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THE KINETIC THEORY OF GASES

BY

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TRANSLATOR'S NOTE

THIS translation is taken from Professor Bloch's work, dated 1921. The original text has, I hope, been faithfully reproduced with a few*minor exceptions. In one or two cases, particularly in the sections dealing with statistical mechanics and probability, the mathematical presentation has been slightly modified where I deemed it advisable in the interest of clearness, but the method has not been changed in any way. Here and there changes have been made in the numerical data in the light of more recent work. At the request of the publishers of this translation I have prepared a more complete bibliography of the subject, which appears at the end of the book, including a list of the more important original papers concerning subjects which commonly find no place in the average text-book. It is hoped the references included will serve as a "point d'appui" for further study.

P. A. S.

NORTON HALL
NORTON-ON-TEES

PREFACE

DISCONTINUOUS STRUCTURE OF MATTER

FUNDAMENTAL HYPOTHESES

THE kinetic theory of gases is merely a branch—albeit the most perfect and most completely developed branch—of the molecular theory of matter. It states that the continuity of matter, solid, liquid, or gaseous, is only apparent, hiding a real discontinuity beyond the limits of our perception. Matter, in all its states, is an agglomeration of very small, distinct particles, whose mutual interactions and movements depend on temperature and pressure, forming an assembly which resembles a continuous medium. In solids the particles oscillate comparatively feebly about their mean positions of equilibrium. In liquids their movements are less restricted and give place to free gliding motions of the particles relative to one another : their mutual interaction still preserves a cohesion of the whole and consequently an approximately constant volume, but its shape no

longer remains invariable as in the case of solids. Finally, in gases, the particles escape almost completely from their mutual interactions, cohesion becomes very weak or negligible, and henceforth the movements which animate the particles become practically rectilinear and are only disturbed by incessant collisions with other particles or with the wall of the containing vessel. These latter collisions are the origin of the pressure which the gas exerts on the wall; the freedom of molecular motions, on the other hand, explains the diffusion of the gas into every space open to it or into another gas.

The theory of gases is more easily developed than that of the other states of matter ; the almost complete absence of cohesive forces, the unknown law of which plays an essential role in the condensed states, and the relatively disperse condition of the molecules, which may, as a first approximation, be considered as material points, introduce great simplifications in our reasoning and calculation. These we shall consider at some length, only discussing the theory of liquids and solids as a subsidiary study.

From the physical point of view, the essential feature of the theory is that heat is no longer considered as a variety of energy distinct from mechanical energy. It is the molecular agitation, or more precisely, the kinetic energy of the molecules, which represents the major part of the heat contained in the gas.

The surplus is accounted for by the potential energy of intermolecular attractions. We see then that the principle of the equivalence of heat and work is, in a sense, visualised from the start by the very conception we hold of heat itself. Hence the name "mechanical theory of gases" which is sometimes given to this doctrine.

On the other hand, since direct experiment does not permit us to distinguish the molecules and their individual movements, the observable properties of gases can only be mean properties, attributable, that is to say, to the simultaneous and more or less similar actions of an immense number of molecules. The physical aim of the theory is to deduce these mean properties from complicated and apparently inextricable molecular motions.

The mathematical calculations to which we are led should, therefore, bear upon these motions, the details of which are unknown to us and whose general characters alone we are able to imagine. They should lead to average results which will depend upon these general characteristics only. In a word, we must appeal to the calculus of probabilities. The mechanics of gases are statistical, and the physical laws to which they lead are statistical laws. We cannot, therefore, hope to obtain laws of certainty, but only laws which are very probable or practically certain. This character of the theory, which at some periods has brought it into disfavour, should,

on the contrary, be regarded as a most suggestive one. As we shall see, it has enabled a new light to be thrown on the second law of thermodynamics, and has cleared our ideas on the fundamental nature of this principle.

Unfortunately, the extreme complication of the molecular motions brings with it a corresponding complication in the mathematical calculation which is necessary for the complete and rigorous development of the theory. This complication is such that it frequently necessitates a resort to simplifications which are sometimes hazardous as a means of pursuing the calculation. It is possible, however, to define at each stage the degree of rigour claimed, and, since by such summary procedure, we are led to results whose agreement with experiment is almost surprising, there is no reason to doubt the accuracy of the principles. In spite of difficulties we are unable to deny, it is very satisfactory on the whole that we may consider the theory as built upon foundations which are almost unassailable.

The small compass of this volume forbidding all purely mathematical developments, we shall be content to study the simplest hypotheses, for example that of elastic collisions, and to arrange the results in logical order ; in a word, to expound the sequence of ideas rather than the detail of calculations. We shall refer the reader anxious to extend his knowledge to the works mentioned in the bibliography at the end of the volume.

A few historical notes may be useful to conclude the generalities which have gone before. Physicists do not consider a theory properly scientific unless it has adequate experimental foundations. It does not appear, therefore, to be of much interest to probe classical antiquity or Greek and Roman philosophies in a search for the origin of atomistic theories. Precise knowledge of the experimental laws of the compressibility of gases dates in reality only from Boyle and Marriotte. It is only just, however, to consider Daniel Bernouilli (1730) as the founder of the modern kinetic theory ; it was he, in fact, who first explained the law of Marriotte by molecular motions. The complete development of atomism, however, only began with the discovery of the fundamental laws of chemistry, in particular the laws of Dalton, Avogadro, and Gay-Lussac, which confirmed the atomistic doctrine at the beginning of the nineteenth century. Since that time progress has been rapid. But it was principally in the middle of the nineteenth century, with Maxwell and Clausius, that the theory received the firm mathematical basis on which it rests to-day. More recently the works of Boltzmann, Kirchhoff, Van der Waals, and, among our contemporaries, those of Lord Rayleigh, H. A. Lorentz, Brillouin, etc., have given it a breadth which, going hand in hand with experimental progress, has made it one of the most vital branches of theoretical physics.

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ERRATA

Page 37, bottom line :—

For $k = 0.3503$ read $k = 0.499$, the value given by Chapman and Enskog for monatomic gases.

Page 156. Table I I . should read :-

Gas.	$C \times 10^{-2}$ cm./sec.	$v \times 10^{-2}$ cm./sec.	$n \times 10^6$	$l \times 10^5$ cm.	$\sigma \times 10^8$ cm.
H ₂	1838	1693	84	11.07	2.88
O₂	461	425	190	6.27	3.56
N ₂	493	454	167	5.89	3.78
Ar	413	380	211	6.21	3.46
He	1307	1204	187	17.45	2.18
CO	493	454	166	5.85	3.83
CO ₂	393	362	137	3.85	4.00
H ₂ O		566	90		3.38
Air	485	447	171	5.92	

Page 157. Table I. should read:

Gas.			$v \times 10^8$
Hydrogen, H ₂			154
Oxygen, O ₂			67.8
Nitrogen, N ₂			77.1
Argon, Ar			61
Helium, He			69
Carbon Monoxide, CO			77.6
Carbon Dioxide, CO ₂			94
Air			75.5

THE KINETIC THEORY OF GASES

CHAPTER I

DISTRIBUTION OF VELOCITIES. LAWS OF PERFECT GASES

I. Molecular Structure of a Gas.—The molecules which constitute a gaseous medium should be considered as particles of extremely small dimensions, animated by rapid and unceasing movements in all directions. The movements of these particles remain sensibly rectilinear and uniform so long as they do not pass sufficiently near one another to be deflected by their mutual interactions or by their collisions. At the moment when an accidental "encounter" of this nature is produced, the velocities of the molecules concerned suffer abrupt changes in magnitude and in direction, changes the duration of which are very short compared with the time during which the molecules move freely. The trajectories of the molecules must therefore be represented as irregular broken lines, of which each element is approximately straight. Collisions of molecules with the walls of the containing vessel introduce in the trajectories perturbations of the same type as those which originate from intermolecular collision.

We shall learn to measure molecular diameters, to calculate the number of molecules contained in a given volume of the gas, as well as their velocities of translation. We shall see also that, at ordinary temperatures and pressures, molecules behave as particles of very small dimensions relative to their mutual distances, projected with velocities comparable to those of rifle-bullets, and accumulated in every element of volume of the gas in enormous numbers. The shape and structural details of the molecules naturally depend on the chemical nature of the gas considered. In a complex gaseous mixture the molecules will be of several kinds. Finally, the translatory motion that the molecule experiences as a whole does not exclude, in the general case, movements of the molecule about its centre of gravity or even internal movements of different parts of the same molecule relative to one another.

2. Distribution of Velocities : Maxwell's Law.

—Let us consider a pure gas in thermal equilibrium contained in a solid envelope at a uniform temperature. We shall assume that molecular motions and collisions do not affect the molecular density of the gas, that is to say, the number of molecules n per cm^3 , and, consequently, that this density remains uniform on the average in the course of time throughout the gas. In the second place, we shall assume that, in each element of volume the molecules possess velocities distributed in all directions, whose magnitudes are themselves distributed according to some law independent of the

The elements of volume with which we are concerned here are always supposed to be very small compared with the total volume of the gas, but sufficiently large to hold an immense number of molecules. This dual condition is realisable since, as we shall see, there are 2.9×10^{16} molecules per cubic millimetre of a gas under normal conditions,

position of the selected element; this law will only be modified by molecular collisions. To simplify the terminology, we shall say that the gas is in a state of molecular chaos.

The preceding hypotheses are fundamental, and indispensable for the application of probability considerations. They lead to a knowledge of the law of distribution of velocities in the state of thermal equilibrium.

