BOLTZMANN'S
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E. A. GUGGENHEIM

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by

E. A. GUGGENHEIM M.A., SC.D., F.R.S.

Professor of Chemistry
in the University of Reading

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PREFACE

"Par ma foi, il y a plus de quarante ans
que je dis de la prose, sans que j'en
susse rien, et je vous suis le plus obligé
du monde de m'avoir appris cela."

MOLIÈRE
"Le Bourgeois Gentilhomme"

This booklet describes a course for students of physics
and chemistry in their first term at a university provided
they have passed G.C.E. at advanced level in pure mathe-
matics, applied mathematics, physics and chemistry.

The idea of such a booklet was conceived at a discussion
meeting arranged by the Low-Temperature Group of the
Physical Society and described in Nature vol. 159, page
626. For eight years I have hoped that it might be written
by someone more experienced than 1 am in elementary
teaching, but I have now lost hope. If some students, after
digesting the text of this booklet, later on react to a formal
course of statistical thermodynamics somewhat as the
Bourgeois Gentilhomme reacted to his lesson on prose I
shall have succeeded in my object.

I am grateful to the publishers for doing everything
possible to keep down the price and I for my part have
aimed at the maximum brevity consistent with what I
hope is an acceptable degree of clarity.

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CONTENTS

Chapter

ELEMENTS OF QUANTUM THEORY

Our present detailed knowledge of the structure of atoms and molecules has been acquired entirely since the turn of the century. Its acquisition has been due to a combination of new experimental techniques with a new theory of mechanics called "quantum theory". Some knowledge of quantum theory is essential for any detailed description of the behaviour of atoms and molecules. This chapter is devoted to a summary of the minimum amount of quantum theory adequate for our purpose. No mention will be made of the history of the development of quantum theory nor of the experiments which led to its development. The justification of the theory is, of course, that it leads to conclusions in agreement with experiment.

As an introduction to quantum theory, we shall recapitulate some of the elements of classical mechanics. We shall then describe the most essential modifications introduced by quantum theory. Classical mechanics is based on Newton's laws of motion. One of the consequences of these laws is the existence of energy which may be of two kinds, kinetic and potential. In an isolated system, e.g. a swinging pendulum, the total energy remains constant. As the potential energy decreases, the kinetic energy increases and vice-versa so that the sum of the kinetic energy and potential energy remains constant. For example the motion of a harmonic oscillator is completely described by the following equations, in which x denotes the positional coordinate, a the amplitude, ν the frequency and t the

time. Further, T denotes the kinetic energy, V the potential energy and E the total energy. The potential energy V has its minimum value, conventionally taken as $V = 0$, at $x = 0$.

$$x = a \sin 2\pi\nu t$$

$$\dot{x} = 2\pi\nu a \cos 2\pi\nu t$$

$$T = \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}m (2\pi a)^2 \cos^2 2\pi\nu t$$

$$V = \tfrac{1}{2}m (2\pi\nu)^2 x^2 = \tfrac{1}{2}m (2\pi\nu a)^2 \sin^2 2\pi\nu t$$

$$E = T + V = \tfrac{1}{2}m (2\pi\nu a)^2$$

Thus the total energy E is proportional to the square of the amplitude a.

Whereas the total energy of an isolated mechanical system such as a harmonic oscillator remains constant, its energy can be changed by interaction with its surroundings. When the system gains energy, then the same amount of energy is lost by the surroundings and we say that work is done on the system by the surroundings. Conversely when the system loses energy then the same amount of energy is gained by the surroundings and we say that work is done by the system on the surroundings.

It is an essential feature of classical mechanics that the possible values of E form a continuum and that E changes continuously. It is an essential feature of quantum theory that E can have only certain discrete values and that E can change only from one of these discrete values to another. It is evident from this that there is in principle a complete contradiction between classical mechanics and quantum theory, but in fact the gaps between successive values of E are so small as to be entirely negligible for planets, projectiles and even the smallest grains of dust. They are however not always negligible for molecules and atoms and they are never negligible for electrons. Hence classical mechanics is an approximation to quantum theory valid for planets, projectiles and grains of dust but

sometimes inadequate for molecules and atoms and completely misleading for electrons.

The restriction of the energy E to discrete values is called "quantization". Quantum theory is largely concerned with the derivation from a few general principles of the rules of quantization. We shall not here be concerned with these derivations, but shall confine ourselves to quoting the derived rules for a few of the simplest and most important kinds of system.

