-1} and the characteristic temperature in K for each mode are shown in parenthesis.

Example 3.6 The three characteristic rotational temperatures for NO_2 are 11.5 K, 0.624 K and 0.590 K and the three vibrational temperatures in Kelvin are 1900, 1980 and 2330. calculate the rotational and vibrational partition functions at 300K.

Solution: The rotational temperature is given by $\Theta_A = \frac{h^2}{8\pi^2 I_A k}$ The rotational partition

$$\text{function becomes, } q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{\Theta_A} \right)^{1/2} \left(\frac{T}{\Theta_B} \right)^{1/2} \left(\frac{T}{\Theta_C} \right)^{1/2}$$

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} (300/11.5)^{1/2} (300/0.624)^{1/2} (300/0.590)^{1/2}$$

$$= (1.772 / 2) \times 5.108 \times 21.97 \times 22.55 = 2242.4$$

The vibrational partition is calculated by taking the zero point energies as the reference points with respect to which the other energies are measured.

$$q_{\text{vib}} = \prod_{i=1}^f \frac{e^{-\Theta_{\text{vib},i}/2T}}{(1 - e^{-\Theta_{\text{vib},i}/T})} \equiv \prod_{i=1}^f \frac{1}{(1 - e^{-\Theta_{\text{vib},i}/T})} = \frac{1}{1 - e^{-1900/300}} \frac{1}{1 - e^{-1980/300}} \frac{1}{1 - e^{-2330/300}}$$

$$= 1.0018 \times 1.0014 \times 1.0004 = 1.0035$$

The implication is that while several rotational state sare accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible

3.4 Ortho and Para Hydrogens

The molecules of hydrogen can exist in two forms depending on the spins on the two hydrogen nuclei. If both the nuclear spins are parallel, the molecule is called ortho and if the spins are antiparallel, it is referred to as para (In disubstituted benzene, para refers to the two groups at two opposite ends, while in ortho, they are adjacent or “parallel” to each other). The spin on the hydrogen nucleus has a magnitude of $\frac{1}{2} \hbar$. The presence of nuclear spins leads to very interesting consequences for the populations of the rotational states and on a macroscopic scale, has consequences on measured entropies and heat capacities as well.

The total partition function of H_2 can be written as

$$Q_{\text{tot}} = Q_{\text{elec}} Q_{\text{vib}} Q_{\text{rot}} Q_{\text{trans}} Q_{\text{nucl}} \quad (3.87)$$

where, the subscripts refer to the respective motions.

After “half” a rotation, the nuclei are superimposed on each other. Since a proton is a spin half nucleus, the total wavefunction must be antisymmetric with respect to the exchange of the particles. i.e.,

$$\Psi(1, 2) = -\Psi(2, 1) \quad (3.88)$$

The translational motion refers to the motion of the molecular center of mass and has no influence on the symmetry of the nuclear wavefunction. Vibrational motion depends on the magnitude of the internuclear distance and has no effect on the particle exchange. The electronic motion also has no effect on the symmetry properties of the nuclear wavefunction. Therefore, the product of the nuclear spin and rotational wavefunctions must be antisymmetric with respect to the particle exchange.

For the nuclear spin functions, there are four combinations. One combination is a singlet

$$\psi_{nu,s} = \alpha(1)\beta(2) - \alpha(2)\beta(1) \quad (3.89)$$

And the other three combinations are the three states of a triplet.

$$\begin{aligned} \psi_{nu,t} = & \alpha(1)\alpha(2) \\ & \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ & \beta(1)\beta(2) \end{aligned} \quad (3.90)$$

The rotational wavefunctions (ψ_r) are given in terms of the associated Legendre polynomials $P_l^{|m|}(x)$ where $x = \cos \theta$.

$$\psi_r = e^{im\phi} P_l^{|m|}(\cos \theta) \quad (3.91)$$

$$P_l^{|m|}(x) = (1-x^2)^{|m|/2} \frac{d^{|m|} P_l(x)}{dx^{|m|}}; \quad P_l(x) = \frac{1}{2^l l!} \frac{d^l (x^2-1)^l}{dx^l} \quad (3.92)$$

When the nuclei are interchanged, θ becomes $\pi - \theta$ and ϕ is changed to $\phi + \pi$. The polynomials change as

$$P_l(-x) = (-1)^l P_l(x); \quad P_l^{|m|}(-x) = (-1)^{l-|m|} P_l^{|m|}(x) \quad (3.93)$$

The exponential function changes as

$$e^{jm(\varphi+\pi)} = e^{jm\pi} e^{jm\varphi} = (-1)^{|m|} e^{jm\varphi} \quad (3.94)$$

Therefore, the rotational wavefunction changes as

$$\psi_r(\pi - \theta, \varphi + \pi) = (-1)^{l-|m|} (-1)^{|m|} \psi_r(\theta, \varphi) = (-1)^l \psi_r(\theta, \varphi) \quad (3.95)$$

$$\psi_r = \text{symmetrical for even } j, \text{ and antisymmetrical for odd } j \quad (3.96)$$

