

10 Probability and Statistics*

The objective of this chapter is to summarize the necessary mathematical concepts employed in the general area of statistical thermodynamics. As molecular systems are composed of a very large number of particles, probability arguments lead to what are essentially exact results. It is useful to begin with some remarks concerning the notion of permutation. It was introduced in Section 8.3, where it was emphasized that it is the permutation of symbols, rather than the permutation of objects, that is basic in the physical application of this mathematical concept. It is with some reservation that in the following sections the word “objects”, or sometimes “things”, will be used (rather than symbols), as it is thus that the subject is presented in virtually all existing textbooks. This point was illustrated in Section 8.3 by the story of the identical twins.

10.1 PERMUTATIONS

Given n identical (but distinguishable) objects, how can they be placed, say, in n different positions along a line? As they are identical, any one of them, say the first, can be placed with equal probability at any given position. There are then $n - 1$ positions open for the second. Hence, these two objects can be arranged in $n(n - 1)$ different ways. Clearly, the third object can be placed at any of the $n - 2$ remaining places, *etc.* The total number of possible solutions is then given by $n(n - 1)(n - 2) \dots 2 = n!$. This result expresses the permutation of n things taken n at a time,

$$P(n, n) = n!. \quad (1)$$

In the simplest case, $n = 2$ and the permutation of two identical objects a and b corresponds to the possibilities a,b and b,a or $P(2, 2) = 2$. If a third object, c , is included in all possible ways, the permutations are then $P(3, 3) = 6$.

*According to Mark Twain (Samuel Clemens), American author (1835–1910) “There are three kinds of lies: lies, damned lies, and statistics”.

The permutation of three identical objects was illustrated in Section 8.3. However, in the application considered there, coordinate systems were used to specify the positions of the particles. It was therefore necessary on the basis of feasibility arguments to include the inversion of coordinates (specified by the symbol #) with those permutations that would otherwise change the handedness of the system. Nevertheless, for the permutation of three particles the order of the group was found to be equal to $3! = 6$.

The application of Eq. (1) can be specifically illustrated by the example of four identical, but distinguishable, objects. The possible permutations can be established with the aid of the following table.

Table 1 Permutation of four distinguishable objects.

a b c d	a c b d	c a b d	b a c d	b c a d	c b a d
a b d c	a c d b	c a d b	b a d c	b c d a	c b d a
a d b c	a d c b	c d a b	b d a c	b d c a	c d b a
d a b c	d a c b	d c a b	d b a c	d b c a	d c b a

Equation (1) is often developed with the use of the following example. In how many ways can n patients occupy n chairs in a doctor's waiting room? The first patient to arrive can choose any one of the n chairs. However, the next patient has only $n - 1$ chairs from which to choose, and so on. Clearly the last patient can take only the single remaining chair. The total number of possibilities is thus given by $n(n - 1)(n - 2) \dots 1 = n!$. In this example each possible permutation involves all n patients.

The result obtained above can be generalized by consideration of the case in which there are but r chairs for n patients, where $r < n$. In this case the question is: In how many ways can a given ensemble of n people be seated in the r chairs? By the same argument, the result

$$P(n, r) = n(n - 1)(n - 2) \dots (n - r + 1) \quad (2)$$

is easily obtained. Clearly, with r chairs filled the following patients cannot be seated. Eq. (2) is usually written in the form

$$P(n, r) = \frac{n!}{(n - r)!}, \quad (3)$$

which represents the permutation of n things taken r at a time, or arrangements.

If four distinguishable objects are taken two at a time, the possible arrangements are shown in Table 2. Thus, $P(4, 2) = 12$, a result that can be compared with $P(4, 4) = 24$, as given in Table 1.

Table 2 Arrangement of four distinguishable objects taken two at a time.

a b	a c	a d
b a	b c	b d
c a	c b	c d
d a	d b	d c

10.2 COMBINATIONS

Now consider an example that is closely related to that presented in the previous section. An ensemble of n prospective clients are waiting to be seated in a restaurant. Here, unlike the case of the doctor's waiting room, there is a hostess, whose role is to select the appropriate ensemble of r clients to be seated at a given table. It is now of interest to determine the number of combinations (or selections) of n things r at a time. In this case the order of the members of the ensemble of r persons has not been considered. It is useful, then, to denote the number of combinations by $C(n, r)$, which can be found by the following argument.

The seating of the r patients in the Doctor's office was determined by the specific order in which they arrived. The solution to this problem was found to be the expression given by Eq. (3). However, in the example of the restaurant the ensemble of r persons was chosen by the hostess and then seated in one of $P(r, r) = r!$ possible ways, according to Eq. (1). The total number of ways of selecting and seating the n hungry clients is then given by

$$P(n, r) = C(n, r)P(r, r). \quad (4)$$

Thus, the number of combinations is equal to

$$C(n, r) = \frac{P(n, r)}{P(r, r)} = \frac{n!}{(n-r)!r!} = \binom{n}{r}. \quad (5)$$

The notation employed in Eq. (5) corresponds to that defined in Section 2.10, namely, the binomial coefficients. Thus, in general the binomial coefficients in the polynomial expansion

$$(a + b)^n = \sum_{r=0}^n \binom{n}{r} a^{n-r} b^r \quad (6)$$

can be identified with the number of combinations of n "objects" taken r at a time.

As an example of the application of Eq. (5), consider four identical objects taken two at a time. The possible combinations are given in Table 3. As

Table 3 Combinations of four identical objects taken two at a time.

a b	a c	a d
(b a)	b c	b d
(c a)	(c b)	c d
(d a)	(d b)	(d c)

the order is not important, the possibilities in parentheses are not counted, yielding $C(4, 2) = 6$. The division by $r! = 2$ in this example arises from the indistinguishability of the objects in each pair. This result should be compared with those given in Tables 1 and 2.

A closely related problem was considered in the seventeenth century. It is the famous arithmetic triangle developed by Pascal* that is shown in Table 4. It is constructed by writing the number one twice as the first line. The first column is then filled with an infinite sequence of the number one. Subsequently, each value in the table is calculated by taking the sum of the number immediately above and the number to the left of the latter. It is then apparent that the second column is given by $C(n, 1) = n$, the third by $C(n, 2) = n(n-1)/2$, and in general as given by Eq. (5).

It will be of interest in the following section to evaluate the sum over all given combinations of n objects taken r at a time, namely,

$$\sum_{r=0}^n C(n, r) = \sum_{r=0}^n \frac{n!}{(n-r)!r!} = \sum_{r=0}^n \binom{n}{r}. \quad (7)$$

By setting $a = b = 1$ in Eq. (6), the desired sum is found in the form

$$\sum_{r=0}^n C(n, r) = 2^n. \quad (8)$$

Table 4 Pascal's triangle.