The quantization rules involve a universal constant called "Planck's constant". This constant, denoted by h, has the dimensions of the product of linear momentum by distance i.e. the same dimensions as angular momentum. The value of h is 6.625×10^{-27} g cm^2 s^{-1} or 6.625×10^{-34} kg m^2 s^{-1}. We shall now quote and discuss several quantization rules in turn.

(a) As our first and simplest example we consider a particle of mass m moving freely back and forth between and normal to two parallel walls distant L apart. The quantization rule is expressed most simply in terms of the momentum $p \equiv m\dot{x}$, where x denotes distance from one of the walls and $\dot{x} \equiv dx/dt$ denotes velocity. The quantization rule for this system is

$$|p|\, 2L = nh$$

where $|p|$ denotes the constant magnitude of the momentum and n is an integer called the "quantum number". The momentum itself is $+\,|p|$ or $-\,|p|$ according to the direction of motion of the particle. The factor 2 occurs because the length of path of the particle over a complete cycle "there and back" is $2L$. We may thus express the quantization rule in the words "The product of the magnitude of the momentum by the length of path over a cycle is equal to an integral multiple of Planck's constant." The allowed values of the energy E, in this case purely kinetic, are immediately derived from the allowed values of $|p|$.

$$E = \tfrac{1}{2}m\dot{x}^2 = \frac{p^2}{2m} = n^2 \frac{h^2}{8mL^2}$$

We may now verify that the gaps between successive energy or momentum values of the particle moving freely between two walls are usually negligible. Let us consider the molecules or atoms of helium gas at room temperature. The magnitude of their average kinetic energy of motion in a given direction is about 2×10^{-14} g cm^2 s^{-2}. The mass of a helium atom is about 7×10^{-24} g. If then the two walls are 1 mm apart the values of E allowed by the quantization rule are

$$\frac{n^2 \times 6.6 \times 10^{-27} \times 6.6 \times 10^{-27}}{8 \times 7 \times 10^{-24} \times 0.1 \times 0.1} \text{ g cm}^2\text{s}^{-2}$$
$$= n^2 \times 7 \times 10^{-29} \text{ g cm}^2 \text{ s}^{-2}$$

Thus the average value of n^2 is about

$$\frac{2 \times 10^{-14}}{7 \times 10^{-29}} \simeq 3 \times 10^{14}$$

and the average value of n is about 1.7×10^7. Hence when n changes to $n + 1$ the energy increases by a fraction $2/n \simeq 1 \times 10^{-7}$. This is so small that we may in this example justifiably ignore the discontinuity in the energy values i.e. ignore quantization. If we had chosen a heavier particle than a helium atom or a larger distance between the walls the effect of quantization would have been still more negligible. At lower temperatures the average energy of a molecule is less but even at a temperature as low as $10°$K quantization of the translational motion of molecules is unimportant. We could easily verify that the effect of quantization is quite trivial for the motion of the lightest visible particles and a fortiori for projectiles and planets.

(b) As our second example we take the harmonic oscillator. Since the magnitude of the momentum is not constant the quantization rule cannot be as simple as for the

free particle. By a natural extension of the previous example we might guess that

$$\int p dx = vh$$

where the integration is over a complete cycle "there and back" and v is an integer. We can transform the left side of this equation as follows

$$\int p dx = \int p \dot{x} dt = \int 2T \, dt = \frac{2\overline{T}}{v}$$

where $\overline{T}$ denotes the average value of T over a complete period of duration $1/v$. But for a harmonic oscillator

$$\overline{T} = \overline{V}$$

where $\overline{V}$ denotes the average value of the potential energy V measured from the equilibrium position as zero. Consequently

$$2\overline{T} = \overline{T} + \overline{V} = E.$$

Our tentative relation may therefore be rewritten as

$$E/v = vh \quad \text{or} \quad E = vhv.$$

We have arrived at this relation by "intelligent guessing" and we have no proof that it is right. According to quantum theory the above formula gives the correct spacing of the energy levels, but the absolute values, when a state of rest at the equilibrium position is taken as zero energy, are

$$E = (v + \tfrac{1}{2}) \, hv$$

where v is an integer. The lowest allowed value of the energy lies $\tfrac{1}{2}hv$ above that of the state of rest in the equilibrium position.