Combining the nuclear spin and the rotational parts, we see that, the product $\psi_r \psi_{nu}$ must be antisymmetrical (with respect to the exchange of nuclei) for half integral nuclear spins and symmetrical for integral spins. To accomplish this, the singlet nuclear states (para) must be combined with the even rotational functions and the triplet nuclear states must be combined with the odd rotational states. The rotational partition functions for ortho and para hydrogens are, thus,

$$q_{ortho} = q_{nu,t} q_{r,odd} = 3 \sum_{j=1,3,5..} (2j+1) e^{-j(j+1)\Theta_R/T} \quad (3.97)$$

And

$$q_{para} = q_{nu,s} q_{r,even} = 1 \sum_{j=0,2,4..} (2j+1) e^{-j(j+1)\Theta_R/T} \quad (3.98)$$

Where Θ_R is the rotational temperature defined by Eq. (3.12).

The total partition function consisting both ortho and para hydrogens is given by

$$q_{rot, nu} = 1 \sum_{j=0,2,4..} (2j+1) e^{-j(j+1)\Theta_R/T} + 3 \sum_{j=1,3,5..} (2j+1) e^{-j(j+1)\Theta_R/T} \quad (3.99)$$

The ratio of ortho to para hydrogens at thermal equilibrium is given by

$$\frac{N_o}{N_p} = \frac{3 \sum_{j=1,2,3..} (2j+1) e^{-j(j+1)\Theta_R/T}}{\sum_{j=0,2,4..} (2j+1) e^{-j(j+1)\Theta_R/T}} \quad (3.100)$$

At high temperature, the two summations become equal and therefore, the high temperature limit of N_o/N_p is 3. At low temperature, the ratio becomes,

$$\frac{N_o}{N_p} = \frac{3(3e^{-2\Theta_R/T} + \dots)}{1(1+5e^{-5\Theta_R/T} + \dots)} \rightarrow 0, \text{ as } T \rightarrow 0 \quad (3.101)$$

A good experimental verification of the above analysis is a comparison between the calculated rotational heat capacities at constant volume $(C_V)_{rot, nu}$ (calculated from $\partial \langle E \rangle / \partial T$, where $\langle E \rangle = \partial \ln q_{rot, nu} / \partial \beta$). The heat capacities are shown as a function of temperature in Fig. 3.4.

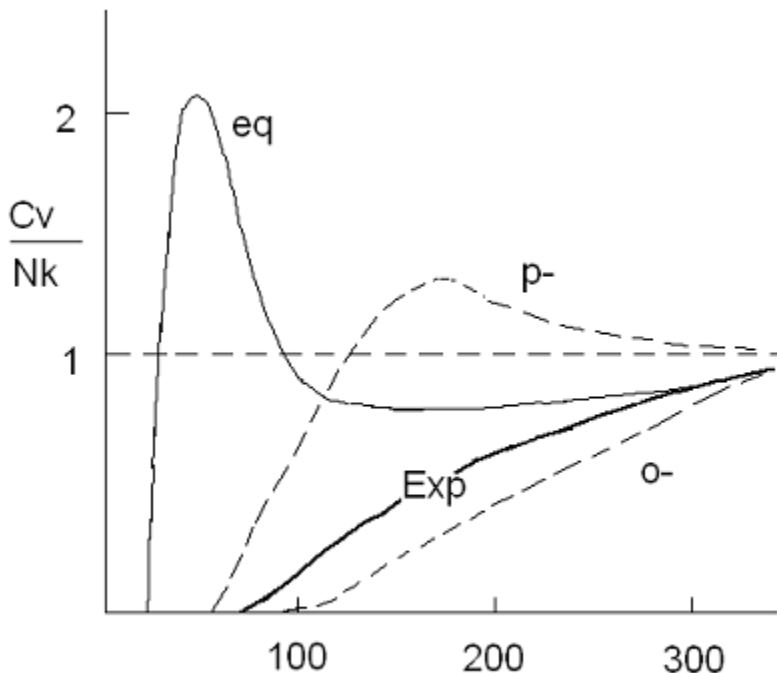


Figure 3.4 The heat capacities of o- and p- hydrogens as a function of temperature. The curve marked Exp depicts the experimental data, the curve eq represents the data for an equilibrated mixture of o- and p- at a given temperature and the curves o- and p- represent the heat capacities of pure o- and pure p- hydrogens.