1	1						
1	2	1					
1	3	3	1				
1	4	6	4	1			
1	5	10	10	5	1		
1	6	15	20	15	6	1	
1	7	21	35	35	21	7	1
⋮							

*Blaise Pascal, French mathematician, philosopher (1623–1662).

10.3 PROBABILITY

The notion of probability is employed in everyday language without, however, a mathematical description. If you say, “it will probably rain today”, you do not know the consequence, namely, should you water your garden? You are then dealing with an unknown outcome of a particular event. Probability theory attempts to specify the state of ignorance of the given event. It is applied in many areas of physical science, in particular in quantum chemistry and statistical mechanics. It can be employed with confidence in these areas, as the number of particles and their possible quantum states is very large, say, of the order of Avogadro’s number.* Its application in the theory of games is more approximate, as the number of events is usually much more limited. These points will be emphasized in the following examples.

In the development of probability theory, as applied to a system of particles, it is necessary to specify the distribution of particles over the various energy levels of a system. The energy levels may be clearly separated in a quantized system or approach a continuum in the classical limit. The notion of probability is introduced with the aid of the general relation

$$\mathcal{W} = \frac{n}{V} \quad (9)$$

where n is the number of “favorable” results and V is the number of possible results.

As a simple example, consider a deck of 52 playing cards. According to Eq. (9), the probability of drawing a heart from the deck is given by

$$\mathcal{W}(\heartsuit) = \frac{13}{52} = \frac{1}{4}, \quad (10)$$

as there are, of course, 13 hearts in the deck. The same result is assumed for the probability of drawing, say, a spade. The probability of drawing either a heart or a spade is then given by the sum

$$\mathcal{W}(\heartsuit) + \mathcal{W}(\spadesuit) = \frac{1}{4} + \frac{1}{4} = \frac{1}{2}, \quad (11)$$

because they are independent results. That the probabilities $\mathcal{W}(\heartsuit)$ and $\mathcal{W}(\spadesuit)$ are equal is an assumption; is it intuitively obvious?

Note, however, that the combined probability of drawing the ace of spades is equal to

$$\mathcal{W}(\heartsuit)\mathcal{W}(\spadesuit) = \frac{1}{13} \times \frac{1}{4} = \frac{1}{52}. \quad (12)$$

*Amedeo di Quaregna Avogadro, Italian chemist (1776–1856).

This result is clear, as there are but four aces in the deck and only one ace of spades.

The probability of a given event is often represented as a function of a random variable, say, x . The random variable can take on various discrete values x_i with probabilities given by $\mathcal{P}(x_i)$. The variable x is then an independent variable that describes a random or stochastic process. The function $\mathcal{P}(x_i)$ in simple examples is discontinuous, although as the number of samples increase, it approaches a denumerable infinity.

Returning now to a game, consider the possible sum of numbers on two dice. Each die has six sides and, assuming that the dice are not loaded, the outcome of the roll of each die has six equally probable possibilities. The probability for each number on a given die is thus equal to $1/6$ and the combined probability for the dice is equal to $1/36$. The possible values of the sum and the corresponding probabilities are then given in Table 5. These results are plotted in Fig. 1, which represents the probability distribution for this example.

The net result for the probability distribution of the sum of the numbers on two dice is then represented in Fig. 1. The well-known significance of the number seven becomes evident, as it has the greatest probability. As a second roll of the dice is independent of the result of the first, the chances of getting an eleven is only $2/36$. However, it is the conditional probability, that is, the

Table 5 The sum of numbers on two dice and the corresponding probability.

Sum	2	3	4	5	6	7	8	9	10	11	12
Probability	$1/36$	$2/36$	$3/36$	$4/36$	$5/36$	$6/36$	$5/36$	$4/36$	$3/36$	$2/36$	$1/36$

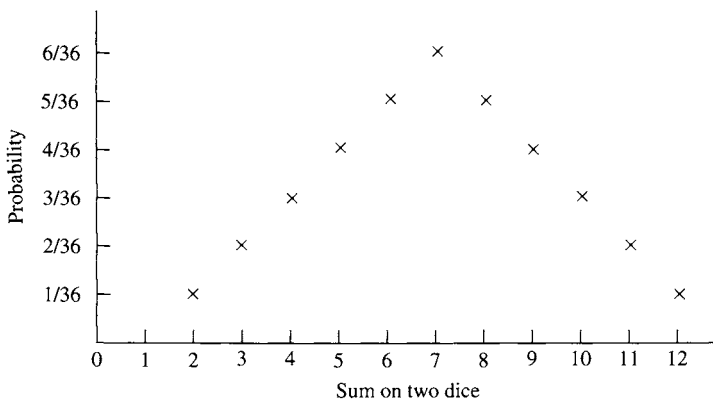


Fig. 1 The probability distribution of the sum of the two numbers on a pair of dice.

chance of obtaining a seven immediately followed by an eleven, that is of interest to the player. The reader is referred to texts on probability theory for discussions of conditional probability, as this subject is usually of less interest in physical applications.

For another game, consider the toss of a coin. If the coin is perfect, the probability of obtaining “heads” (and that of obtaining “tails”) is of course equal to one-half. If the coin is tossed five times, the probability of any particular sequence of heads and tails is given by $(\frac{1}{2})^5$ because the tosses are independent and the order is unimportant in this case. The number of sequences containing three heads is given by the number of ways of selecting three positions out of five heads, namely, the combination $C(5,3)$. The probability of three heads in five tosses is then given by $(\frac{1}{2})^5 C(5,3)$. This result is expressed in general by the probability function

$$\mathcal{W}(x) = \left(\frac{1}{2}\right)^n C(n, x), \quad (13)$$

where x represents the number of heads and n the number of tosses.

In the example presented in the previous paragraph, two results of each event have been considered. In this problem, an event has been repeated with two possible outcomes. One of them is usually referred to as the “success” (p) and the other as “failure” ($q = 1 - p$). These independent events are known as Bernoulli trials, after the Bernoulli brothers.* The general expression for the probability is then given by

$$\mathcal{W}(x) = p^x q^{n-x} C(n, x). \quad (14)$$

For a coin $p = q = \frac{1}{2}$, and Eq. (14) reduces to Eq. (13).

In the examples described above the resulting probability distributions were discontinuous functions. However, it is not difficult to imagine cases in which the distributions become continuous in the limit of an infinite – or at least a very large – number of trials. Such is the case in the application of statistical arguments to problems in thermodynamics, as outlined in Section 10.5.

10.4 STIRLING'S APPROXIMATION

Factorial numbers enter often in the equations developed in the previous sections. They are not very conveniently evaluated in the applications considered below. However, there exists an approximation due to Stirling[†] that is

*The Bernoulli family of Belgian–Swiss mathematicians, of whom Daniel (1700–1782) is probably the best known.