If all the molecules initially possessed the same velocities, this uniformity would be destroyed immediately by collisions. With the aid of the hypothesis of molecular chaos, Maxwell has shown that, when the state of thermal equilibrium is attained, the magnitudes of the molecular velocities distribute themselves according to a law which is no longer modified by collisions. His demonstration, claiming little rigour at first, has been improved and generalised by himself, and subsequently by Boltzmann, Jeans, and others. It is valid whatever may be the complexity of molecular structure and mutual interaction. For the present we shall assume the truth of the result obtained, considering it as verified by its consequences.*

Let

$$dn = nf(u, v, w)dudvdw \quad . \quad (I)$$

be the number of molecules per cm^3 whose velocities have components comprised within the limits, u , v , w and $u + du$, $v + dv$, $w + dw$. To ascertain the law of distribution of velocities we must determine the function n . The velocity c of a molecule is often represented graphically by a point in space whose co-ordinates are equal to the components of its

The elements of a general deduction are given in Chapter V.

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velocity u, v, w ; such a point is called a velocity-point. The product $du dv dw$, therefore, represents an element of volume which may conveniently be abridged to dr . According to this, we shall be able to say that the number of molecules per cm.^3 whose velocity-points lie within the element dr is $n f(u, v, w) dr$, or again that the probability that one molecule should have its velocity-point in the element dr is $f(u, v, w) dr$.

With this assumption the law of permanent distribution obtained by Maxwell for the state of thermal equilibrium is the following:—

$$f(u, v, w) = ae^{-b(u^2 + v^2 + w^2)} = ae^{-bc^2}.$$

a and b are constants the significance of which will appear later.

Expressing the total number of molecules per cm.^3 by n , we find

$$\int f(u, v, w) du dv dw = 1,$$

the sign of integration representing a triple integral extending from $-\infty$ to $+\infty$ for each variable. Replacing f by its mathematical expression and making use of well-known mathematical formulae,* we get the relation

$$a = \sqrt{\frac{b^3}{\pi^3}}.$$

It is convenient to replace b by hm , in which m is the mass of a molecule and h is a new constant. We may therefore put

$$a = \sqrt{\frac{h^3 m^3}{\pi^3}} \quad . \quad . \quad . \quad (2)$$

$$f(u, v, w) = \sqrt{\frac{h^3 m^3}{\pi^3}} e^{-hm(u^2 + v^2 + w^2)} \quad . \quad (3)$$

$$dn = n \sqrt{\frac{h^3 m^3}{\pi^3}} e^{-hm(u^2 + v^2 + w^2)} du dv dw \quad . \quad (4)$$

Integrating equation (4) with respect to v and w from $-\infty$ to $+\infty$, we obtain the number of molecules per cm.³ whose components of velocity parallel to a given direction Ox are comprised within the limits u and $u + du$. The result obtained,* which is frequently of service, is

$$dn_1 = n \sqrt{\frac{hm}{\pi}} e^{-hmu^2} du \quad . \quad . \quad (5)$$

We can interpret formula (4) by saying that the probabilities that the components of velocity of a molecule shall lie between u and $u + du$, v and $v + dv$, w and $w + dw$, are independent; the probability $f(u, v, w)dr$ is the product of three probabilities which depend on u , v , and w respectively.

Formula (4) enables us to obtain quite easily the number dn_c of molecules whose velocities lie between c and $c + dc$, without any reference to their direction. It is sufficient to note that for these molecules, $u^2 + v^2 + w^2$ is a constant equal to c^2 , so that their number is obtained by integrating the

* See Note I at the end of the volume. Formula I.

The formula (5) is identical with that which Gauss has given for the Law of Errors, and which is occasionally referred to as the Law of Large Numbers. If we measure a quantity, and if u is the error in one measurement taken among a large number of others, the number dn of measurements for which the error lies between u and $u + du$ is given by formula (5).

element of volume $dudvdw$ for the whole space between spheres of radii c and $c + dc$, which is therefore $4\pi c^2 dc$. We find in this way

$$dn_c = 4n \sqrt{\frac{h^3 m^3}{\pi}} e^{-hmc^2} c^2 dc \quad (6)$$

The curve opposite (Fig. I), which represents the

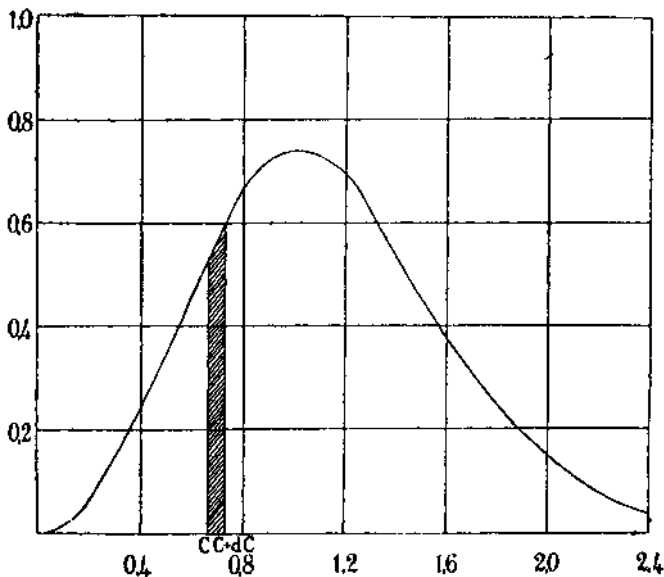


FIG. I.

function $2x^2 e^{-x^2}$, gives a concrete idea of the law of distribution of velocities: the number of velocities, the magnitudes of which lie between two neighbouring abscissae c and $c + dc$, is proportional to the shaded area.

3. Average Velocities.—If G is any quantity whatever corresponding to a molecule, the arith-

metical mean of the values G may take for all the molecules in a given element of volume is referred to as the mean value of this quantity in this element of volume, and is represented by $\bar{G}$:

Formula (6) enables us to calculate the mean square velocity, that is to say the velocity C , the square of which is equal to the average of the squares of all the velocities. We obtain actually *

$$C^2 = \bar{c^2} = \frac{1}{n} \int_0^{\infty} c^2 dn_c = \frac{3}{2hm} \quad . \quad . \quad (7)$$

This velocity C plays an important part in everything that follows, and it is important to guard against confusing it with the real mean velocity, v , given by

$$v = \bar{c} = \frac{1}{n} \int_0^{\infty} c dn_c = \sqrt{\frac{2}{\pi hm}} \quad . \quad (8)$$

or with the most probable velocity c_0 , which makes the expression (6) a maximum, and consequently has the value

$$c_0 = \frac{1}{\sqrt{hm}}$$

We see that

$$\frac{v}{C} = \sqrt{\frac{8}{3\pi}} \quad . \quad . \quad . \quad (8a)$$

and

$$\frac{c_0}{C} = \sqrt{\frac{2}{3}}$$

* Note I. Formula 5. The arithmetical mean of the values of c^2 , which is, rigorously speaking, an ordinary sum, has been replaced by a definite integral. This method of calculation is justified by the remark contained in the note on page 3.

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It is interesting, as an application of the preceding formulae, to calculate the number ν of molecules which cross an element of surface of one cm.² in one second (or which strike one cm.² of the wall per second) in a given direction. If the axis of x is perpendicular to the element considered, referring to formula (5) we have

$$\nu = \int_0^{\infty} udn = \frac{n}{2\sqrt{\pi hm}} = \frac{nv}{4} = \frac{nC}{\sqrt{6\pi}} \quad (9)$$

4. Calculation of the Pressure of a Gas.—We shall make this calculation assuming the molecules to be elastic solids of negligible dimensions, and thereby assuming the gas to be a perfect gas. The wall itself will be supposed perfectly elastic. Let f be the component, normal to the wall, of the force exerted upon it by a molecule in the process of striking it; and let Σf be the resultant of all the forces f for all the molecules in contact with the element s of the wall at an instant t . The average force exerted on the wall s during a time T , which is very great compared with the duration of a collision, will be

$$F = \frac{1}{T} \sum_0^T f dt.$$

Let us consider the pressure p on the element s as due to molecular collisions; the foregoing relation, supposing T equal to one second for simplicity, will give us

$$p = \frac{F}{s} = \frac{1}{s} \sum_0^1 f dt.$$

Now the integral $\int f dt$, extended over the period of one collision, is nothing more than the impulse conveyed to the wall by the molecule during this time. We know also, from the laws of impact, that this impulse is equal to the rate of change of the momentum of the molecule striking it. In consequence the total force ps which the gas exerts on the wall s is equal to the total variation of momentum suffered in one second by all the molecules which have struck the element s in this time. The axis of x being perpendicular to the element s , we shall let u be the component, considered positive, of the velocity of a molecule perpendicular to the wall. Since the collision is elastic, the change of momentum of this molecule in consequence of the collision is $2ma$, and we may write

$$ps = 2m \sum u \quad . \quad . \quad . \quad (10)$$

the sum $\sum$ being extended over all the molecules which have struck the element s in one second.

Of these molecules, we shall consider first of all only those which are endowed with a velocity completely defined in magnitude and direction. Let v be the number of these molecules per cm^3 of the gas, a number which is everywhere the same by virtue of the assumption of molecular chaos. The molecules of the category considered which strike s in the time dt are evidently contained, at the beginning of this time, in an oblique cylinder of base s and sides parallel to the direction of the velocity c and equal to cdt . The volume of this cylinder is $sadt$ and the number of molecules of the type considered which are contained in it is $vsadt$. Furthermore, they all strike the element s , since the smallness of the molecules allows us to neglect their mutual collisions.