The curve marked Exp gives the experimental data, the curve eq represents the data for an equilibrated mixture of o- and p- at a given temperature. The curves o- and p- represent the heat capacities of pure o- and pure p- hydrogens calculated from the o- and p- partition functions given by Eqs. (3.97) and (3.98) respectively. Initially it was a puzzle as to why the experimental data differs from the calculated values. In fact, the experimental data seemed to agree very well with the following equation.

$$(C_V)_{rot,nu} = \frac{3}{4}(C_V)_{rot,nu} (ortho) + \frac{1}{4}(C_V)_{rot,nu} (para) \quad (3.102)$$

The reason for this is that, when H_2 is cooled down from a higher temperature, the ortho para ratio continues to remain 0.75 / 0.25 (the high temperature value) because the ortho para interconversion rate is very very small and we do not reach the equilibrium composition unless a catalyst such as activated charcoal is added to the gas mixture. Eq. (3.102) corresponds to a “frozen high temperature mixture” of ortho para hydrogens. In the presence of the catalyst, the experiments also give the curve labeled as eq in the graph. This is indeed a very nice case where the experiments support not only the methods of statistical thermodynamics but also of the antisymmetry principle for bosons and fermions. If we consider the case of O_2^{16} , where the nuclear spins are zero, the rotational wavefunction has to be symmetric as only symmetric wavefunctions are permitted for bosons. Thus, only even rotational states contribute to the partition function.

$$q_{rot,nu}(O_2^{16}) = \sum_{j=0,2,4..} (2j+1)e^{-j(j+1)\Theta_R/T} \quad (3.103)$$

Chemical Equilibria

Consider a reaction which may be represented as



The equilibrium constant K_{eq} for the reaction is given by

$$\Delta G^\ominus = -RT \ln K_{eq} \quad (3.105)$$

Where the superscript \ominus represents the standard state, i.e., the state at 1 bar pressure at each temperature. The free energy of a species is given by eq. (3.39) as

$$G = G(0) - n RT \ln \frac{q_m}{N_A} \quad (3.106)$$

And the molar free energy in the standard state for a species J is given by

$$G_{J,m}^\ominus = G_{J,m}^\ominus(0) - n RT \ln \frac{q_{J,m}^\ominus}{N_A} \quad (3.107)$$

The standard free energy change for this reaction is given by

$$\begin{aligned} \Delta G_{reaction}^\ominus = \Delta G_r^\ominus = & c G_{C,m}^\ominus(0) + d G_{D,m}^\ominus(0) + e G_{E,m}^\ominus(0) - a G_{A,m}^\ominus(0) - b G_{B,m}^\ominus(0) \\ & - c RT \ln \frac{q_{C,m}^\ominus}{N_A} - d RT \ln \frac{q_{D,m}^\ominus}{N_A} - e RT \ln \frac{q_{E,m}^\ominus}{N_A} + a RT \ln \frac{q_{A,m}^\ominus}{N_A} + b RT \ln \frac{q_{B,m}^\ominus}{N_A} \end{aligned} \quad (3.108)$$

But since $G(0)$ is the same as $E(0)$,

$$\left(\Delta G_0^\ominus\right)_r = \left(\Delta E_0^\ominus\right)_r = c G_{C,m}^\ominus(0) + d G_{D,m}^\ominus(0) + e G_{E,m}^\ominus(0) - a G_{A,m}^\ominus(0) - b G_{B,m}^\ominus(0) \quad (3.109)$$

And the equilibrium constant is given by

$$-RT \ln K = \left(\Delta E_0^\ominus\right)_r - RT \ln \frac{\left(q_{C,m}^\ominus/N_A\right)^c \left(q_{D,m}^\ominus/N_A\right)^d \left(q_{E,m}^\ominus/N_A\right)^e}{\left(q_{A,m}^\ominus/N_A\right)^a \left(q_{B,m}^\ominus/N_A\right)^b} \quad (3.110)$$

$$K = \left\{ \frac{\left(q_{C,m}^\ominus/N_A\right)^c \left(q_{D,m}^\ominus/N_A\right)^d \left(q_{E,m}^\ominus/N_A\right)^e}{\left(q_{A,m}^\ominus/N_A\right)^a \left(q_{B,m}^\ominus/N_A\right)^b} \right\} e^{-\left(\Delta E_0^\ominus\right)_r / RT} \quad (3.111)$$

It is instructive to analyse K of Eq. (3.111) in terms of molecular energy levels and their populations. Consider the energy levels for the following equilibrium,



The energy levels of systems containing only A, only B and both A and B are schematically shown in Fig. 3.5.