†James Stirling, British mathematician (1692–1770).

very useful in the evaluation of factorials of large numbers. It can be derived in several ways. For example, the Gamma function was defined by Eq. (5-143) in the form

$$\Gamma(z) = \int_0^{\infty} e^{-t} t^{z-1} dt. \quad (15)$$

If z is replaced by $n + 1$, a positive integer, Eq. (15) becomes

$$\begin{aligned} \Gamma(n+1) = n! &= \int_0^{\infty} e^{-t} t^n dt \\ &= \int_0^{\infty} e^{n \ln t - t} dt. \end{aligned} \quad (16)$$

With the substitution $t = n + y\sqrt{n}$, and hence $dt = \sqrt{n} dy$, Eq. (16) becomes

$$n! = \int_{-\sqrt{n}}^{\infty} e^{n \ln(n+y\sqrt{n}) - n - y\sqrt{n}} \sqrt{n} dy. \quad (17)$$

It should be noted that at $t = 0$, $y = -\sqrt{n}$. The logarithm appearing in the exponent in Eq. (17) can be developed in the form

$$\ln(n + y\sqrt{n}) = \ln n + \ln \left(1 + \frac{y}{\sqrt{n}} \right) = \ln n + \frac{y}{\sqrt{n}} - \frac{y^2}{2n} + \dots \quad (18)$$

(see problem 1). Substitution of Eq. (18) into Eq. (17) leads to the approximation

$$\begin{aligned} n! &\approx \int_{-\sqrt{n}}^{\infty} e^{n \ln n + y\sqrt{n} - y^2/2 - n - y\sqrt{n}} \sqrt{n} dy \\ &\approx e^{n \ln n - n} \sqrt{n} \int_{-\sqrt{n}}^{\infty} e^{-y^2/2} dy. \end{aligned} \quad (19)$$

The integral in Eq. (19) can be evaluated in terms of the error function, but for practical purposes it can be replaced by $\sqrt{2\pi}$ in the limit of large values of n (see Section 3.4.5). Then,

$$n! \approx n^n e^{-n} \sqrt{2\pi n}. \quad (20)$$

In applications in statistical mechanics it is the logarithm of large factorials that is of primary interest. The logarithm of Eq. (20) can be written in the limit of large values of n as

$$\ln n! = \left(n + \frac{1}{2} \right) \ln n - n + \frac{1}{2} \ln 2\pi. \quad (21)$$

$$\approx n \ln n - n. \quad (22)$$

Equation (22) is employed repeatedly in the applications illustrated in the following sections. It should be noted that this relation can also be obtained by evaluation of $\int_1^n \ln x dx$ (see problem 2).

10.5 STATISTICAL MECHANICS

In physical chemistry the most important application of the probability arguments developed above is in the area of statistical mechanics, and in particular, in statistical thermodynamics. This subject supplies the basic connection between a microscopic model of a system and its macroscopic description. The latter point of view is of course based on the results of experimental measurements (necessarily carried out in each experiment on a very large number of particles) which provide the basis of classical thermodynamics. With the aid of a simple example, an effort will now be made to establish a connection between the microscopic and macroscopic points of view.

Consider a system composed of n identical, but distinguishable, particles. The distinguishability of the particles may result, for example, from their positions in space, *e.g.* their coordinates. It is useful in this simplified model to assume, furthermore, that the energy of interaction between the particles can be neglected. Thus, n_1 particles in the ensemble have energy ε_1 *etc.*, and n_i the energy ε_i . The number of ways of choosing n_1 out of the ensemble of n particles is given by Eq. (5), with $r = n_1$, namely,

$$C(n, n_1) = \frac{n!}{(n - n_1)!n_1!} . \quad (23)$$

There remain but $n - n_1$ particles from which to choose the number n_2 . This result is easily generalized to obtain the probability distribution involving all n particles in the form

$$\mathcal{W} = \frac{n!}{n_1!n_2!n_3! \cdots} = n! \prod_i \frac{1}{n_i!} . \quad (24)$$

It should be noted that each factorial appearing in the denominator of Eq. (24) arises from the permutation of the n_i identical particles of energy ε_i .

In the derivation of Eq. (24) the possibility of degeneracy was not considered. However, if there are g_i states with the same energy ε_i , this result can be generalized. In effect, the first particle among the n_i can be placed in g_i ways among the states of energy ε_i . As there is no limitation here on the number of particles in each state, there are $g_i^{n_i}$ ways to place the n_i particles. Thus,

the more general form of Eq. (24) becomes

$$\mathcal{W} = n! \prod_i \frac{g_i^{n_i}}{n_i!}. \quad (25)$$

With the use of Stirling's approximation, as given by Eq. (22), the logarithm of Eq. (25) can be written as

$$\ln \mathcal{W} = \sum_i n_i \ln g_i - \sum_i (n_i \ln n_i - n_i) + n \ln n - n. \quad (26)$$

It should be pointed out that the n particles have been assumed here to be distinguishable. However, in an ideal gas the molecules cannot be distinguished, as their positions are random in space. Therefore, to be applied to the case of an ideal gas, Eqs. (24) and (25) should be divided by $n!$. Equation (26) becomes simply,

$$\ln \mathcal{W} \approx \sum_i n_i \ln g_i - \sum_i (n_i \ln n_i - n_i). \quad (27)$$

It might seem that the most probable distribution could be found by setting the differential $\delta \mathcal{W}$ equal to zero. Or, as \mathcal{W} and $\ln \mathcal{W}$ are maximum at the same point (if $\mathcal{W} \neq 0$), the differential of Eq. (27) can also be considered. The needed result is given by (see problem 3)

$$\delta \ln \mathcal{W} = \ln \frac{g_i}{n_i} \delta n_i. \quad (28)$$

Note, however, that the condition that Eq. (28) vanishes is subject to two constraints, namely,

$$n = \sum_i n_i \quad (29)$$

and

$$E = \sum_i \varepsilon_i n_i \quad (30)$$

which must be imposed to obtain a statistical description of an ideal gas. Equations (29) and (30) express the conservation of the number of particles (and, hence, mass) and the energy, respectively. The problem is then to maximize $\ln \mathcal{W}$ and at the same time assure the conditions given by Eqs. (29) and (30).

10.6 THE LAGRANGE MULTIPLIERS

Before the results obtained in the previous section can be applied, it is necessary to describe briefly the method of underdetermined multipliers. Given a function $f(x_1, x_2, \dots, x_k)$ of variables x_i , for which it is desired to find stationary values, the chain rule leads to the expression

$$df = \left(\frac{\partial f}{\partial x_1} \right) dx_1 + \left(\frac{\partial f}{\partial x_2} \right) dx_2 + \dots + \left(\frac{\partial f}{\partial x_k} \right) dx_k, \quad (31)$$

as given in Section 2.12. If the variables x_1, x_2, \dots, x_k are independent, the stationary values of $f(x)$ can be found by setting each partial derivative in Eq. (31) equal to zero. However, if there are constraints on the system, that is, if the variables x_i are not independent, the problem becomes more complicated.