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They contribute, therefore, a term $2msv\bar{u}^2$ to the second member of (10). To determine the total value of this second term, it is now sufficient to sum the preceding expression for all magnitudes and directions of the molecules which collide with s in unit time. Remembering that by virtue of the definition of mean values already given in Art. 3, we may write

$$2 \sum v u^2 = n \bar{u}^2; *$$

we get finally

$$p = n m \bar{u}^2.$$

It is obvious from considerations of symmetry, that

$$\bar{u}^2 = \bar{v}^2 = \bar{w}^2 = \frac{1}{3} \bar{c}^2.$$

We may thus write

$$p = \frac{1}{3} n m \bar{c}^2 = \frac{1}{3} n m C^2 \quad . \quad . \quad (11)$$

If we introduce the absolute density or specific mass of the gas $\rho = nm_t$ we find

$$(11\phi) \quad p = \frac{1}{3} \rho C^2 = \frac{2}{3} \frac{\rho c^2}{2} \quad . \quad .$$

We see, therefore, that the pressure of a perfect gas is numerically equal to two-thirds of the total kinetic energy of the molecules contained in one cm.³ of the gas.

The preceding demonstration is absolutely independent of any particular form of the law of

* To obtain the mean value of u^2 the sum must be extended to all values of u from $-\infty$ to $+\infty$. We must, therefore, double the sum extending over positive values of u alone.

distribution of velocities. It involves only the hypothesis of molecular chaos and that of elastic collisions.

If we take account of Maxwell's law, the formula obtained (n) may be completed by means of the formula (7), and assumes the form

$$p = \frac{n}{2h} \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

5. Laws of Perfect Gases. Kinetic Interpretation of Temperature.—If V represents the molecular volume of the gas and M its molecular weight, equation (ua) may be written

$$pV = \frac{1}{3} VC^2 = \frac{1}{3} MC^2 \quad \cdot \quad \cdot \quad (13)$$

From this are derived the laws of Marriotte and Gay-Lussac, or the laws of perfect gases. The well-known formula for perfect gases may, in fact, be written

$$pV = RT \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

representing by T the absolute temperature and by R the gas constant referred to one gramme-molecule (8.32×10^7 in C.G.S. units). It becomes identical with formula (13) if we put

$$\frac{1}{3} MC^2 = RT \quad \cdot \quad \cdot \quad (15)$$

or again, calling N the ratio $\frac{M}{m}$, that is the number of molecules contained in a gramme-molecule, and equating α with the factor $\frac{3R}{2N}$

$$\frac{mC^2}{2} = \frac{3R}{2N} T = \alpha T \quad \cdot \quad (16)$$

We are therefore compelled to consider the absolute temperature of a gas as proportional to the mean kinetic energy of translation of its molecules: to every uniform temperature there is a corresponding uniform distribution of kinetic energy, and molecular collisions furnish the mechanism which leads to the equalisation of temperature.

6. Mixture of Gases. Equipartition of Kinetic Energy of Translation.—The kinetic definition of temperature which is implicit in formula (16) stands in need of a supplement and justification. Up to the present we have only studied a gas composed of identical molecules. If we mix several different gases, whose molecules have masses $m_1, m_2 \dots$ we know that equilibrium is established, after complete diffusion, with a uniform distribution of temperature and pressure throughout the mixture. In applying to the mixture the same lines of reasoning which have culminated in the law of distribution of velocities for a simple gas, we are led to the law of distribution of velocities for each of the groups of molecules which form the mixture. These laws are expressed by formulae analogous to (4) and (6). For molecules of mass m_1 , for example, the number per cm.³ whose velocity lies in the range c_x and $c_x + dc_x$ is given by

$$dn_1 = 4n_1 \sqrt{\frac{h^3 m_1^3}{\pi}} e^{-h m_1 c_1^2} c_1^2 dc_1$$

calling n_x their "molecular density". The formulae valid for molecules of mass $m_2, m_3 \dots$ are derived from the same expression by replacing the suffix 1 by 2, 3, . . . and keeping the same constant h .

This last result is essential. If, in fact, we work out, as in Art. 3, the mean square velocities C_1, C_2

... of the different kinds of molecules, we find

$$C_1^2 = \frac{3}{2hm_1}, \quad C_2^2 = \frac{3}{2hm_2} \dots$$

and we conclude therefrom that the mean kinetic energies will have identical values in the state of equilibrium

$$\frac{m_1 C_1^2}{2} = \frac{m_2 C_2^2}{2} = \dots = \frac{3}{4h} \quad \cdot \quad (17)$$

This important result permits us to complete the kinetic interpretation of temperature. We know that, in practice, the mixture of several gases, taken at equal temperatures and pressures, occurs without change of temperature. Therefore, if the kinetic definition of temperature given by formula (16) has any real significance, the mean molecular kinetic energy should have in the mixture precisely the same value as before. Now we have just seen that it becomes identical for all the gases. Therefore it must have been so initially, and the constant a of formula (16) is a universal constant. Comparison of formulae (16) and (17) allows us to express it in the form

$$a = \frac{3R}{2N} = \frac{3}{4hT} \quad \cdot \quad \cdot \quad (18)$$

It appears that the number h contained in the formula for the distribution of velocities according to Maxwell is inversely proportional to the absolute temperature.

The kinetic energy of each molecule of the mixture under consideration only depends on three degrees of freedom, to wit the three components of its translational velocity, u , v , w . From a consideration of symmetry, the mean values of the kinetic energies

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$\frac{mu^2}{2}$, $\frac{mv^2}{2}$, $\frac{mw^2}{2}$, corresponding to each of the degrees of freedom, are the same, and consequently equal to one-third of the mean total kinetic energy, $\frac{mC^2}{2}$. According to (16) and (18) their common value is $\frac{RT}{3N}$ or $\frac{I}{4h}$. This result is a particular case of a principle which we shall meet later under the name of the Equipartition of Kinetic Energy, and is susceptible to an important generalisation.

The train of reasoning which has been applied to the calculation of the pressure of a gas may be utilised without difficulty in the case of a mixture of several gases. The formula to which we are led is an obvious generalisation of formula (na), and, taking no account of the law of distribution of velocities, may be written

$$p = \frac{I}{3} (\rho_1 C_1^2 + \rho_2 C_2^2 + \rho_3 C_3^2 + \dots).$$

On the other hand, if this law is taken into account, formula (12) gives place to the generalisation

$$p = \frac{I}{2h} (n_1 + n_2 + \dots).$$

In this form we see that the pressure of the mixture is equal to the sum of the pressures which the different gases would have exerted if they occupied the volume of the mixture separately. This is Dalton's Law of gas mixtures. We see also that the pressure of a gaseous mixture at a given temperature only depends on the total number of molecules per cm.³

7. The Law of Avogadro.—Formula (ia) shows

that, at the same temperatures and pressures, all gases have the same molecular density ; that is to say they contain the same number of molecules per cm.³ This is the Law of Avogadro, which is thereby intimately connected with the laws of perfect gases.

In the same way formula (r8) shows that, like a , the number N is a universal constant. This constant, which represents the number of molecules per gramme-molecule (or atoms per gramme-atom) is often called Avogadro's Constant. Its numerical value, determined by numerous distinct and concordant methods, some of which will be described later, is known nowadays with some accuracy ; it is in the neighbourhood of 65×10^{22} . From it the numerical values of h and n^* are easily deduced.

8. Numerical Values of Molecular Velocities.—

Formula (na) enables us to calculate the mean square velocities of the molecules of all gases, since the pressure and the absolute density are easily determined by experiment. The following table gives a few values obtained under normal conditions of temperature and pressure:—

Hydrogen	.	.	1838 metres per second.
Oxygen	.		461
Nitrogen	.		- 493

It is worthy of note that the calculated velocities are, as they should be, of the same order as the velocities of flow of the gases into a vacuum through small openings, and also of the same order as the velocity of sound in the gases.

9. Dilute Solutions. Osmotic Pressure.—The properties of dilute solutions are very similar to those of a gas. The dissolved molecules exert upon

See Chapter XI for a collection of all the numerical results,
t See the more complete numerical results in Chapter XI.

a surface immersed in the solution a pressure, called the osmotic pressure, which is analogous to the pressure of a gas. Van't Hoff has confirmed this analogy by showing that the dissolved substance exerts an osmotic pressure numerically equal to that which it would exert in the same volume if it could assume the gaseous state without change of temperature. In other words, the equation (14) valid for perfect gases is applicable to dilute solutions with the same value of the constant R , if the osmotic pressure is represented by p .

The kinetic theory enables us to understand this result. In a solution we can no longer neglect intermolecular actions, but we may assume that the molecules of a substance in dilute solution are subject to the action of forces exerted by the solvent, which balance on the average. Their movements will, therefore, be approximately the same as those of the molecules of a gas mixed with another, and we shall be able to calculate the pressure they exert by the same methods of argument as in the case of a gas.*

We shall, therefore, be led to admit the validity, not only of formula (14) but also that of formulae (n), (16) and (17). In other words, the mean kinetic energy of a dissolved molecule will be the same as that of a gaseous molecule at the same temperature ; the principle of equipartition will apply to dissolved molecules.

We shall see later that the validity of the principle has been verified even for very large particles in suspension in colloidal emulsions.

* In the well-known experiments where the osmotic pressure is demonstrated by means of a semi-permeable membrane, the actions between molecules of the solvent and molecules of the dissolved substance no longer compensate one another in the general case, and consequently assume a great importance. In this connection the reader is referred to a note by M. Langevin in the *Journal de Chiquie Physique* for 1912.