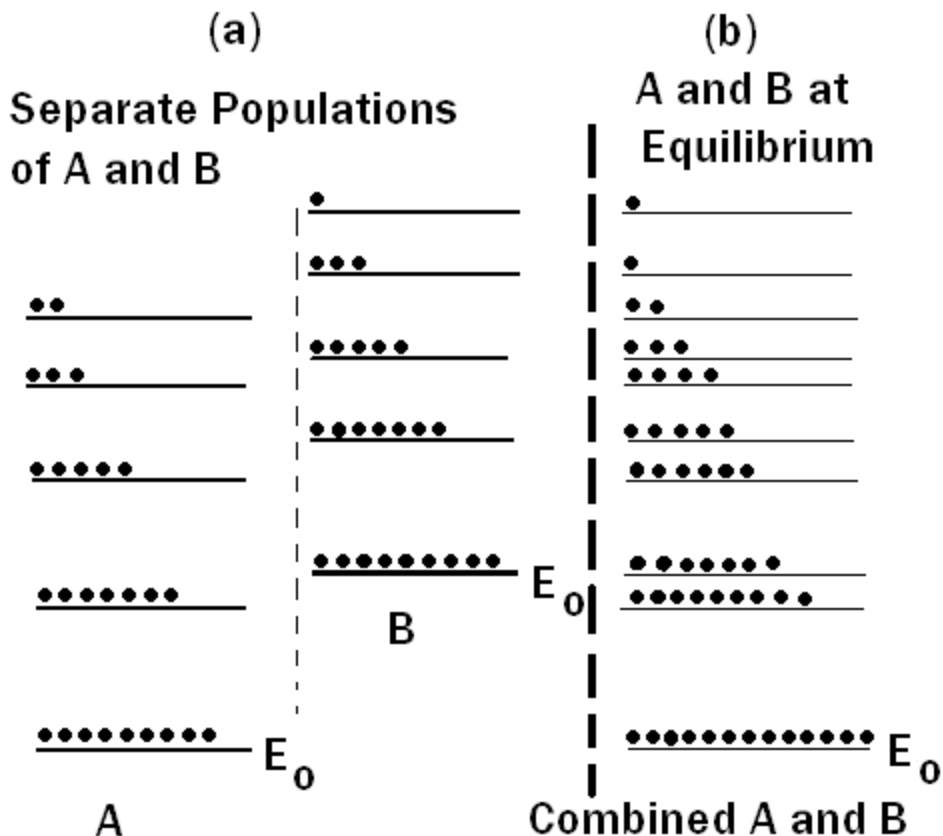


Figure 3.5 (a) Energy levels of individual molecules A, B and the individual populations of these levels, (b) Energy levels of the combined system A and B and the relative populations of the combined levels at equilibrium (schematic).

If the molecules of A and B are kept in separate containers, each container will be in a state of equilibrium with the populations of A and B given by their separate Boltzmann distributions. This is shown in Fig 3.5(a). The partition functions of the systems A and B are given by q_A and q_B . Fig 3.5(b) shows the combined system and the population of the levels of the combined system. The population of the i th level of the combined system is given by

$$n_i = N P_i = N \frac{e^{-\beta E_i}}{q} \quad (3.113)$$

Where q is the partition function of the combined system and E_i is the energy of the i th level of the combined system. In the combined system, the total population of A molecules at equilibrium is given by summing n_i for A molecules. Similarly, for B. We thus have,

$$N_A = \sum_{\text{All levels of A}} n_i = \frac{N}{q} \sum_{\text{levels of A}} e^{-\beta(E_i)_A} = \frac{N}{q} q_A \quad (3.114)$$

$$N_B = \sum_{\text{All levels of B}} n_i = \frac{N}{q} \sum_{\text{levels of B}} e^{-\beta(E'_i)_B} = \frac{N}{q} \sum_{\text{levels of B}} e^{-\beta[(E_i)_B + \Delta E_0]} = \frac{N}{q} q_B e^{-\Delta E_0 / RT} \quad (3.115)$$

The prime in eq (33.16) indicates that the levels $(E_i)'_B$ are now measured from the lowest level of the combined states of A and B, which is $(E_0)_A$. Expressing E'_i in terms of E_i , we have,

$$(E'_i)_B = (E_i)_B + (E_0)_B - (E_0)_A = (E_i)_B + \Delta E_0 \quad (3.116)$$

The equilibrium constant is now given by

$$K = N_B / N_A = (q_B / q_A) e^{-\Delta E_0 / RT} \quad (3.117)$$

For a more general reaction $A + B \rightleftharpoons C + D$, the equilibrium constant is given by

$$K = [q_C q_D / q_A q_B] e^{-\beta \Delta E_0} \quad (3.118)$$

Where,

$$\Delta E_0 = (E_0)_C + (E_0)_D - (E_0)_A - (E_0)_B \quad (3.119)$$

3.5 Activated Complex theory

In many reactions, mixing the reactants does not lead to products instantaneously. A short lived high energy configuration of molecules, referred to as the activated complex is formed which may lead to products or the reactants depending on the specific motions in the activated complex. Although the terms transition state and activated complex are often used synonymously, the transition state does not have a chemically significant life time. Consider the reaction



The potential energy diagram for this reaction is given in Fig 3.6. In Eq. (3.120), C^\ddagger is the activated complex which forms the products P with a unimolecular rate constant k^\ddagger .