Consider the case in which there are two implicit relations among the variables, *e.g.*

$$g(x_1, x_2, \dots, x_k) = 0 \quad (32)$$

and

$$h(x_1, x_2, \dots, x_k) = 0. \quad (33)$$

Expressing Eqs. (32) and (33) with the use of the chain rule leads to three relations which must be simultaneously satisfied, *viz.*

$$\sum_i \frac{\partial f}{\partial x_i} dx_i = 0, \quad (34)$$

$$\sum_i \frac{\partial g}{\partial x_i} dx_i = 0 \quad (35)$$

and

$$\sum_i \frac{\partial h}{\partial x_i} dx_i = 0. \quad (36)$$

If Eqs. (35) and (36) are each multiplied by an arbitrary constant, say $-\alpha$ and $-\beta$, respectively, and added, the result is given by

$$\sum_i \left(\frac{\partial f}{\partial x_i} - \alpha \frac{\partial g}{\partial x_i} - \beta \frac{\partial h}{\partial x_i} \right) dx_i = 0. \quad (37)$$

As the various differentials dx_i are not identically zero, the expression in parentheses must be, leading to the expression

$$\frac{\partial f}{\partial x_i} = \alpha \frac{\partial g}{\partial x_i} + \beta \frac{\partial h}{\partial x_i}. \quad (38)$$

In this example α and β are the Lagrange multipliers, which can be determined from the expressions for the constraints, although it is not always necessary to do so. Clearly, this approach can be generalized and the number of multipliers is equal to the number of constraints on the system.

10.7 THE PARTITION FUNCTION

The statistical description of an ideal gas, a system of n identical, indistinguishable (nonlocalized) particles, can now be obtained from Eqs. (28) to (30). The differentials of Eqs. (29) and (30) are given by

$$\sum_i \delta n_i = 0 \quad (39)$$

$$\sum_i \varepsilon_i \delta n_i = 0, \quad (40)$$

respectively. The problem of maximizing $\ln \mathcal{W}$ subject to these constraints can be expressed by

$$\sum_i \left(\ln \frac{g_i}{n_i} - \alpha - \beta \varepsilon_i \right) \delta n_i = 0, \quad (41)$$

where α and β are Lagrange multipliers. As the quantity in parentheses must vanish in each term, the number of particles with energy ε_i is given by

$$n_i = g_i e^{-\alpha - \beta \varepsilon_i}. \quad (42)$$

The evaluation of the Lagrange multipliers requires additional information.

From Eqs. (42) and (29) the fraction of particles in energy level i becomes

$$\frac{n_i}{n} = \frac{g_i e^{-\beta \varepsilon_i}}{\sum_i g_i e^{-\beta \varepsilon_i}}. \quad (43)$$

The denominator of Eq. (43), $\sum_i g_i e^{-\beta \varepsilon_i} \equiv \mathcal{Z}$, is known as the partition function (French: *fonction de partition*) or state sum (German: *Zustandssumme*). It will be shown later that $\beta = 1/kT$, where T is the absolute temperature and k is the Boltzmann constant.* The partition function is thus a function of the absolute temperature.

*In classical thermodynamics the (inexact) differential change in heat, δq , is related to the (exact) differential change in entropy, dS , by $dS = k\beta \delta q = T^{-1} \delta q$. Thus, $k\beta = 1/T$ is an integrating factor for the heat change (see Section 3.5).

The substitution of Eq. (43) in Eq. (30) yields the expression for the internal energy of the system,

$$\begin{aligned} E &= \frac{n}{\mathcal{Z}} \sum_i \varepsilon_i g_i e^{-\varepsilon_i/kT} \\ &= \frac{nkT^2}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial T}. \end{aligned} \quad (44)$$

The energy per mole of gas is then equal to

$$\tilde{E} = RT^2 \frac{\partial \ln \mathcal{Z}}{\partial T}, \quad (45)$$

where the tilde indicates a molar quantity. The heat capacity per mole is then given by

$$\tilde{C}_V \equiv \left(\frac{\partial \tilde{E}}{\partial T} \right)_V = R \frac{\partial}{\partial T} \left(T^2 \frac{\partial \ln \mathcal{Z}}{\partial T} \right). \quad (46)$$

From Eqs. (45) and (46) it is apparent that the calculation of the energy and heat capacity of a system depends on the evaluation of the partition function as a function of temperature. In the more general case of molecules with an internal structure, the energy distributions of the various degrees of freedom must be determined. This problem is outlined briefly in the following section.

10.8 MOLECULAR ENERGIES

It was argued in the introduction to Chapter 9 that the energy of a molecule can be written in a first approximation as the sum

$$\varepsilon_i \approx \varepsilon_i(\text{electrons}) + \varepsilon_i(\text{translation}) + \varepsilon_i(\text{rotation}) + \varepsilon_i(\text{vibration}), \quad (47)$$

where the last three terms refer to displacement of the nuclei and all interaction terms have been neglected. For an ensemble of independent molecules, as in an ideal gas, it is apparent from Eq. (45) that the partition function can be written as the product of the appropriate partition functions. Thus,

$$\mathcal{Z} = \mathcal{Z}(\text{translation}) \cdot \mathcal{Z}(\text{rotation}) \cdot \mathcal{Z}(\text{vibration}), \quad (48)$$

where $\mathcal{Z}(\text{electrons}) = 1$, if the molecules are in their (nondegenerate) ground state. However, at very high temperature the population of excited electronic states cannot be neglected and the electronic partition function must be evaluated.

10.8.1 Translation

The displacement of the center of mass of a molecule gives rise to the external or translation energy of the molecule. It corresponds to the energy associated with the movement in three-dimensional space of a particle whose mass is equal to that of the molecule. In each of the three directions in space the problem can be treated as a particle in a box, as presented in Section 5.4.1. It was shown that the energy is given by

$$\varepsilon_i = \frac{h^2 n_x^2}{8ma^2}, \quad (49)$$

where the notation has now been modified so that $n_x = 1, 2, 3, \dots$ is the quantum number associated with the translation in the x direction and a is the corresponding dimension of the box. With the use of the definition of the partition function, as given below Eq. (43), the partition function associated with the x degrees of translational freedom of the molecules is given by

$$\mathcal{Z}^{(x)} = \sum_{N_x} e^{-\frac{h^2 n_x^2}{8ma^2 kT}}, \quad (50)$$

where β has been replaced by $1/kT$, as before, and the system is nondegenerate ($gn_x = 1$ for all values of n_x). From Eq. (49) it is apparent that the separation between successive energy levels decreases as the quantity ma^2 increases. As the dimension a is very large on a molecular scale, for virtually all molecules the energy distribution given by Eq. (49) approaches a continuum. In other words, the deBroglie wavelength of the particle is very short compared with a , the dimension of the container. At moderate temperatures almost all of the molecules are to be found in the lower levels. Thus, to a good approximation, the sum in Eq. (50) can be replaced by an integral over the energy levels, namely,

$$\begin{aligned} \mathcal{Z}^{(x)} &\approx \int_0^\infty e^{-\frac{h^2 n_x^2}{8ma^2 kT}} dn_x \\ &= \frac{a\sqrt{2\pi mkT}}{h}. \end{aligned} \quad (51)$$