CHAPTER II

REAL GASES. EQUATION OF STATE OF VAN DER WAALS' THEORY OF THE VIRIAL

10. Equation of State of a Real Gas.—We have been led to the laws of perfect gases by neglecting the molecular dimensions together with the forces which may be operative between the molecules, except in the case of their collisions. Now molecular dimensions evidently come into consideration at high pressures, tending to diminish the compressibility, and cannot remain negligible indefinitely, compared with the distances between the molecules themselves. On the other hand, liquids can only maintain an approximately constant volume under the influence of internal cohesive forces or forces of intermolecular attraction. The continuity of the gaseous and liquid states, proved by the experiments of Andrews, leads to think that forces of cohesion much more feeble in gases than in liquids since the mean displacement of the molecules is much greater there, now assume appreciable values. We find a confirmation of this idea in the fact that real gases, at fairly high pressures are more compressible than Boyle's Law would lead us to expect.

It is by developing this dual point of view that we may attempt to introduce corrections to the equation of perfect gases in order to make it an

equation of state of a real gas. Unfortunately, these corrections can only be made approximately, and only if the gas does not deviate too much from the ideal state. The numerous assumptions made in this way have led to equations of state which, without representing the facts with rigorous precision, give, on the whole, so exact a representation of the actual properties of gases, that they have constantly served as guide in all experimental research carried out in this domain.

II. The Formula of Van Der Waals. — The oldest and best-known of the formulae which have been derived in this way is that of Van der Waals, and we shall proceed to indicate how it is derived.

First, to take account of the dimensions of the molecules, a sphere is drawn concentrically with each of them, the radius of which is equal to the molecular diameter a . This sphere, called the "sphere of influence" of the molecule, is that within which the centre of no molecule can penetrate. The movements of a given molecule may, therefore, be studied by considering it as a point at its centre, subject to the condition that this point is denied admission within the spheres of influence of the other molecules. If V is equal to the total volume of the gas (which we will take equal to the molecular volume), N the total number of molecules (Avogadro's constant), and therefore $\frac{N}{V}$ or n the molecular density defined above, each molecule carries with it in its motion a sphere of influence of volume $\frac{4}{3}\pi\sigma^3$, so that, for the centre of a given molecule, the volume excluded is $\frac{4}{3}\pi\sigma^3(N-1)$, or what comes to the same thing since N is very large,

$\frac{4}{3} \pi \sigma^3 N$. The volume remaining is consequently only $V - \frac{4}{3} \pi \sigma^3 N$, so that the real molecular density in the whole gas is increased, assuming the value

$$n' = \frac{N}{V - \frac{4}{3} \pi \sigma^3 N}.$$

We notice now that the centres of the molecules which collide with the wall never get nearer to it than $\frac{\sigma}{2}$. Let us draw a surface parallel to the wall at this distance. The centres of the molecules strike this imaginary wall, in the same way as the molecules themselves struck the real wall when they were considered as points. Therefore we must apply to an element s of this surface * the same argument as in § 4 of Chapter I for the calculation of the pressure.

Consider a cylindrical element of volume dv of infinitely small height $u dt$, and base s , such as occupied our attention on page 9.

If we denote by dv' the fraction of its volume which is freely accessible to the centre of a molecule, the number of molecules contained in it will be obviously $n' dv'$. Now the reasons which exclude a part $dv - dv'$ of the element dv are analogous to those which exclude a fraction of the total volume, with the difference, however, that, the element dv being at the distance $\frac{\sigma}{2}$ from the wall, those hemispheres

* The volume included between this surface and the wall is also "out of bounds," but we may neglect it in comparison with the total volume, if the latter is sufficiently great.

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of the spheres of molecular protection which are furthest from the wall at the moment when the molecules arrive in its neighbourhood, are excluded a priori, leaving only the remaining hemispheres to be accounted for, with volumes of $\frac{2}{3} \pi \sigma^3 c h$. We deduce immediately that

$$\frac{dv - dv'}{dv} = \frac{\frac{2}{3} \pi \sigma^3 N}{V}$$

or

$$dv' = dv \left(1 - \frac{2}{3} \pi \sigma^3 \frac{N}{V} \right).$$

The number of molecules contained in the element dv is therefore

$$n' dv' = \frac{N dv \left(1 - \frac{2}{3} \pi \sigma^3 \frac{N}{V} \right)}{V - \frac{4}{3} \pi \sigma^3 N} = \frac{N dv}{V - b}$$

where

$$b = \frac{2}{3} \pi \sigma^3 N^* \quad . \quad . \quad . \quad (19)$$

and neglecting powers of b higher than the first. We see that the gas behaves exactly as if its total volume were simply diminished by an amount b .

The equation of state thus becomes

$$p (V - b) = RT.$$

The constant b is called the "co-volume"; it re-

* If the element dv were taken inside the gas, we should obviously have arrived at the equation $ridv^* = \frac{N dv}{V} = ndv$.

presents a volume four times as large as the total volume of the molecules.

Secondly, to take account of the intermolecular cohesive forces, we will consider them as central forces of attraction acting over fairly large distances and operating from each molecule. Their mean effect in the interior of the gas is nil, by symmetry. But it is no longer so near the wall; in this region the molecules are evidently acted upon by a mean force of attraction directed normally to the interior, superposed on the action of the wall itself. The effect is the same as it would be if the pressure p were augmented by a supplementary term p_i called the internal pressure. Without knowing the law of molecular attraction, we are able to predict the form of this term. The supplementary force referred to unit surface of the wall, is at the same time proportional to the density of the molecules attracted and to that of the attracting molecules.

It is therefore proportional to n^2 or to $\frac{1}{V^2}$. We shall henceforward put

$$p_i = \frac{a}{V^2}$$

and the equation of state becomes

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad . \quad (20)$$

by including this new correction. This is Van der Waals' equation.

The very imperfect arguments which have led to it show that this equation only expresses the truth to a first approximation, valid at the most for quite low pressures. It also explains quite easily the fact that numerical agreement with experiment

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remains unsatisfactory in detail. But the equation furnishes so complete a qualitative representation of the isotherms of actual fluids, that it may be considered, nevertheless, as one of the most beautiful justifications of the kinetic theory.

It is very remarkable, in particular, that Andrews' isotherms for carbon dioxide are represented in their general form by Van der Waals' equation, even in the range where the fluid is very highly condensed. We must be content to recall that the formula also aids us to an interpretation of the critical phenomena and the existence of metastable states (retrograde vaporisation and condensation), and that it leads for the first time to the law of corresponding states.

12. Other Equations of State.—Since the formula of Van der Waals explained and illuminated Andrews' results, experimental research on the gaseous state has developed very rapidly. Simultaneously many further attempts have been made to improve the equation of state and to attain still more accuracy in agreement with fact. Leaving aside all purely empirical work, we will give a few indications of the suggestions based on the kinetic theory.

In the first place, we notice that in Van der Waals' theory the ratio $\frac{b}{V}$ is small compared with unity, and we may therefore write the formula in the form

$$p + \frac{a}{V^2} = \frac{RT}{V} \left(1 + \frac{b}{V} \right) . \quad (20a)$$

The expression in brackets on the right-hand side of the equation is the beginning of a development in series of increasing powers of $\frac{b}{V}$. Various formulae

have been proposed containing terms of higher order and furnishing in consequence a closer approximation to the estimate of the influence of molecular dimensions. Similar modifications have been introduced in the term $\frac{a}{\sqrt{V}}$, expressing, for example, the term a as a function of the temperature.

One form of equation, proposed initially by Dieterici and firmly supported by a theory due to Jeans, is the following :

$$p(V - b) = RTe^{-\frac{a}{RTV}};$$

a and b are approximately constant, but, strictly speaking, they are unknown functions of V and T . The particular interest of this new equation is that, without being much more complicated than that of Van der Waals, it is clearly a generalisation of it. It reduces to the same form when a and b are small, and seems to give, if anything, better concordance with experiment. The agreement still remains imperfect however.

13. Equation of State deduced from the Virial Theorem.—Let x, y, z be the co-ordinates of the centre of gravity of a molecule, u, v, w the components of its velocity c , and X, Y, Z the components of the force acting upon it. The equations of its movement are of the type

$$m \frac{du}{dt} = x.$$

Now

$$\begin{aligned} \frac{d(mxu)}{dt} &= m \left(u \frac{dx}{dt} + x \frac{du}{dt} \right) \\ &= mu^2 + xX. \end{aligned}$$

If we integrate this equation between two arbitrary

instants 0 and t , and divide the result by t , we find, employing the usual notation for mean values,

$$\frac{m}{t}(x_t u_t - x_0 u_0) = m\overline{u^2} + \overline{Xx}.$$

The co-ordinates and velocities of the molecules remaining finite, the first term tends towards zero as t increases indefinitely. It is only necessary, then, to extend the averages over a sufficiently long time to be able to write

$$m\overline{u^2} + \overline{Xx} = 0.$$

If we add to this equation the two analogous relations

$$\begin{aligned} m\overline{v^2} + \overline{Yy} &= 0 \\ m\overline{w^2} + \overline{Zz} &= 0 \end{aligned}$$

relative to the other axes of co-ordinates, we find

$$m\overline{c^2} + \overline{Xx} + \overline{Yy} + \overline{Zz} = 0$$

and summing once again for all the molecules of the gas

$$\sum m\overline{c^2} + \sum (\overline{Xx} + \overline{Yy} + \overline{Zz}) = 0 \quad . \quad (21)$$

The expression $\frac{1}{2}\Sigma(\overline{Xx} + \overline{Yy} + \overline{Zz})$ has been called by Clausius the virial of the forces acting on the gas, and the remarkable equation derived above expresses the virial theorem; the total kinetic energy of translation of the molecules of the gas is equal and opposite in sign to the virial of the forces acting on it.