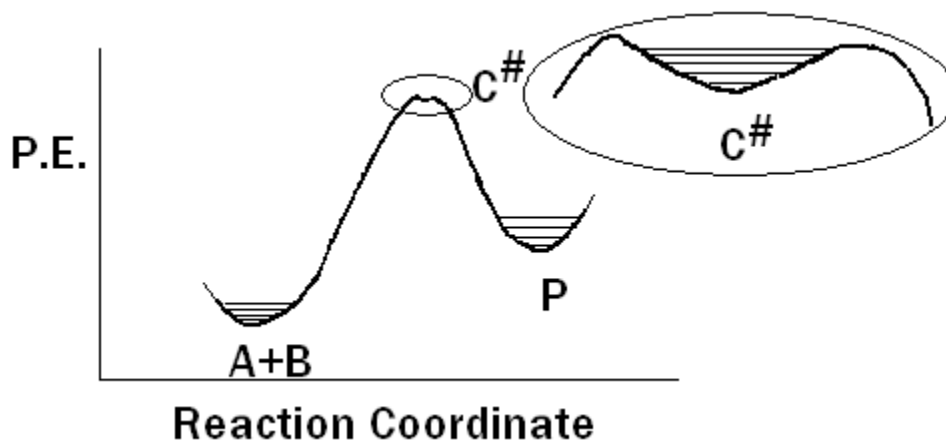


Figure 3.6. Potential energy of reaction as a function of the reaction coordinate. The energy levels of the shallow activated complex C^\ddagger are shown in the inset to the right.

The ordinate is the potential energy (PE) and the abscissa is the reaction coordinate. At a specific configuration of the reactants, the potential energy is maximum, the slope is zero and the PE falls to lower values in both the forward and the reverse direction. All the structures in the vicinity of this transition state or configuration may be considered as the "activated complex", which is very reactive. A motion along the "forward" direction will

lead to the products. The activated complex theory or the transition state theory provides a way to calculate the rate constant for the reaction. The assumptions involved in the transition state theory are:

- 1) The electronic motion (which can only be described only quantum mechanically) may be separated from the motion of the nuclei and a classical description of the nuclear motion is used to evaluate the rate constant.
- 2) The energy distribution of the reactants is described by the equilibrium Boltzmann distribution throughout the reaction.
- 3) The activated complex which has crossed the transition state can not return to the reactant configuration. In the transition state, motion along the reaction coordinate may be separated from all other motions.
- 4) The activated complex is also distributed according to the Boltzmann distribution. The rate of the reaction can thus be expressed as

$$d [C^\ddagger] / dt = k^\ddagger [C^\ddagger] \quad (3.121)$$

The concentration of C^\ddagger is expressed in terms of the concentrations of A and B through the proportionality constant K^\ddagger (which is not an equilibrium constant).

$$[C^\ddagger] = K^\ddagger [A] [B] \quad (3.122)$$

substituting Eq. (3.122) into Eq. (3.121), we have,

$$d [C^\ddagger] / dt = k_2 [A] [B] \text{ where } k_2 = k^\ddagger K^\ddagger. \quad (3.123)$$

We now will determine the values of the constants k^\ddagger and K^\ddagger . It should be obvious that the process represented in Eq. (3.122) is not a regular equilibrium process because, as the products are formed, $[A]$ and $[B]$ are decreasing with time and $[C^\ddagger]$ is not increasing with time since the collisions responsible for the formation of C^\ddagger are themselves decreasing in frequency as the reaction evolves. The activated complex can exhibit several motions such as translations, rotations and vibrations, since it has a finite life time. The motion leading to the product is assumed to be a specific vibration with a frequency ν . This vibrational motion along the reaction coordinate is equated to the constant k^\ddagger . The transition state is in a shallow well with a vibrational frequency much smaller than that of the reactants and the products. The energy levels of the shallow activated complex C^\ddagger are shown to the right in Fig. 3.6.

$$k^\ddagger \approx \nu \quad (3.124)$$

Our next task is the determination of the concentration of C^\ddagger . Let us express the equilibrium constant for the reaction $A + B \rightarrow C^\ddagger$ in terms of the partial pressures of A, B and C^\ddagger (p_A , p_B and p_{C^\ddagger} , written simply as p_C).

$$K = [C^\ddagger] / [A] [B] = [p_{C^\ddagger} / \bar{p}] / [(p_A / \bar{p}) (p_B / \bar{p})] \quad (3.125)$$

Where \bar{p} is the standard pressure of 1 bar. These partial pressure can be expressed in terms of molar concentrations of A, B and C as follows.

$$[A] = n_A / V; V = n RT / p; p_A = x_A p = n_A p / n \quad (3.126)$$

$$[A] = n_A p / nRT = x_A p / R T = p_A / RT \text{ or } p_A = RT [A] \quad (3.127)$$