(c) As our third example we shall consider a particle free to move in a container. We require three coordinates to describe the position of the particle. We might use cartesian coordinates or spherical polar coordinates, but whatever our choice the required number of coordinates is

three. We describe this situation by the statement that the particle has three "degrees of freedom". According to quantum theory each quantum state is specified by as many quantum numbers as there are degrees of freedom. Let us assume for the sake of simplicity that the container is a rectangular box with edges a, b, c. It is then most convenient to use cartesian coordinates, x, y, z with respect to axes parallel to the edges of the box. With this particular choice of coordinates the problem, in quantum theory as well as in classical theory, can be resolved into three independent sets of relations for the motion in the three directions defined by x, y, z respectively. In mathematical terminology the motion of the particle is "separable" when these coordinates are used. The quantization rules are now

$$|p_x| \times 2a = n_x h$$
$$|p_y| \times 2b = n_y h$$
$$|p_z| \times 2c = n_z h$$

where n_x, n_y, n_z are three independent integral quantum numbers. There are three of them because the particle has three degrees of freedom, and each is of the form already quoted for one-dimensional motion. The energy, being purely kinetic, is given by

$$E = T = \frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

If the box is cubic with an edge of length L

$$a = b = c = L$$

and the formula for the energy becomes

$$E = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8mL^2}$$

All states n_x, n_y, n_z such that $n_x^2 + n_y^2 + n_z^2$ has the same value will have equal energy. For example all the following states have energy $E = 66\ h^2/8mL^2$.

n_x	n_y	n_z	n_x	n_y	n_z
8	1	1	4	1	7
1	8	1	7	1	4
1	1	8	4	7	1
7	4	1	1	4	7
1	7	4			

In this case there are 9 distinct quantum states having equal energy and we say that this energy level is "ninefold degenerate".

As already mentioned it is sometimes, but by no means always, allowable to ignore the discreteness of quantum states and regard them as forming a continuum. This is allowable when the separation between the energy levels is negligibly small compared with the energy differences or energy changes with which one is concerned. When this condition is satisfied, we say that the system behaves classically. When the condition is satisfied with respect to a particular degree of freedom we say that this degree of freedom behaves classically.

If a certain degree of freedom behaves classically, we may and usually shall treat it classically, i.e. as if the states formed a continuum. Even so it will sometimes be necessary to know how many quantum states are included in an element of the continuum. In the simplest case of a single translational degree of freedom described by the coordinate x and momentum $p_x \equiv m\dot{x}$, the number of quantum states included between x and $x + dx$ and between p_x and $p_x + dp_x$ is $dx dp_x/h$. If we draw a diagram in which the abscissa represents x and the ordinate represents p_x, such a diagram is called a "phase plane". We may then say that there is one quantum state per element of area h in the phase plane.

We may extend this statement to three dimensions. If we imagine x, y, z, p_x, p_y, p_z as a six-dimensional coordinate system this is called phase space for the particle. Then the

number of quantum states is one per element h^3 of six-dimensional phase space.

The statement can be further extended to a system of f degrees of freedom described by coordinates q_1, q_2, ...q_f and momenta p_1, p_2, ...p_f. Then in the 2f-dimensional phase space in which the q's and p's are plotted as coordinates, there will be one quantum state per 2f-dimensional element h^f, provided of course all f degrees of freedom are classical. If they are not classical the statement is still true on the average, but may not be true for an arbitrarily chosen element of phase space.

TEMPERATURE AND PARTITION FUNCTIONS

We shall not attempt to give here a logical definition of temperature. We shall rather state its most important properties.

When two macroscopic systems are placed in contact with each other in such a manner that interchange of energy is possible, then over and above any work that the one system may do on the other, energy will always move from the system at the higher temperature to the system at the lower temperature and this exchange of energy is called a flow of heat. In particular if the two systems have equal temperatures, there will be no flow of heat and they are then said to be in thermal equilibrium. Moreover when heat flows into a system its temperature either increases or remains constant and when heat flows out of a system its temperature either decreases or remains constant. (The case where it remains constant is related to the term "latent heat", but discussion of this is postponed.) Other things being equal (in the interest of simplicity we are deliberately using vague terminology at this stage) increase of temperature involves increase of energy in the system and vice-versa. Consequently, at least in a loose way, temperature is a measure of the energy in a given system.