Obviously, the above derivation can be repeated for the other two Cartesian directions. As the energies are additive, the partition function for the three-dimensional translation of the molecule can be written as a product, *viz.*

$$\begin{aligned} \mathcal{Z}(\text{translation}) &= \mathcal{Z}^{(x)} \cdot \mathcal{Z}^{(y)} \cdot \mathcal{Z}^{(z)} \\ &= \frac{abc(2\pi mkT)^{3/2}}{h^3} = \frac{V}{h^3} (2\pi mkT)^{3/2}, \end{aligned} \quad (52)$$

where $V = abc$ is the volume of the rectangular container. Equation (52) leads to

$$\ln \mathcal{Z}(\text{translation}) = \frac{3}{2} \ln T + \text{constant} \quad (53)$$

and

$$\frac{\partial \ln \mathcal{Z}(\text{translation})}{\partial T} = \frac{3}{2T}. \quad (54)$$

Then, from Eqs. (45) and (46)

$$E(\text{translation}) = \frac{3}{2}nkT \quad (55)$$

and the energy per mole is given by

$$\tilde{E}(\text{translation}) = \frac{3}{2}RT. \quad (56)$$

This result is identical to that obtained in elementary kinetic theory. There is, in effect a contribution of $\frac{1}{2}RT$ to the energy per mole for each of the three directions in space. Furthermore, this result allows the identification $\beta = 1/kT$, as suggested earlier.

10.8.2 Rotation

It was shown in the previous chapter that the Schrödinger equation for molecular rotation depends on the type of rotator, as defined in Section 9.2.2. For linear molecules and, hence, diatomics, the energy is given by Eq. (9-40),

$$\varepsilon_J = \frac{h^2}{8\pi^2 I} J(J+1), \quad (57)$$

with $J = 0, 1, 2, \dots$. As the degree of degeneracy is equal to $g_J = 2J + 1$, the rotational partition function can be written as

$$\mathcal{Z}(\text{rotation}) = \sum_J (2J+1) e^{-h^2 J(J+1)/8\pi^2 I kT}. \quad (58)$$

If the molecule does not have a center of symmetry, the sum appearing in Eq. (58) extends over all values of the quantum number J . It should be noted, however, that in the case of centrosymmetric molecules the role of nuclear spins must be considered.

For linear molecules that lack a center of symmetry, Eq. (58) is applicable and at temperatures significantly greater than the "rotational temperature", $\theta \equiv h^2/8\pi^2 I k$, the sum in Eq. (58) can be replaced by an integral. This

operation is equivalent to the passage from the quantum-mechanical to the classical description of the rotational motion of the molecule. It yields

$$\mathcal{Z}(\text{rotation}) \approx \frac{8\pi^2 I k T}{h^2} = \frac{T}{\theta} \quad (59)$$

for $T \gg \theta$ (problem 5). The derivative of the logarithm of Eq. (59) is then given by

$$\frac{\partial \ln \mathcal{Z}(\text{rotation})}{\partial T} = \frac{1}{T}, \quad (60)$$

which leads to RT as the rotational energy per mole of a gas composed of linear (noncentrosymmetric) molecules. This result corresponds to a contribution of $\frac{1}{2}RT$ for each of the two degrees of rotational freedom of a linear molecule.

If a linear molecule contains a center of symmetry, the quantum number J is restricted to either odd or even values. Thus, the sum in Eq. (58) is composed of two parts that approach the same value as J increases, *viz.*

$$\sum_{J \text{ even}} (2J + 1) e^{-J(J+1)\theta/T} \approx \sum_{J \text{ odd}} (2J + 1) e^{-J(J+1)\theta/T} \approx \frac{T}{2\theta}. \quad (61)$$

In effect, the division by two is the result of the molecular symmetry, as specified by the character table for the group $\mathcal{D}_{\infty h}$. In general it is useful to define a symmetry number σ ($= 2$ in this case), as shown below. The well-known example of the importance of nuclear spin is that of *ortho*- and *para*-hydrogen (see Section 10.9.5).

Nonlinear polyatomic molecules require further consideration, depending on their classification, as given in Section 9.2.2. In the classical, high-temperature limit, the rotational partition function for a nonlinear molecule is given by

$$\mathcal{Z}(\text{rotation}) \approx \frac{\sqrt{\pi}}{\sigma h^3} \sqrt{I_a I_b I_c} (8\pi^2 k T)^{3/2}, \quad (62)$$

where $I_a = I_b = I_c$ for spherical rotators and $I_a = I_b$ for symmetric rotators. The symmetry number depends on the structure of the molecule. For example, a molecule such as H_2O , which belongs to point group \mathcal{C}_{2v} , has a two-fold axis of symmetry, leading to $\sigma = 2$. For ammonia (\mathcal{C}_{3v}), $\sigma = 3$, while for methane (\mathcal{T}_d) and benzene (\mathcal{C}_{6v}), $\sigma = 4 \times 3 = 12$ (4 three-fold axes) and $\sigma = 6 \times 2 = 12$ (6 two-fold axes), respectively. In all cases Eq. (62) yields $\frac{3}{2}RT$ for the energy per mole of a gas composed of nonlinear molecules.