In Eq. (3.126), V = total volume, p = total pressure, n = total number of moles, n_A = number of moles of A , $x_A = n_A / n$, the mole fraction, R is the gas constant and T absolute temperature. Substituting each partial pressure in terms of the mole fractions, we have

$$K = RT [C^\ddagger] / \bar{p} / [(RT [A] / \bar{p}) (RT [B] / \bar{p})] \quad (3.128)$$

$$= [C^\ddagger] \bar{p} / [A] [B] RT \quad (3.129)$$

$$\text{or } C^\ddagger = [A] [B] RT / \bar{p} K \quad (3.130)$$

Comparing this equation with Eq. (3.122), we have

$$\text{or } K^\ddagger = K RT / \bar{p} \quad (3.131)$$

In Eq. (3.122), K^\ddagger was merely a proportionality constant and now it has been related to the equilibrium constant for the formation of the activated complex

Specific vibration of the activated complex along the reaction coordinate leads to product formation. When we have a reaction such as $A + B \rightleftharpoons C^\ddagger$, the equilibrium constant given in terms of partition functions by (see Eq. 3.111).

$$K = (N_A q_{C^\ddagger} / q_A q_B) e^{-\beta \Delta E_0^\ddagger} \quad (3.132)$$

Where $\Delta E_0 = (E_0)_{C^\ddagger} - (E_0)_A - (E_0)_B$. Here N_A is the Avogadro number. In the above equation, we have suppressed the standard state and molarity labels \ominus and m of Eq. (3.111). Returning to Eq. (3.123), $k_2 = k^\ddagger K^\ddagger$, the unimolecular rate constant k^\ddagger is taken as proportional to the vibrational frequency along the reaction coordinate $k^\ddagger = \nu$. The partition functions for this vibrational motion of the transition state is

$$(q_V)_{C^\ddagger} = 1 / (1 - e^{-h\nu/k_B T}) \quad (3.133)$$

Usually this frequency is quite small because the transition state falls apart into products with this frequency. Very high frequencies of the transition state are improbable and they would lead, not to the usual products but to rather highly disintegrated products.

Expanding the denominator, $e^{-h\nu/k_B T} \approx 1 - h\nu/k_B T$,

$$(q_V)_{C^\ddagger} = k_B T / h \nu \quad (3.134)$$

Writing q_{C^\ddagger} in terms of the vibrational modes $(q_V)_{C^\ddagger}$ [which is approximated as $k_B T / h \nu$] and all the other remaining modes [\bar{q}_{C^\ddagger}], we have for q_{C^\ddagger} ,

$$q_{C^\ddagger} = (k_B T / h \nu) \bar{q}_{C^\ddagger} \quad (3.135)$$

Combining Eqs. (3.123), (3.131) and (3.132), we have,

$$k_2 = k^\ddagger K^\ddagger = \nu (RT / \bar{p}) K = (\nu k_B T / h \nu) [(N_A \bar{q}_{C^\ddagger} / q_A q_B) e^{-\beta \Delta E_0^\ddagger} RT / \bar{p}] \quad (3.136)$$

$$= k_B T / h \bar{K} \quad (3.137)$$

Where \bar{K} is the second, square bracketed expression in Eq. (3.136) which is akin to an equilibrium constant with the vibrational mode of C^\ddagger removed. There are often factors not included in Eq. (3.137) and they are included through a transmission coefficient κ and the rate constant in the transition state theory becomes,

$$k_2 = \kappa (k_B T / h) \bar{K} \quad (3.138)$$

We want to express \bar{K} in terms of molecular partition functions. Let us obtain a formula for simple species of A and B where A and B are atoms. The partition function of atoms is simply the translational partition function (as rotations and vibrations are absent). The translational partition function of A, using the molar volume, becomes

$$q_{tr,A} = (2\pi m_A k_B T)^{3/2} V_m^0 \quad (3.139)$$

$$q_{tr,A} = V_m^0 / \Lambda_A^3, \text{ where } \Lambda_A = h / (2\pi m_A k_B T)^{1/2} \quad (3.140)$$

Where V_m^0 is the standard molar volume, given by RT / \bar{p} . For the activated complex, the partition function is the product of translational, vibrational and rotational partition functions, because in our present model, AB is a diatomic. However, we have already considered the vibrational partition function in Eq. (3.135) and we need to consider \bar{q}_C^\ddagger now which includes only rotation and translation.

This is given by

$$\bar{q}_{C^\ddagger} = (2 I k_B T / h^2) V_m^0 / \Lambda_{C^\ddagger}^3 \quad (3.141)$$

The first term in the brackets is the rotational partition function of the activated complex. The moment of inertia I is given by μr^2 where r is the "bond length" of the activated complex and $\mu = (m_A m_B) / (m_A + m_B)$ is the reduced mass. Substituting the values of q_A , q_B and q_C in equations (3.136) and (3.138), we get

$$k_2 = \kappa (k_B T / h) (RT / \bar{p}) N_A \Lambda_A^3 \Lambda_B^3 / \Lambda_{C^\ddagger}^3 V_m^0 (2 I k_B T / h^2) e^{-\beta \Delta E_0^\ddagger} \quad (3.142)$$

Canceling RT / \bar{p} and V_m^0 (which are equal) and substituting the values of Λ_A , Λ_B and Λ_{C^\ddagger} , we get

$$k_2 = N_A (8 k_B T / \pi \mu)^{1/2} (\kappa \pi r^2) e^{-\beta \Delta E_0^\ddagger} \quad (3.143)$$