In order to deduce the equation of state of the gas from the relation (21), suppose the gas to be placed in a parallelepiped, the edges of which, of length α , β , γ , are taken as axes of co-ordinates. We will

neglect first of all the internal forces. The only external forces which act on the gas are supposed to be the pressures exerted by the walls. The walls perpendicular to Ox exert forces $+p\beta\gamma$ and $-p\beta\gamma$ (p representing the pressure of the gas). As their abscissae are 0 and a , the corresponding term in the virial is $-\frac{pa\beta\gamma}{2}$. If, as before, N is the total number of molecules of the gas, equation (21) becomes

$$Nm\bar{c}^2 - 3pa\beta\gamma = 0$$

or again, introducing the molecular density n ,

$$p = \frac{1}{3} nm\bar{c}^2.$$

We have thus arrived at equation (n), which expresses the law of perfect gases.

To consider the effect of internal forces, we will let $f(r)$ represent that acting between two molecules a distance r apart, whose co-ordinates are x, y, z and x', y', z' . The force acting on the first molecule has components

$$f(r) \frac{x' - x}{r}, \quad f(r) \frac{y' - y}{r}, \quad f(r) \frac{z' - z}{r}.$$

It contributes to the virial the terms

$$\frac{f(r)}{2r} [x(x' - x) + y(y' - y) + z(z' - z)].$$

The expression referring to the second molecule is

$$\frac{f(r)}{2r} [x'(x - x') + y'(y - y') + z'(z - z')],$$

and if we add it to the preceding expression, we get

$$-\frac{r(f)r}{2}, \quad \begin{array}{l} \text{be station.} \\ \text{h we shall draw} \end{array}$$

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The equation of the virial gives, therefore,

$$3p = n \cdot m \bar{c}^2 - \sum r f(r)$$

the sum Σ extending to all pairs of molecules contained in unit volume. By introducing the molecular volume V and extending the sum over all this volume, we may write

$$pV = RT - \frac{1}{3} \sum r f(r).$$

Such is the correction which must be made to the equation of perfect gases in order to take account of intermolecular forces.

If these forces are forces of cohesion or attractive forces with a large radius of action, such as those introduced by Van der Waals, we arrive once more, as shown by H. A. Lorentz, at the same formula as Van der Waals, in the form (20a). But we may develop the calculation more completely in various ways. For example, we may replace elastic collisions by large repulsive forces acting between molecules at very small distances, taking precedence over the attractive forces of cohesion at that moment; they will contribute a term to the virial which will be superposed on the cohesion term. Carrying out the calculation in the way Reinganum has done, we find the equation of state

$$pV = RT \left(1 + \frac{be^c}{V} \right) + \frac{k}{V} \phi(T).$$

This is a generalisation, both interesting and new, of Van der Waals' equation, and one which reduces to the same form when $c = 0$ and $R\phi(T) = -a$.

CHAPTER III

MEAN FREE PATH. VISCOSITY. THERMAL CONDUCTIVITY. DIFFUSION

14. Mean Free Path.—The space traversed by a molecule between two successive collisions is an extremely variable quantity, but we may endeavour to evaluate its mean value, following Clausius. This value has been given the name of the "mean free path," or the "mean path" of a molecule. The problem is easily stated if the molecules are elastic spheres. At least, only one difficulty is encountered; the numerical coefficient of the result depends upon the definition adopted of the term "mean," a fact which has no great importance in its applications. But, if we dispense with the hypothesis of elastic collisions and consider the molecules as centres of force acting at a distance and deflecting one another from their respective courses, the free paths are no longer precisely defined and the conception of mean free path disappears. In spite of this difficulty the idea has rendered great service, and must still preserve an important place, particularly in an elementary exposition.

First of all let us attempt the evaluation of the mean free path, using a simplified train of argument. We shall consider all the molecules to be stationary, with the exception of one, about which we shall draw

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a sphere, the sphere of influence, of radius equal to the diameter a of a molecule. It is clear that this molecule will move in straight lines, in such a way that the surface of its protective sphere never meets the centre of any other. If v is the velocity, supposed constant, of the mobile molecule, the volume swept out in one second by the surface of its sphere of influence will be $\pi a^2 v$, and, representing by n the molecular density, $\pi a^2 v n$ centres of other molecules will be included within this volume. This number therefore gives us the number of collisions ν suffered by the moving molecule in one second. Its mean free path is deduced from it directly; it is the average of the paths traversed between two collisions, that is,

$$l = \frac{v}{\nu} = \frac{1}{n\pi a^2}.$$

It is evident that it is inversely proportional to n , that is to the density $p = nm$ of the gas. At constant temperature it is inversely proportional to the pressure.

This argument presupposes every molecule to be immobile with one exception. To improve it, consider all the molecules endowed with a common velocity v . We may now revise the preceding calculation by replacing the absolute velocity of the molecule considered separately by its mean velocity r relative to the others. The number of collisions per second becomes $\pi a^2 r n$ and the mean free path

$$l = \frac{v}{\nu} = \frac{1}{n\pi a^2} \frac{v}{r}.$$

The calculation of the ratio $\frac{v}{r}$, effected by Clausius,

has given

$$\frac{v}{r} = \frac{3}{4}$$

and consequently

$$l = \frac{3}{4n\pi\sigma^2}.$$

Finally we may dispense with the assumption of a common molecular velocity v , and introduce the real law of distribution discovered by Maxwell. A new correction must, therefore, be applied to the foregoing result, giving Maxwell's formula, which is the one we shall adopt

$$l = \frac{1}{\sqrt{2}n\pi\sigma^2} \quad \cdot \quad \cdot \quad \cdot \quad (22)$$

The number of collisions per second is therefore

$$\nu = \sqrt{2}n\pi\sigma^2v \quad \cdot \quad \cdot \quad \cdot \quad (23)$$

for a molecule of velocity v , and the duration of a mean free path is

$$\tau = \frac{l}{v} = \frac{1}{\sqrt{2}n\pi\sigma^2v} \quad \cdot \quad (24)$$

Maxwell's argument may be applied to the more general case of a mobile molecule of mass m' in the midst of a gas whose molecules are of mass m (impurity in a gas). If σ_2 represents the average $\frac{\sigma + \sigma'}{2}$

* See Note II at the end of the book (p. 167).

By taking the average over the time instead of in space, Tait found, instead of the numerical factor $\sqrt{2}$, the factor 1.477 .

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of the diameters of the two types of molecule, the mean free path of the molecule of mass m' is

$$l' = \frac{1}{n\pi\sigma_1^2 \sqrt{1 + \frac{m'}{m}}} \quad \cdot \quad \cdot \quad (25)$$

15. Law of Distribution of Free Paths.—Since the molecular velocities differ, generally speaking, from their mean, being distributed about it according to Maxwell's law, the free paths also differ from the mean free path l , and we may now set out to determine how they are distributed about it.

Suppose that the molecules which have travelled a distance x without collision all have equal chances of suffering no collision for a further distance dx *. In other words, the probability of suffering no collision in the path $x + dx$ is composed of two independent probabilities: 1st the probability of no collision in the path x , which we may call $f(x)$; 2nd the probability of no collision in the further path dx ; this latter is obviously of the form $1 - adx$ (a being a constant), since the probability of collision in the small distance dx is necessarily proportional to this distance.

The rule of independent probabilities gives, therefore, the functional equation

$$f(x + dx) = f(x) + f'(x)dx = f(x)(1 - adx)$$

or
$$f'(x) = -af(x).$$

This is a form of the hypothesis already utilised under the name of "molecular chaos."

The constant a is independent of the path x , but may depend on the velocity of the molecule.

Hence

$$f(x) = be^{-ax}$$

in which b is a constant of integration.

The constant b is readily determined when we notice that the probability of a path without collision becomes absolute certainty if the path traversed is zero. The function $f(x)$ should therefore reduce to 1 when $x = 0$, which implies that $b = 1$.

To determine the significance of the constant a , write v as the total number of collisions experienced by one molecule in one second, that is the total number of its free paths. Of these there will be a number

$$vf(x) = ve^{-ax}$$

which exceed x . The number of those comprised between x and $x + dx$ is, therefore,

$$ve^{-ax} - ve^{-a(x+dx)} = ve^{-ax} (1 - e^{-adx}) = vadxe^{-ax}$$

using the expansion of e^{-adx} in a power series of dx , and neglecting higher powers than the first.

The sum of their lengths is

$$vax \, dx \, e^{-ax}$$

and, if we extend this sum to all the paths traversed in one second, we find for the velocity of the molecule

$$v = va \int_0^{\infty} e^{-ax} x \, dx = \frac{v}{a}.$$

The mean free path is consequently

$$l = \frac{v}{a} = \frac{1}{a}.$$

In fine, the probability that a molecule travels a distance x without collision

$$f(x) = e^{-\frac{x}{l}}$$

where l is the mean free path. The proportion of the molecules whose free paths are comprised within the limits x and $x + dx$ is, therefore,

$$\frac{dx}{l} e^{-\frac{x}{l}}$$

The consequence of this is that the number of molecules whose free paths exceed the value l is very small; thus only one molecule in 148 has a free path above $5l$, one in 22,027 has a free Path greater than $10l$, etc.

16. Viscosity of a Gas.—Imagine that a thin rigid lamina whose surface is large moves in its own plane with a uniform velocity U ,* parallel to another fixed plane, separated from the first by a thin layer of gas. Experiment shows that the gas does not behave in the manner of a perfect fluid, but that it adheres in some way to the moving sheet, and that by means of internal friction, transmitted from place to place, it tends to communicate its motion to the fixed plane.