10.8.3 Vibration

The vibrational energy of a diatomic molecule is given in the harmonic approximation by

$$\varepsilon_v(\text{vibration}) = h\nu^0 \left(v + \frac{1}{2} \right), \quad (63)$$

where $v = 0, 1, 2, \dots$ is the vibrational quantum number and ν^0 is the classical frequency of vibration (see Sections 5.4.4 and 6.5.2). The corresponding partition function is then equal to

$$\mathcal{Z}(\text{vibration}) = e^{-h\nu^0/2kT} \sum_v e^{-(h\nu^0/kT)v}. \quad (64)$$

The summation appearing in Eq. (64) can be written in the form

$$\begin{aligned} \sum_v e^{-(h\nu^0/kT)v} &= \sum_v (e^{-h\nu^0/kT})^v \\ &= \sum_v \zeta^v = 1 + \zeta + \zeta^2 + \dots = \frac{1}{1 - \zeta}, \end{aligned} \quad (65)$$

where $\zeta = e^{-h\nu^0/kT}$. In Eq. (65) ζ^v has been developed as a geometric series (see problem 6). Thus,

$$\ln \mathcal{Z}(\text{vibration}) = -\frac{h\nu^0}{2kT} - \ln(1 - e^{-h\nu^0/kT}) \quad (66)$$

and from Eq. (45) the energy per mole is given by

$$\tilde{E} = N_0 \left(\frac{1}{2} h\nu^0 \right) + \frac{N_0 h\nu^0 e^{-h\nu^0/kT}}{e^{-h\nu^0/kT} - 1}. \quad (67)$$

The first term on the right-hand side of Eq. (67) is known as the zero-point energy, as it remains even at $T = 0$. It does not, however, contribute to the heat capacity, as Eq. (46) leads to

$$\tilde{C}_V(\text{vibration}) = \left(\frac{\partial \tilde{E}}{\partial T} \right)_v = R \left(\frac{h\nu^0}{kT} \right)^2 \frac{e^{h\nu^0/kT}}{(e^{h\nu^0/kT} - 1)^2} \quad (68)$$

(problem 7). The function

$$f(x) = \frac{x^2 e^x}{(e^x - 1)^2} \quad (69)$$

appearing in Eq. (68) with $x \equiv h\nu^0/kT$ is known as the Einstein function.* In the limit as $kT \gg h\nu^0$, $f(x) \rightarrow 1$ (see problem 8), and the heat capacity becomes equal to R in the high-temperature limit. On the other hand the heat capacity is equal to zero at zero Kelvin.

The results obtained above for a diatomic molecule can be generalized for polyatomic molecules. Each of the $3N-6$ normal modes of vibration (or $3N-5$ for linear molecules) will contribute an energy given by an expression analogous to Eq. (63), namely,

$$\varepsilon_{v_k} = h\nu_k^0 \left(v_k + \frac{1}{2} \right), \quad (70)$$

where v_k is the vibrational quantum number for the k^{th} mode and ν_k^0 is its frequency. Thus, there will be a partition function \mathcal{Z}_{v_k} for each mode such that

$$\mathcal{Z}(\text{vibration}) = \prod_{v_k=1}^{3N-6} \mathcal{Z}_{v_k}. \quad (71)$$

The various contributions to the energy of a molecule were specified in Eq. (47). However, the fact that the electronic partition function was assumed to be equal to one should not be overlooked. In effect, the electronic energy was assumed to be equal to zero, that is, that the molecule remains in its ground electronic state. In the application of statistical mechanics to high-temperature systems this approximation is not appropriate. In particular, in the analysis of plasmas the electronic contribution to the energy, and thus to the partition function, must be included.

10.9 QUANTUM STATISTICS

10.9.1 The indistinguishability of identical particles

A basic principle in quantum mechanics is the indistinguishability of particles. Thus, as indicated in Section 10.5, two particles of the same type in an ideal gas are characterized by a wavefunction, say $\psi(r_1, \theta_1, \varphi_1; r_2, \theta_2, \varphi_2)$, where r, θ, φ are the usual spherical polar coordinates. If for simplicity this wavefunction is written as $\psi(1, 2)$, the permutation of the coordinates of the two identical particles can be represented by

$$\hat{P}\psi(1, 2) = \psi(2, 1), \quad (72)$$

*Albert Einstein, German-American theoretical physicist (1879–1955).

where \hat{P} is the permutation operator (see Section 10.1). Clearly, if this operation is carried twice in succession the result is to re-establish the original description of the system, namely,

$$\hat{P}\hat{P}\psi(1, 2) = \hat{P}\psi(2, 1) = \psi(1, 2). \quad (73)$$

It is useful at this point to define the eigenvalue λ of this operator by the relation

$$\hat{P}\psi(1, 2) = \lambda\psi(1, 2). \quad (74)$$

The successive application of this operation yields

$$\hat{P}\hat{P}\psi(1, 2) = \lambda\hat{P}\psi(1, 2) = \lambda^2\psi(1, 2). \quad (75)$$

Comparison of Eqs. (73) and (75) shows that $\lambda^2 = 1$; thus, $\lambda = \pm 1$.

The result of the above argument is that the wavefunctions can be classified as either:

(i) symmetric, with no change in sign under the permutation; $\psi(1, 2) = \psi(2, 1)$

or

(ii) antisymmetric, with change in sign, *viz.* $\psi(1, 2) = -\psi(2, 1)$.

The conclusion is then that the wavefunction representing a system composed of indistinguishable particles must be either symmetric or antisymmetric under the permutation operation. On purely physical grounds, this result is apparent, as the probability density must be independent of the permutation of indistinguishable particles; or $|\psi(1, 2)|^2 = |\psi(2, 1)|^2$.

Most particles of interest to physicists and chemists are found to be antisymmetric under permutation. They include electrons, protons and neutrons, as well as positrons and other "antiparticles". These particles, which are known as Fermions,* all have spins of one-half. The relation between the permutation symmetry and the value of the spin has been established by experiment and, in the case of the electron, by application of relativistic quantum theory.

10.9.2 The exclusion principle

The symmetry of particles [(i) or (ii), above] determines the rules under which they occupy the various quantum states of a system. In the case of Fermions, for example, no more than one particle can occupy a given quantum state.

*Enrico Fermi, Italian physicist (1901–1954).

This statement, as applied to electrons, provides the basis for the exclusion principle of Pauli.*

The method of assuring the antisymmetry of a system of electrons, as for example in a polyelectronic atom, is to construct what is often called the Slater determinant.† If the N electrons are numbered 1, 2, 3, ... and each can occupy a state a, b, c, \dots , the determinant

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_b(1) & \psi_c(1) & \cdots & \psi_N(1) \\ \psi_a(2) & \psi_b(2) & \psi_c(2) & & \vdots \\ \psi_a(3) & \psi_b(3) & \psi_c(3) & & \\ \vdots & & & & \\ \psi_a(N) & \cdots & & & \psi_N(N) \end{vmatrix} \quad (76)$$

provides a description of the system. If any two electrons are permuted, the result is to exchange the corresponding two rows in the determinant. The determinant thus changes sign and the wavefunction ψ is necessarily antisymmetric, as required. Furthermore, if any two electrons are found in the same state, e.g. $\psi_a = \psi_b$, two columns are identical and the determinant vanishes. Thus, the system does not exist and this possibility is excluded.

The properties of the Slater determinant demonstrate immediately the Pauli exclusion principle, as usually taught. It reads: No two electrons can have all four quantum numbers equal, that is to say that they cannot occupy the same quantum state. It is the direct result of the more general argument that the wavefunction must be antisymmetric under the permutation of any pair of (identical and indistinguishable) electrons.