If we identify the reaction cross section as $\kappa \pi r^2$, this equation is identical to the equation derived using a simple collision theory. It is indeed remarkable that two very different approaches give the same result! Does it mean that this result is more "correct" than the result that is usually obtained from a single theory? While it would be tempting to say yes, what this means is that we have captured some of the essential features relevant in the dynamics of chemical reactions in both approaches. Further improvements will come when we consider the cross sections of each of the states of the reacting species and also when we remove the requirement that C^\ddagger is not in equilibrium with A and B . In the next section, we relate k_2 to the activation parameters for the reaction

Activation Parameters

In the Arrhenius theory, the only activation parameter that was introduced was the activation energy. In the transition state theory developed in this chapter, we have related the concentration of the activated complex to the reactant concentrations through an equilibrium constant K . Treating $(\bar{P} / RT) \bar{K}$ of Eqs. (3.129) and (3.136) as an equilibrium constant (although one vibrational mode is removed from C^\ddagger), we can define the Gibbs free energy of activation ΔG^\ddagger as

$$\Delta G^\ddagger = -RT \ln (\bar{K} \bar{P} / RT) \quad (3.144)$$

the rate constant k_2 becomes

$$k_2 = \kappa k_B T / h (RT / \bar{P}) e^{-\Delta G^\ddagger / RT} \quad (3.145)$$

The free energy of activation can be divided into enthalpy and entropy terms (analogous to $G = \Delta H - TS$) through

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (3.146)$$

For the time being let us either take $\kappa = 1$ or include it in the entropy term. The rate constant then becomes

$$k_2 = B e^{\Delta S^\ddagger / R} e^{\Delta H^\ddagger / RT} \text{ with } B = (k_B T / h) (R T / \bar{P}) \quad (3.147)$$

The activation energy of the Arrhenius equation $k_2 = A e^{-E_a/RT}$, E_a is defined through

$$E_a = R T^2 (d \ln k_2 / dT). \quad (3.148)$$

Substituting k_2 into this, we get

$$E_a = \Delta H^\ddagger + 2RT \quad (3.149)$$

Substituting this in Eq. (3.147), we get

$$k_2 = e^{-2} B e^{\Delta S^\ddagger / R} e^{-E_a / RT} \quad (3.150)$$

and the Arrhenius factor A becomes

$$A = e^{-2} e^{\Delta S^\ddagger / R} \quad (3.151)$$

Usually, when A and B form a complex $(AB)^\ddagger$, more ordering is created and entropy is reduced. ΔS^\ddagger is thus negative. This is based on a collision complex model for the reaction. In addition to this decrease, there is a further orientational or steric decrease due to the preference of only certain configurations for the activated complex (as in the case of a reaction between molecules such as C_2H_4 and H_2). The steric factor P of collision theory may be associated with $e^{\Delta S_{steric}^\ddagger / R}$, i.e.,

$$P = e^{\Delta S_{steric}^\ddagger / R}, \quad (3.152)$$

where,

$$\Delta S^\ddagger = \Delta S_{collisional}^\ddagger + \Delta S_{steric}^\ddagger \quad (3.153)$$

Similar to activation enthalpies and entropy, activation volume can also be defined through

$$\partial(\Delta G^\ddagger) / \partial p = \Delta V^\ddagger \quad (3.154)$$

For reactions in solution, these ΔV^\ddagger values are small, but for gas phase reactions, they may be approximated by the ideal gas values

$$P \Delta V^\ddagger = \Delta n^\ddagger RT \quad (3.155)$$

Example 3.10

For the $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$ reaction at 300 K, find the thermodynamic activation parameters ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger of the transition state theory. The Arrhenius parameters for the above reaction are given to be $A = 1.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ and $E_a = 0 \text{ kJ/mol}$.

Solution: $\Delta S^\ddagger = R \ln \left\{ \frac{h A \bar{p}}{N_A e^2 k_B^2 T^2} \right\}$

Here $h = 6.65 \times 10^{-34} \text{ Js}$, $\bar{p} = 1 \text{ bar} = 10^5 \text{ J/m}^3$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$k_B = 1.38 \times 10^{-23} \text{ J/K}$, $A = 10^{12} \text{ M}^{-1} \text{ s}^{-1} = 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

Substitute all these values and show that

$$\frac{h A \bar{p}}{N_A e^2 k_B^2 T^2} = 7.812 \times 10^{-11} (\text{A/M}^{-1}\text{s}^{-1}) / (\text{T/K})^2$$

Substituting the above value in the equation for ΔS^\ddagger , we have

$$\Delta S^\ddagger = R \ln \left\{ 7.812 \times 10^{-11} \times 10^{12} \times 300^2 \right\} = -58 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta H^\ddagger = E_a - 2 RT = 0 - 2 \times 8.314 \times 300 \text{ J/mol} = -2.5 \text{ kJ/mol}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger = -2.5 - 300 \times (-58) / 10^3 \text{ kJ/mol} = 15 \text{ kJ/mol}$$