In the steady state we may verify that: 1. The velocity of each layer of gas is proportional to its distance z from the fixed plane. It is therefore of the form

$$U = Az \quad . \quad . \quad . \quad (26)$$

2. Each unit of surface of the fixed plane is subjected to a dragging force parallel to the direction of motion,

* Small compared with the velocity of thermal motion of the molecules.

whose value, proportional to the velocity gradient, A or $\frac{dU}{dz}$, is of the form

$$R = \eta \frac{dU}{dz} \quad . \quad . \quad . \quad (27)$$

This same force per cm.² is also exerted by that portion of the gas situated on one side of an imaginary plane, parallel to our fixed and movable sheets, upon the portion of the gas on the other side of it. The coefficient η , which may depend upon conditions of temperature and pressure as well as upon the nature of the gas, is called the "coefficient of viscosity" or the "coefficient of internal friction" of the gas.

An analogous definition may be given for a liquid. The classical equations of the hydrodynamics of perfect fluids must be corrected by the introduction of viscosity terms proportional to the coefficient η , if they are required to account for the properties of real fluids, for example, for the phenomenon of the dragging of a rigid plane just described. Conversely, the experimental study of actual fluids will enable us, by comparison with theoretical formulae, to gain some knowledge of its coefficient of viscosity. It will be sufficient to mention, in this connection, the case of the flow of a fluid moving with moderate velocity through a narrow tube. The laws of this flow, experimentally discovered by Poiseuille, are easily interpreted by means of the hydrodynamical equations of viscous fluids. They are adequately expressed by the formula

$$I = \frac{\pi r^4}{8\eta l} (p_1 - p_2) \quad . \quad . \quad (28)$$

in which I represents the loss in volume of the fluid, and l the radius and the length of the tube, $p_1 - p_2$

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the drop in pressure or head between the two extremities of the tube. If we wish to introduce the loss in mass G in place of the loss in volume I , we must multiply the preceding expression by the absolute density p , which, according to formulae (na) and (15), will give for a gas

$$G = \frac{\pi r^4}{8\eta l} (p_1 - p_2) \frac{pM}{RT} . \quad (28a)$$

in which p is the mean pressure of the issuing gas. The loss in mass G is therefore proportional, not only to the pressure drop, but also to the average pressure of discharge.

Formula (28) furnishes an experimental method for the measurement of the coefficient of viscosity of a fluid. Applied in the first case to liquids, it gives the value 0.013 C.G.S. for water at 10° C. For gases the numerical values obtained are much smaller. A few such results are :—

Hydrogen	.	84 X 10^{-6}	C.G.S. under normal	
			[conditions.	
Carbon Dioxide		137 X 10^{-6}	„	
Air	.	171 x 10^{-6}	„	„

A more complete series will be given in Chapter XI.

17. Theory of Viscosity.—The kinetic interpretation of the internal friction of a gas is due to Maxwell. Let us consider once more the fundamental experiment, and choose as xy plane the plane of the fixed sheet, in which the x . axis is parallel to the direction of motion, the z . axis being perpendicular to the sheets and directed towards the mobile sheet (upwards, for example).

It is a consequence of the fundamental equation of dynamics that the total force acting on a definite

mass is numerically equal to the increase of momentum of this mass in unit time. Since the part of the gas immediately above a plane P , whose ordinate is z , parallel to the plane of the two sheets, exerts an accelerating force on the portion of the gas below it, and consequently suffers an equal and opposite retardation, there must be an exchange of momentum between these two regions. By virtue of the existence of a velocity-gradient perpendicular to the sheets, the molecules above the plane P have a momentum greater on the average than that of the molecules below it. Through the agency of thermal agitation they carry a quantity of momentum from the upper layer to the lower, which is greater than that transported in the same time in the opposite direction by the molecules which cross the plane P from the lower layer to the upper. The algebraic sum of these momenta, taken over unit surface for unit time, gives a measure of the force of internal friction R , and consequently allows the coefficient of viscosity to be determined.

In order to simplify the calculation, suppose that all the molecules have a common velocity equal to their mean velocity v , and that between the instants they cross the plane P , and that when they last suffered a collision they have travelled the same distance l equal to their mean free path. If θ is the angle made by the direction of one of them with the positive direction of the z . axis, the last collision it suffered must have occurred in the plane P' , whose ordinate is

$$z' = z - l \cos \theta.$$

The velocity u' parallel to Ox , which the molecule possessed at that time, is the resultant of that due to thermal motion, say u , and the velocity with which

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the gas is drawn along in the plane P' , say Az (formula 26). We may therefore write

$$u' = u + Az' = u + (z - l \cos \theta) \frac{dU}{dz}.$$

We can obviously neglect the term u in the evaluation of the momentum transported across the plane P , since the transfer of momentum due to thermal agitation is zero on the whole. The quantity of useful momentum transferred across the plane P parallel to Ox is, therefore, simply

$$m(z - l \cos \theta) \frac{dU}{dz}$$

and only depends on the variable θ . Now, if n is the molecular density of the gas, the number of these molecules per cm.³ whose directions make angles with Oz comprised within the limits θ and $\theta + d\theta$ is*

$$\frac{n \sin \theta d\theta}{2}.$$

The number of these which cross unit surface of the plane P in unit time is the same as the number of molecules of the category considered which are contained in an oblique cylinder whose generatrix is inclined at an angle θ to Oz , of unit base and height $v \cos \theta$. Therefore

$$dn = \frac{nv}{2} \sin \theta \cos \theta d\theta.$$

Finally the total useful momentum transferred in one second across unit surface of the plane P parallel

* Since the solid angle of the conical annular space comprised within the two cones of angle θ and $\theta + d\theta$ is $2\pi \sin \theta d\theta$.

to the axis of x and in the direction of decreasing z is

$$R = - \int_0^\pi m(z - l \cos \theta) \frac{dU}{dz} \times \frac{nv}{2} \sin \theta \cos \theta d\theta$$

or

$$R = \frac{nmvl}{2} \frac{dU}{dz} \int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{nmvl}{3} \frac{dU}{dz} \quad (27a)$$

We find, therefore, for the force of viscosity R referred to unit surface, an expression consonant with formula (27), and comparison with this formula leads to the following expression for the coefficient of viscosity

$$\eta = \frac{1}{3} nmvl = \frac{1}{3} \rho vl \quad . \quad (29)$$

The calculation may be carried out more rigorously, taking account of the law of the distribution of velocities about the mean velocity v and also of the distribution of the free paths about the mean free path l . We are thus led to a formula of the same type

$$\eta = k\rho vl \quad . \quad (29a)$$

with a numerical value of the coefficient k very little different from the former

$$k = 0.3503.$$

This result brings several important consequences in its train: 1. We know (Art. 14) that the mean free path is inversely proportional to the absolute density p of the gas. Therefore, if the temperature of the gas is fixed (the mean velocity v of the molecules constant), the coefficient of viscosity is independent of the density of the gas, that is, in this

case, independent of the pressure. This very remarkable and unexpected result has been verified by experimental means with convincing accuracy for reasonable pressures ; it is a striking success for the kinetic theory (Chapter XI, Table I). At high pressures discrepancies are observed, which are, after all, to be expected when it is remembered that inter-molecular forces can be no longer neglected under such conditions. We shall return later (Chapter IX) to the deviations observed at very low pressures.

2. Thanks to formula (29a) the experimental determination of the coefficient of viscosity η permits the evaluation of the mean free path λ of a molecule : we know the absolute densities ρ and the mean square velocities c (Art. 8) and consequently the average velocities v (formula 8a).

Thus we find for hydrogen under normal conditions 15.8×10^{-6} cm., for air 8.45×10^{-6} cm., etc. The mean paths are, therefore, of the order of one-tenth of a micron. At a pressure of $\hat{v}$ of a mm. of mercury we find for the same two gases, 1.20 cms. and 0.64 cm. Under low pressures, therefore, the mean paths are comparable with the dimensions of the apparatus which contains the gas.

3. A knowledge of the mean free path, together with formula (22) enables us to calculate the product $n\bar{a}^2$ of the molecular density of the gas and the square of the molecular diameter. To determine the values of n and a separately another relation is necessary. First of all we may use formula (19) established in connection with Van der Waals' equation of state. The experimental study of the isotherms of a fluid will furnish the co-volume b of this fluid, and consequently the product $n\sigma^3$. It

was in this way that a satisfactory estimate was first made of the molecular density of gases under normal conditions and, simultaneously, of molecular dimensions. (See Chapter XL)

More recently, with the assistance of numerous concordant methods, several of which will be expounded later, it has been possible to determine directly Avogadro's constant N (the number of molecules per gramme-molecule) and consequently the molecular density n of a gas under normal conditions. In this way it has been found that $N = 60 \cdot 64 \times 10^{22}$ and $n = 2 \cdot 9 \times 10^{19}$ and these numbers may be considered within an error of one per cent. Formula (22) therefore determines the molecular dimensions; the numbers obtained for a are $2 \cdot 4 \times 10^{-8}$ cm. for hydrogen, $3 \cdot 1 \times 10^{-8}$ cm. for nitrogen, $2 \cdot 9 \times 10^{-8}$ cm. for argon, etc. The values corresponding to the monatomic gases (argon) are particularly important, because formula (22) only has a clear and definite meaning for a perfect monatomic gas.

As soon as the mean free paths of the molecules are known, and their mean velocity determined in the manner indicated previously, we may determine from formulae (23) and (24) the number of collisions made in one second by each molecule, together with the average duration of a free path. All the numerical results are collected in Chapter XL

4. According to formula (29a) the coefficient of internal friction of a gas should be proportional to the average velocity, that is to say (formula 8a and 15) to the square root of the absolute temperature T . In actual fact experiment shows an increase of the coefficient r) with the temperature, a remarkable verification of the theory when one reflects that for liquids the viscosity decreases when the temperature

risers. The law of variation observed for η , however, is in reality more rapid than formula (29a) would demand, particularly at moderate temperatures.