10.9.3 Fermi–Dirac‡ statistics

These restrictions, imposed above on electrons, apply equally to all particles that are represented by antisymmetric wavefunctions, the so-called Fermions. The condition that no more than one particle can occupy a given quantum state leads immediately to the expression for the number of possible combinations. If $C(n_i, g_i)$ is the number of combinations that can be made with g_i particles taken n_i at a time,

$$C(n_i, g_i) = \frac{g_i!}{n_i!(g_i - n_i)!}, \quad (77)$$

as they are indistinguishable and the order in which they are taken is immaterial. For an ensemble of n particles the total number of combinations is

*Wolfgang Pauli, Austro-American physicist (1900–1958).

†John C. Slater, American theoretical physicist (1900–1976).

‡P. A. M. Dirac, British theoretical physicist (1902–1984).

given by

$$\mathcal{W} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}, \tag{78}$$

the product of the number of possible combinations for each energy level. This result is appropriate to Fermi–Dirac statistics, which is applicable to antisymmetric particles.

It is the logarithm of the number of combinations that enters in the appropriate statistics; thus it is the quantity

$$\ln \mathcal{W} = \sum_i [\ln g_i! - \ln n_i! - \ln(g_i - n_i)!] \tag{79}$$

that is of interest. Applying Stirling’s approximation, Eq. (79) reduces to

$$\ln \mathcal{W} = \sum_i \left[n_i \ln \left(\frac{g_i}{n_i} - 1 \right) - g_i \ln \left(1 - \frac{n_i}{g_i} \right) \right]. \tag{80}$$

As a simple illustration of Eq. (77), consider a system composed of three particles of the same energy that can occupy four quantum states. The case of Fermi–Dirac statistics is shown in Fig. 2a.

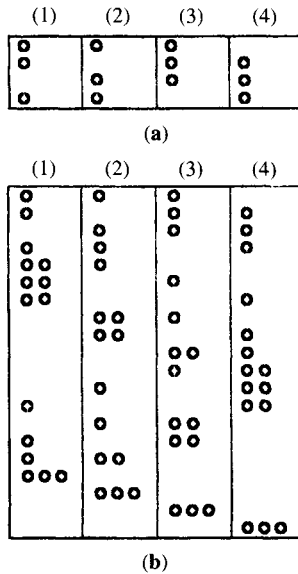


Fig. 2 The distributions of three particles in four quantum states (1) . . . (4) following (a) Fermi–Dirac statistics (b) Bose–Einstein statistics.

10.9.4 Bose*–Einstein statistics

Under the conditions determined by the symmetric permutation of identical particles, any number of particles can be placed in each quantum state. To distribute n_i of a given energy in g_i quantum states, consider the following model. To create g_i little boxes (“all in a row”) only $g_i - 1$ barriers separating the boxes are necessary. There are then n_i particles and $g_i - 1$ barriers. Therefore, there are $n_i + g_i - 1$ Bosons that can be permuted and $(n_i + g_i - 1)!$ possible permutations. However, as the particles are indistinguishable, the elements of each ensemble of n_i can be permuted, leading to $n_i!$ possibilities. Clearly, the indistinguishability of the barriers corresponds to $(g_i - 1)!$ permutations. The number of combinations is then given by

$$C(n_i, n_i + g_i - 1) = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \quad (81)$$

Again, by analogy with Eq. (78), for an ensemble of n_i Bosons the number of combinations is given by

$$\mathcal{W} = \prod_i \frac{(n_i + g_i - 1)}{n_i!(g_i - 1)!}. \quad (82)$$

In the applications of this result in statistical mechanics $g_i \gg 1$ and Eq. (81) reduces to

$$\mathcal{W} = \prod_i \frac{(n_i + g_i)!}{n_i!g_i!}. \quad (83)$$

Here, again, it is the logarithm of this function that is of interest. It is given by

$$\ln W = \sum_i \left[n_i \ln \left(\frac{g_i}{n_i} + 1 \right) + g_i \ln \left(1 + \frac{n_i}{g_i} \right) \right]. \quad (84)$$

Equations (80) and (84) can be written as a single expression, *viz.*

$$\ln W = \sum_i \left[n_i \ln \left(\frac{g_i}{n_i} - \iota \right) - \iota g_i \ln \left(1 - \iota \frac{n_i}{g_i} \right) \right], \quad (85)$$

where ι is equal to ± 1 .

With the use of the method developed in Section 10.7, Eq. (85) leads to

$$n_i = \frac{g_i e^{-\alpha - \beta \epsilon_i}}{1 + \iota e^{-\alpha - \beta \epsilon_i}}, \quad (86)$$

*Satyendranath Bose, Indian physicist (1894–1974).

where α and β are the Lagrange multipliers, as before. If the number of particles of a given energy is much smaller the number of quantum states that they can occupy, $e^{-\alpha-\beta\epsilon_i} \ll 1$ and Eq. (86) becomes identical to Eq. (42).

In summary, Eq. (86) is a general expression for the number of particles in a given quantum state. If $\iota = \pm 1$, this result is appropriate to Fermi–Dirac statistics, or to Bose–Einstein statistics, respectively. However, if ι is equated to zero, the result corresponds to the Maxwell–Boltzmann distribution. In many cases the last is a good approximation to quantum systems, which is, furthermore, a correct description of classical ones – those in which the energy levels form a continuum. From these results the partition functions can be calculated, leading to expressions for the various thermodynamic functions for a given system. In many cases these values, as obtained from spectroscopic observations, are more accurate than those obtained by direct thermodynamic measurements.

10.10 ORTHO- AND PARA-HYDROGEN

In Section 10.8 it was assumed that the total energy of a molecule can be written as the sum given in Eq. (47). Accordingly, the partition function was written as a product of the corresponding partition functions. However, a particular problem arises in the case in which the molecule possesses a center of inversion. The simplest case is of course a homonuclear diatomic molecule. The inversion operation with respect to the center of symmetry results in the exchange of the identity of the two nuclei. The effect of this permutation on the wavefunction for the nuclear spins is either symmetric or antisymmetric. If this wavefunction is symmetric, the molecule is called *ortho* and if it is antisymmetric, it is called *para*. It can be shown that the number of independent spin wavefunctions (spin degeneracy or statistical weight) is given by $g_i(\textit{ortho}) = (i + 1)(2i + 1)$ if the wavefunction is symmetric under the permutation and $g_i(\textit{para}) = i(2i + 1)$ if it is antisymmetric. Here, i is the spin of one of the identical nuclei. It has integer values or half-integer values, depending on the nature of the nucleus. In the former case, it is called a Boson, while in the latter it is known as a Fermion. The proton, for example, has a spin of one-half and is thus a Fermion (see Section 10.9.1).