Summary

The populations or the occupation numbers of different levels that are available for molecules are expressed in terms of partition functions which measure the number of available states with each state weighted by the Boltzmann factor, $e^{-E/kT}$. Since the total molecular energy can be written as a sum over electronic vibrational, rotational and translation energies, the total partition function was expressed as the product of electronic, rotational, vibrational and translational partition functions. Separate expressions were obtained for these partition functions their estimates were given. The partition function for a collection of molecules and the average energy of a system was obtained in terms of partition functions. The relation of partition functions to thermodynamic functions and equilibrium constants was outlined. The ratio of ortho and para hydrogens in a H_2 mixture, their heat capacities was derived in terms of their partition functions and the interesting connection with experiment was shown. The use of partition functions in chemical kinetics and their use in estimating activation parameters of chemical reactions has been illustrated.

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Problems

- 1) If the nucleus has a spin of s_n , then its spin degeneracy $g_n = 2s_n + 1$. The diatomic molecule formed from such a nucleus will have g_n^2 spin functions which have to be combined to form symmetric and antisymmetric functions. Carry out an analysis similar to that of H_2 for D_2 where the deuterium nucleus has a spin of 1.
- 2) Derive the thermodynamic functions from the polyatomic rotational partition function.
- 3) Carry out the integration for the rotational partition function of the symmetric top.
- 4) Calculate the total partition function and the thermodynamic functions of water at 1000K. The three moments of inertia of water are 1.02, 1.91 and 2.92 in 10^{-47} kg m^2 . The symmetry number is 2. The vibrational data is given in Fig. 3.5. Assume a non-degenerate electronic ground state.
- 5) Verify that the symmetry numbers for methane, benzene and SF_6 are 12, 12 and 24 respectively.
- 6) The ground state of Na is a doublet (two states with the same energy). Assuming this to be the zero of energy and assuming that the next energy level to be 2 eV higher than the ground state, calculate q_{el} .
- 7) The bond length r_e of O_2 is 1.2 Å. The moment of inertia I is $m r_e^2 / 2$ where m of O is $16 \times 1.66 \times 10^{-27} \text{ kg}$. Calculate B and the rotational partition function of O_2 at 300 K.
- 8) The vibrational frequency ν of ICl is 384 cm^{-1} . What is its vibrational partition function at 300 K? What is the fraction of molecules in the ground state ($n = 0$) and the first excited state $n = 1$?
- 9) Calculate the translational partition function of N_2 at 300 K. For volume, use the molar volume at 300 K.
- 10) An isotope exchange reaction between isotopes of bromine is $^{79}Br^{79}Br + ^{81}Br^{81}Br \rightleftharpoons 2^{79}Br^{81}Br$. The fundamental vibrational frequency of $^{79}Br^{81}Br$ is 323.33 cm^{-1} . All the molecules can be assumed to have the same bond length and have a singlet ground electronic state. Calculate the equilibrium constant at 300K and 1000K.
- 11) For the reaction $I_2 \leftrightarrow 2I$, calculate the equilibrium constant at 1000K. The relevant data are as follows. The ground electronic state of I is $^2P_{3/2}$ whose degeneracy is 4. The rotational and vibrational frequencies of I_2 are 0.0373 cm^{-1} and 214.36 cm^{-1} respectively. The dissociation energy of I_2 is 1.5422 eV.
- 12) The representative molecular data for a few molecules is given in table 3.1. Using the relevant data, calculate the equilibrium constant for the reaction $H_2 + Cl_2 \rightleftharpoons 2HCl$ at 1000K. What is the value of the equilibrium constant as $T \rightarrow \infty$?

13) Eq. (3.50) is related to the Giauque function. Estimate the total molar Giauque function for molecules that behave as harmonic oscillators-rigid rotors.

14) The energy of a molecule in the rigid rotor – harmonic oscillator approximation is $E_{\text{vib, rot}}$ is $(n + 1/2) h\nu + \bar{B} J(J+1)$. Real molecules deviate from this behaviour due to the existence of anharmonicity (anharmonicity constant x_e), centrifugal distortion (centrifugal distortion constant \bar{D}) and the interaction between vibration and rotation (α is the coupling constant between the vibrational and rotational modes). The expression for the energy when these affects are included is

$$E_{\text{vib, rot}} = (n + 1/2) h\nu + \bar{B} J(J+1) - x_e (n + 1/2)^2 h\nu + \bar{D} J^2 (J+1)^2 - \alpha (n + 1/2) J(J+1)$$

Here, the third term is due to anharmonicity, the fourth term is due to centrifugal distortion and the last term is due to the interaction between vibration and rotation. Calculate the $q_{\text{vib, rot}}$ which includes the effects of these distortions.