This may be ascribed to the fact that the mean free path has been calculated without taking account of any intermolecular forces of attraction, which have already been seen to give rise to the internal pressure term in the equation of Van der Waals. Sutherland has shown, by quite a simple argument, that these actions may be taken into consideration, preserving the hypothesis of elastic collision, by replacing the mean free path of Maxwell (formula 22), which is independent of the temperature, by the following expressions, which does depend on it—

$$l = \frac{1}{\sqrt{2}n\pi\sigma^2\left(1 + \frac{B}{T}\right)}$$

in which B is a constant. The coefficient of viscosity becomes, in consequence,

$$\eta = \frac{k\rho v}{\sqrt{2}n\pi\sigma^2\left(1 + \frac{B}{T}\right)}$$

and its relation with the temperature is of the form

$$\eta = \frac{A\sqrt{T}}{1 + \frac{B}{T}}$$

This law is borne out by experiment in a remarkable manner over a very wide range of temperatures; it is particularly noticeable in the case of nitrogen from -190° to $+300^\circ$. (See Chapter XT, Table II.)

18. Transport of any Magnitude.—In the preceding paragraph we have calculated the trans-

port of momentum effected by molecular agitation across a fixed plane in the gas, when the absolute molecular velocities differ on the average from one side to the other of this plane. We have been led in this way to the theory of internal friction.

The reasoning may be generalised by imagining a gas in which any magnitude G attached to each molecule, instead of having the same value on an average throughout the gas, varies progressively from one region to another. The aim of the calculation will be to estimate the amount of the magnitude G which is transported across unit surface of a given plane in unit time by the influence of thermal agitation.

We shall suppose, as in the preceding paragraph, that the magnitude G has the same average value for all the molecules in a plane P parallel to the xy plane, and that it increases from one plane to another according to the linear law,

$$G = Az \quad . \quad . \quad . \quad (30)$$

Its gradient of variation is therefore the constant

A molecule crossing the plane P in a direction making an angle θ with the z axis last suffered a collision in a plane P' whose ordinate is

$$z' = z - l \cos \theta$$

assuming, as before, that the free paths of all the molecules are equal to their mean path l . It carries with it an amount of the magnitude G equal to

$$Az' = (z - l \cos \theta) \frac{dG}{dz}.$$

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If n is the molecular density, it is easily seen that, as before, the number of molecules crossing unit surface in unit time and in a direction within the limits θ and $\theta + d\theta$ is

$$dn = \frac{nv}{2} \sin \theta \cos \theta d\theta \quad . \quad . \quad (31)$$

The consequence is that the total amount of the magnitude G carried across unit surface of the plane P during unit time and in the direction in which z decreases is

$$\Gamma = - \int_0^\pi (z - l \cos \theta) \frac{dG}{dz} \times \frac{nv}{2} \sin \theta \cos \theta d\theta$$

or

$$\Gamma = \frac{nvl}{2} \frac{dG}{dz} \int_0^\pi \cos^3 \theta \sin \theta d\theta = \frac{nvl}{3} \frac{dG}{dz} \quad . \quad (32)$$

19. Thermal Conductivity.—If G is the momentum mU parallel to Ox , formula (32) gives equation (27a) once more, relating to the coefficient of viscosity.

If G represents the mean molecular energy in a plane of ordinate z , we arrive at the equation for the thermal conductivity of a gas. Suppose, in fact, that the absolute temperature T increases with the ordinate of the plane P according to the law

$$T = T_0 + z \frac{dT}{dz},$$

the gradient $\frac{dT}{dz}$ being constant. Unit surface of the

plane P will be crossed from the upper to the lower side by a quantity of heat

$$\Gamma = k \frac{dT}{dz} \quad \bullet \quad (33)$$

in unit time, the coefficient k being, by definition, the coefficient of conductivity of the gas.

Further, let c_v be the specific heat of the gas at constant volume. The heat energy transferred by one molecule of mass m which crosses the plane P is, on the average (see paragraph 27, Chapter V),

$$mc_v T = mc_v \left(T_0 + z \frac{dT}{dz} \right).$$

The only term which contributes anything, on the whole, to a transfer of heat across unit surface of the plane P is the second,

$$\Gamma = mc_v \frac{dT}{dz} z,$$

and it is of the form (30) indicated in the preceding paragraph. We may, therefore, apply to it the general formula (32) and say that the transfer of heat per unit surface and unit time is

$$\Gamma = \frac{nv}{3} mc_v \frac{dT}{dz}.$$

Comparison with the expressions (29) and (33) gives, for the coefficient of thermal conductivity, the expression

$$k = \frac{nmv}{3} c_v = \eta c_v \quad \bullet \quad (34)$$

The kinetic theory of gases, therefore, predicts the existence of a remarkably simple **relation** between

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the coefficient of viscosity η , the coefficient of thermal conductivity k , and the specific heat c_v at constant volume. A more complete argument leads to a formula which contains a more complicated numerical coefficient B ,

$$k = B\eta c_v . \quad (34a)$$

The coefficient B , calculated by Chapman and by Enskog, should be approximately equal to 2.5 for monatomic gases, and less for polyatomic gases. Averaging the reasonable hypotheses, Chapman finds for B the value 1.90 for diatomic gases, 1.75 for triatomic gases. Experiment appears to confirm these predictions in a very satisfactory manner. (See Chapter XI, Table III.)

20. Mutual Diffusion of Two Gases.—If any two gases are brought into contact, one above the other, at the same temperature and the same pressure, in such a way that the lighter of them is uppermost, after the lapse of quite a short period of time the mixture of the two gases is found to be complete, without causing any alteration in the temperature or the pressure. The experiment may be performed, for instance, as Berthollet showed long ago, with hydrogen and carbon dioxide, the densities of which are in the ratio of 1 to 22. It affords a striking demonstration of a qualitative kind of molecular agitation. The phenomenon has received the name of the mutual diffusion of two gases.

To attack the problem mathematically we may, as a first approximation, employ the same simplified methods as were used in the preceding paragraphs. Let l_1 and v_1 represent the mean free path and the average velocity supposed common to all the molecules of the first gas. Similarly let l_2 and v_2 represent the corresponding quantities for the second

gas. The molecular densities n_1 and n_2 of the two gases must be considered as varying from point to point; we shall assume them to be linear functions of z , such that the distribution of the two gases is uniform in each plane parallel to the xy plane, and diffusion will be assumed to proceed parallel to the z . axis. Further, the process will be supposed to have attained a steady state, such that n_x and n_2 do not depend explicitly on the time. According to these assumptions we may write for any plane P parallel to the xy plane,

$$n_1 = \frac{n}{2} - az$$

$$n_2 = \frac{n}{2} + az.$$

In these relations a is the constant gradient of the two molecular densities

$$a = -\frac{dn_1}{dz} = \frac{dn_2}{dz}$$

and n is the total molecular density

$$n = n_1 + n_2.$$

The constancy of n is a consequence of Avogadro's hypothesis (Art. 7), and the equality, in absolute value, of the two gradients is necessitated by the constancy of 11.

Of the molecules of the first kind, those which cross unit surface of the plane P in unit time making an angle with the z .axis within the limits θ and $\theta + d\theta$, are given by relation (31) as

$$dv_1 = \frac{n_1' v_1}{2} \sin \theta \cos \theta d\theta;$$

n_1 represents the molecular density of the molecules of the first kind in a plane P' where they suffered their last collision, that is in the plane whose ordinate is

$$z' = z - l \cos \theta.$$

In other words,

$$n_1' = \frac{n}{2} - \alpha(z - l_1 \cos \theta),$$

and consequently

$$dv_1 = \left[\frac{n}{2} - \alpha(z - l_1 \cos \theta) \right] \frac{v_1}{2} \sin \theta \cos \theta d\theta.$$

Integration with respect to θ extended from $\theta = 0$ to $\theta = \pi$ will give the total number of molecules of the first kind which have crossed unit surface of the plane P in unit time and in the direction in which z increases. The result is easily found to be

$$v_1 = \frac{\alpha l_1 v_1}{3}.$$

Similarly we should find for the number of molecules of the second kind which cross the same surface in the same time but in the opposite direction

$$v_2 = \frac{\alpha l_2 v_2}{3}.$$

As the difference $v_1 - v_2$ in the general case, differs from zero, in order to keep the pressure of the gas constant there must be a movement of the gas as a whole in the direction in which z decreases, to compensate for the change in molecular density $v_1 - v_2$. The number of molecules of the first kind which, from this cause, must cross unit surface of the plane

P in unit time and in the direction in which z decreases will be

$$\frac{(\nu_1 - \nu_2)n_1}{n_1 + n_2}$$

so that the total number of the molecules of the first kind transferred finally will be

$$p_1 = \nu_1 - \frac{(\nu_1 - \nu_2)n_1}{n_1 + n_2} = - \frac{dn_1}{dz} \cdot \frac{l_1\nu_1n_2 + l_2\nu_2n_1}{3(n_1 + n_2)}.$$

We see that this number is proportional to the gradient $-\frac{dn_1}{dz}$ and we may therefore put

$$p_1 = -D \frac{dn_1}{dz} \quad \cdot \quad \cdot \quad (35)$$

in which

$$D = \frac{l_1\nu_1n_2 + l_2\nu_2n_1}{3(n_1 + n_2)} \quad \cdot \quad \cdot \quad (36)$$

Equation (35) is the fundamental equation for the diffusion of two gases into one another. It may also be written

$$V_1 = - \frac{D}{n_1} \cdot \frac{dn_1}{dz} \quad \cdot \quad \cdot \quad (37)$$

V_1 being the velocity of diffusion of the first gas. Equation (36) gives the value of the "coefficient of diffusion" D , which is evidently the same for the two gases.