Energy, like volume, is a typically "extensive property" by which we mean that the energy (or volume) of the whole system is equal to the sum of the energies (or volumes) of the parts of the system. The temperature, like

pressure, on the other hand is a typically "intensive property" by which we mean that in a homogeneous system the temperature (or pressure) of any part is the same as that of the whole. Whereas the energy of the whole system is, as just mentioned, an extensive property, the average energy per molecule in the system is an intensive property. We might then reasonably expect the temperature to be related to the average energy per molecule. We shall see that the temperature in fact determines not only the average energy per molecule, but moreover determines the distribution of the molecules over all possible quantum states.

There is an infinite choice of temperature scales such that everything we have so far said about temperature is valid. There is however one particular kind of temperature scale in terms of which the distribution law over quantum states takes an especially simple form. The temperature on such a scale is called the "absolute temperature" and it is denoted by the symbol T. The distribution law for molecules over quantum states 1, 2, 3, ..., each specified by as many quantum numbers as the molecule has degrees of freedom, may then be expressed as follows. Let N_1, N_2, N_3, ..., denote the number of molecules in the states 1, 2, 3, ..., with energies E_1, E_2, E_3, ..., then

$$N_1 : N_2 : N_3 : ... = e^{-E_1/kT} : e^{-E_2/kT} : e^{-E_3/kT} : ...$$

where k is a constant, called Boltzmann's constant, which is a scaling factor fixing the size of the degree. When the temperature of the triple point of water is defined as 273.16 degrees the scale is called the Kelvin scale and we write for the triple point of water $T = 273.16°K$. On this scale the value of Boltzmann's constant is

$$k = 1.38 \times 10^{-16} \text{ erg deg}^{-1}.$$

The above statement, known as Boltzmann's distribution law, describes by far the most important property of

absolute temperature and it will be our starting point for all problems involving temperature. This statement tells us nothing about how absolute temperature can be measured practically. That is a problem which must be postponed to a later chapter when we shall find it quite easy.

It is sometimes convenient to write Boltzmann's distribution law in the alternative form

$$N_i = \lambda\, e^{-E_i/kT} \qquad \text{(all } i)$$

where λ has the same value for every quantum state. (Note that we do not call λ a "constant" because that might give the false impression that λ were independent of temperature.) The coefficient λ is called the "activity", or the "absolute activity".

It may happen that we are interested not so much in the number of molecules in a single quantum state i but rather in the number in a certain group of quantum states. In particular we may be interested in the distribution of molecules over the different energy levels, some or all of which may be degenerate. If then we denote by p_r the degeneracy, i.e. the number of independent quantum states, of the energy level E_r and by N_r the number of molecules in this energy level at the temperature T we have

$$\frac{N_r}{p_r e^{-E_r/kT}} = \frac{N_s}{p_s e^{-E_s/kT}} = \frac{N_t}{p_t e^{-E_t/kT}} = \cdots$$

or

$$N_r = \lambda\, p_r e^{-E_r/kT}$$

where the activity λ has the same value for all energy levels.

If we denote by f_i the fraction of molecules in a particular quantum state i, specified by as many quantum numbers as the molecule has degrees of freedom, then we have

$$f_i = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}$$

where the summation in the denominator extends over all quantum states. This sum plays an important role in determining the equilibrium properties of molecules. It is sometimes called the "sum of states" (German "Zustandsumme") of the molecule but more usually in English the "partition function" of the molecule. It is denoted by the symbol Q. Thus

$$Q = \Sigma_j \mathrm{e}^{-E_j/kT}$$

where Σ_j denotes summation over states, or by

$$Q = \Sigma_r\, p_r\, \mathrm{e}^{-E_r/kT}$$

where Σ_r denotes summation over energy levels.

An important property of a partition function is that it can be factorized whenever the energy is separable with respect to several degrees of freedom. For example if each energy E_i can be expressed as a sum

$$E_i = E'_l + E''_m + E'''_n$$

where the single dash, double dash and triple dash relate to different degrees of freedom or groups of degrees of freedom, each specified by its appropriate quantum numbers, then we have

$$Q = Q'\ Q''\ Q'''$$

where

$$Q' = \Sigma_l\, \mathrm{e}^{-E'_l/kT}$$

$$Q'' = \Sigma_m\, \mathrm{e}^{-E''_m/kT}$$

$$Q''' = \Sigma_n\, \mathrm{e}^{-E'''_n/kT}$$

We shall call call Q', Q'', Q''' the partition functions for the respective degrees of freedom or groups of degrees of freedom.