According to the argument presented above, any molecule must be described by wavefunctions that are antisymmetric with respect to the exchange of any two identical particles. For a homonuclear diatomic molecule, for example, the possibility of permutation of the two identical nuclei must be considered. Although both the translational and vibrational wavefunctions are symmetric under such a permutation, the parity of the rotational wavefunction depends on the value of J , the rotational quantum number. It can be shown that the wavefunction is symmetric if J is even and antisymmetric if J is odd. The overall

symmetry of a homonuclear diatomic molecule is determined by the symmetry of the product of the rotational and nuclear-spin wavefunctions. Thus, for the *ortho* species, the rotational wavefunction is antisymmetric, corresponding to odd values of J . On the other hand, only even values of J are involved in the partition function for the *para* molecules. The specific forms of the partition functions are then

(i) *Ortho* molecules:

$$\mathcal{Z}(\text{nuclear})\mathcal{Z}(\text{rotation}) = (i + 1)(2i + 1) \sum_{J \text{ odd}} (2J + 1)e^{-J(J+1)\theta/T} \quad (87)$$

and

(ii) *Para* molecules:

$$\mathcal{Z}(\text{nuclear})\mathcal{Z}(\text{rotation}) = i(2i + 1) \sum_{J \text{ even}} (2J + 1)e^{-J(J+1)\theta/T}, \quad (88)$$

where \mathcal{Z} (nuclear) is the partition function for nuclear spin and θ is the rotational temperature. It should be noted from Eq. (87) that the energy of the ground state ($J = 1$ for *ortho* molecules) is not, in this case, equal to zero.

As an example, consider now the hydrogen molecule. With $i = \frac{1}{2}$ for the protons, the statistical weights are given by $(i + 1)(2i + 1) = 3$ and $i(2i + 1) = 1$ for the *ortho* and *para* species, respectively. As the translational and vibrational partition functions are identical for the two types of hydrogen, the partial-pressure ratio approaches three at high temperatures ($T \gg \theta$), as the two sums in Eqs. (87) and (89) are equal in this limit. At low-temperatures, as $T \rightarrow 0\text{K}$, the sum in Eq. (87) becomes equal to zero and at equilibrium only *para*-H₂ can exist. This, result, as expressed by the percentages of the two types of molecular hydrogen, are presented as a function of temperature in Fig. 3. However, the equilibrium between these two species is only very slowly established in the absence of a catalyst.

For molecular hydrogen the evaluation of the various thermodynamic quantities from the partition functions is direct. However, for the rotational contribution the partition function must be considered to be the weighted sum of those for the *ortho* and *para* species. For example, the rotational part of the heat capacity is calculated from Eq. (46) with $\tilde{C}_v(\text{rotation}) = \frac{1}{4}\tilde{C}_v(\text{para}) + \frac{3}{4}\tilde{C}_v(\text{ortho})$. At ordinary temperatures the equilibrium constant for the reaction *ortho*-H₂ \leftrightarrow *para*-H₂ has almost reached its limiting value of $\frac{1}{3}$, as determined by the quantity $i/(i + 1)$. At lower temperatures the sums involved in the rotational partition functions must be evaluated term-by-term. The calculated

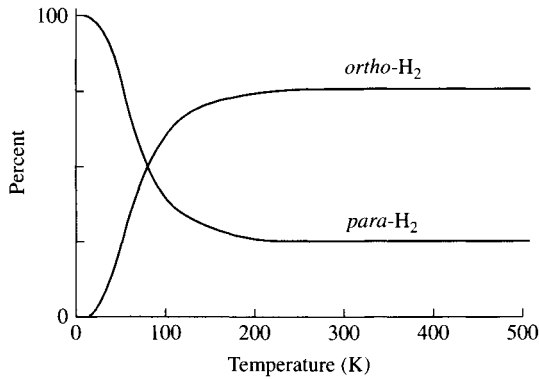


Fig. 3 Relative equilibrium percentages of *ortho*- and *para*-hydrogen as a function of temperature.

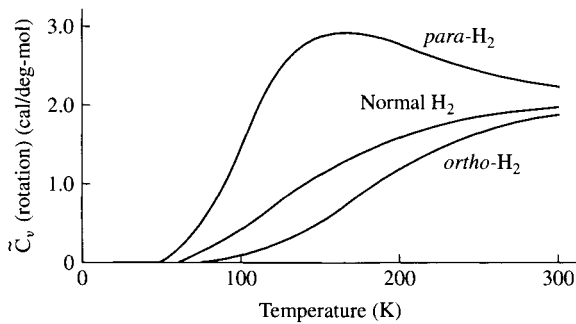


Fig. 4 Rotational contribution to the molar heat capacity \tilde{C}_v for *ortho*, *para* and normal hydrogen. Note that $1 \text{ cal/deg-mol} = 4.18 \text{ J K}^{-1} \text{ mol}^{-1}$.

rotational molar heat capacity is shown as a function of temperature in Fig. 4 for both *ortho*-H₂ and *para*-H₂, as well as for the equilibrium mixture.

If only the spins of the nuclei are altered in a given transition, the translational and vibrational contributions to the partition function are identical. Thus, for the reaction *ortho*-H₂ \rightarrow *para*-H₂, the partial-pressure ratio at equilibrium is given by

$$K = \frac{[\textit{para}\text{-H}_2]}{[\textit{ortho}\text{-H}_2]} = \frac{\mathcal{Z}_{\textit{para}}(\textit{rotation})}{3\mathcal{Z}_{\textit{ortho}}(\textit{rotation})}. \quad (89)$$

However, it should be emphasized that the equilibrium between these two types of hydrogen is not easily established. In fact, under ordinary conditions, equilibrium is achieved only after a period of some years. It was for this reason

that the early experimental determinations of the heat capacity of ordinary hydrogen were not in agreement with the values predicted from the elementary theory, in which the symmetry considerations presented above were not taken into account. Furthermore, the spectra of molecular hydrogen obtained at that time displayed anomalous line intensities that suggested the presence of two types of hydrogen, as indicated in this simple theoretical analysis.

It was subsequently shown that the presence of a catalyst accelerates the attainment of the *ortho-para* equilibrium. Measurements of properties such as the heat capacity and the thermal conductivity as a function of temperature then indicate that an equilibrium between the two species has been established.

PROBLEMS

1. Develop the series given by Eq. (18).
2. Evaluate $\int_1^n \ln^m x$ by parts and show that for $m = 1$ it becomes equal to $n \ln n - n$ in the limit as $n \gg 1$.
3. Derive Eq. (28).
4. Verify Eq. (51).
5. Carry out the integration over J to obtain Eq. (59).
6. Derive the sum given in Eq. (65).
7. Verify Eq. (68).
8. Show that the function $f(x) = x^2 e^x / (e^x - 1)^2$ approaches zero as $x \rightarrow \infty$ and one as $x \rightarrow 0$. (Hint, use L'Hospital's rule.)
9. Verify Eq. (86).