A particularly important case is that in which one of the gases is simply an impurity in the other, that is where one of the molecular densities, n_2 , is

very small compared to the other, n_1 . In this case the coefficient D reduces to

$$D = \frac{l_2 v_2}{3} \quad \cdot \quad \cdot \quad \cdot \quad (38)$$

The experimental measurement of the coefficient of diffusion of a gas diluted to a very low molecular density in a second gas, provides, by the use of this formula, a new means of determining the mean free path. It is worthy of note also, that formula (38) has been of great service in the study of the electrical conductivity of gases.

Another case of special interest is that in which the two kinds of molecule become identical. The coefficient of diffusion D of the gas into itself now takes the form

$$D = \frac{lv}{3} = \frac{\eta}{\rho}.$$

As might have been expected, it is proportional to the coefficient of viscosity.

In conclusion, we must notice that the phenomena, of which a brief theoretical study has just been outlined, cannot be treated rigorously by the method of mean free paths. In fact, as soon as the temperature or the pressure of a gas are no longer uniform, the molecular velocities cease to be distributed according to Maxwell's law. In this case it is necessary to introduce a correction to the law of distribution which complicates the theory very considerably. Still worse, the correction which is a consequence of it in the calculations given above is, in certain cases, of the same order of magnitude as the principal terms ; the method of mean free paths then loses all practical value.

Maxwell first developed a rigorous method of cal-

culatation which would permit the study of viscosity, diffusion and thermal conductivity; abandoning the idea of free paths, he studied very closely the mechanism of the transport of momentum, matter and energy by the molecules, by considering in detail the dynamics of molecular collisions. His calculations—which are very complicated—could only achieve his object in the case of a particular law of intermolecular action, that of a repulsion varying inversely as the fifth power of the distance. The theory has been perfected and generalised by various w⁷riters among whom the names of Boltzmann, Brillouin, Jeans, Langevin, Chapman, and Enskog deserve special mention. The last three have been able to dispense with the particular law of force acting between the molecules, which Maxwell was compelled to introduce.

From their studies it appears that, if it is expedient to introduce mean free path considerations in the calculations as a first approximation, because of their extreme simplicity, the numerical values of the coefficients in the formulae obtained are frequently inaccurate, and the formulae themselves occasionally incorrect.

For more complete developments special treatises and original memoirs must be consulted.

CHAPTER IV

SPECIFIC HEATS OF GASES. EQUIPARTITION OF ENERGY

ai. The Case of Perfect Monatomic Gases.—As before, let m and C represent the mass and the mean square velocity of a molecule of a perfect gas, and let N be Avogadro's constant. The total kinetic energy of translation of the molecules contained in a gramme-molecule of the gas is

$$Q = N \frac{mC^2}{2}.$$

By the application of formula (16) we may write

$$Q = \frac{3}{2} RT \quad \cdot v \quad (39)$$

«

If, as in monatomic gases, the molecules are considered as homogeneous elastic spheres, any quantity of heat communicated to the gas at constant volume can only increase the kinetic energy of translation of the molecules through the agency of collisions. The above expression may, therefore, be regarded as the total quantity of heat or the total internal energy contained in a gramme-molecule of the gas at constant volume.

The increase of this quantity of heat for a rise in

temperature of one degree is the " molecular heat at constant volume,"

$$C_v = \frac{3}{2} R \quad . \quad . \quad . \quad (40)$$

To raise the temperature of a gramme-molecule of the gas by one degree at a constant pressure p , we may first work at constant volume V , and then increase the volume by the amount ΔV requisite to restore the pressure to its initial value. The total energy expended, which is simply the molecular heat at constant pressure C_{pt} is manifestly expressed by the relation

$$C_p = C_v + p\Delta V.$$

The formula for perfect gases

$$pV = RT$$

shows that, to preserve the initial pressure p during a rise of temperature of one degree, the volume must vary by

$$\Delta V = \frac{R}{p}.$$

We have then

$$C_p = C_v + R \quad . \quad . \quad . \quad (41)$$

and consequently

$$C_p = \frac{5}{2} R \quad . \quad . \quad . \quad (42)$$

Of the three formulae (40), (41), and (42), the second is a consequence of the principle of the conservation of energy (Mayer's formula), but the first and the third give very simple expressions for the two specific heats of a perfect monatomic gas which are peculiar to the kinetic theory of gases and susceptible to experimental verification.

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The molecular heats C_v and C_p should be constants independent of the temperature and of the nature of the gas. The numerical value of these constants is, for the first

$$C_v = \frac{3}{2} R = \frac{3 \times 8.32 \times 10^7}{2} \text{ ergs} = 2.97 \text{ calories}$$

and for the second

$$C_p = \frac{5}{2} R = 4.95 \text{ calories.}$$

The ratio of the specific heats should have the invariable value,

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.666.$$

These predictions are amply confirmed by experience. Thus for argon, the molecular heat at constant volume has the value 2.97 at all temperatures. For the following monatomic gases the values of γ obtained are tabulated opposite:

Mercury vapour		1.666
Argon		1.667
Krypton		1.666
Helium		1.652

22. Perfect Polyatomic Gases.—If the molecules are no longer homogeneous elastic spheres, and if, moreover, they are at liberty to exercise actions at a distance upon one another, any heat communicated to the gas will no longer merely serve to increase the kinetic energy of translation of the molecules; a certain part of it may be converted into intramolecular kinetic energy, or into potential energy.

In the particular case of a perfect polyatomic gas

we shall suppose that no forces acting at a distance between the molecules are operative, and that all the collisions are elastic. From the moment of its dissemination by collisions the heat energy can only distribute itself as kinetic energy of translation and intramolecular energy ; the intermolecular potential energy will be zero.

Let dQ be the quantity of heat, expressed in units of energy, necessary to raise the temperature of one gramme-molecule of the gas by dT at constant volume. We may, therefore put

$$dQ = dQ_1 + dQ_2$$

representing by dQ_x the amount of heat transformed into kinetic energy of translation and by dQ_2 the amount converted to intramolecular energy

The expression for dQ_v already calculated above is

$$dQ_1 = \frac{3}{2}RdT.$$

The expression for dQ_2 is unknown, but it is obviously proportional to dT and it may be assumed that the coefficient of proportionality is a simple function of the temperature.*

The calculation which permits the deduction of

* In fact, the mean energy accumulated by the internal mechanism of a molecule from molecular collisions, cannot, in the steady state, depend on the frequency of the collisions (pressure) but only on their intensity (temperature).

We may therefore put

$$dQ_2 = adQ_1 = \frac{3Ra}{2}dT$$

in which a represents an unknown function of the temperature. In accordance with this expression, the molecular heat of the gas at constant volume becomes

$$C_v = \frac{dQ}{dT} = \frac{3R}{2}(1 + a) \quad . \quad . \quad . \quad (43)$$

the molecular heat at constant pressure is in no way changed. The relation expressed by (41) is always valid and leads to the formula,

$$C_p = \frac{R}{2} (5 + 3a).$$

These formulae imply certain consequences differing slightly from those we have deduced in connection with monatomic gases;

1, The molecular heats, C_p and C_v , are no longer necessarily independent of the temperature. In actual fact they depend upon it only to a very slight extent, and a is practically constant over a wide range of temperature for polyatomic gases in the neighbourhood of the perfect state.

2. To gain some knowledge of the value of a , it is necessary to refer to two series of experimental results, to wit, the values of C_p and those of the ratio:

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{3(1+a)} \quad \text{".} \quad (44)$$

The molecular heats at constant pressure, expressed in calories, approximate to a constant value 7 for most polyatomic gases (the law of Delaroche and Berard), whilst for monatomic gases we found a value in the neighbourhood of 5. From these results a must have a numerical value near $\frac{2}{3}$.

On the other hand the ratio γ is approximately $1.40 = \frac{7}{5}$ for quite a large number of diatomic gases (H_2 , O_2 , N_2 , NO , CO , . . .). The value of a , therefore, again appears to be $\frac{2}{3}$. For certain gases, generally triatomic (N_2O , CO_2 . . .) the value of γ is approximately $1.33 = \frac{4}{3}$. In this case $a = 1$. For gases with more complex molecules the value of γ is sometimes near $1.25 = \frac{5}{4}$, corresponding to

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$a = \frac{5}{3}$. Finally, it may happen that y is much less, and a , consequently, much greater. But in all cases y is without exception somewhere between 1 and $\frac{5}{3}$, a result completely in accordance with formula (44). (See Table IV, Chapter XL)

En resume, for diatomic gases the intramolecular energy is, on an average, two-thirds of the kinetic energy of translation. In certain more complex cases, such as triatomic gases, it may reach the same value as the translational energy, and even exceed it. But—and this is a most remarkable fact—the distribution of energy between these two types seems to occur, without exception, in a simple ratio.

23. The General Law of the Distribution of Energy between Molecules.—It was to interpret this very striking result that Maxwell and Boltzmann were led to propound the celebrated doctrine of the equipartition of energy.

The origin of the principle of equipartition is to be found in Maxwell's law of the distribution of velocities, which has already occupied our attention in Chapter I. Successive generalisations have extended its field of application to all material systems whatever their complexity of structure. Since it would be impossible to attempt a complete exposition we shall limit ourselves to giving a general idea of the subject, as precisely as possible, illuminating it with several applications. Later we shall be compelled to realise that this principle has been the origin of several important difficulties in connection with the kinetic theory, difficulties which must now set definite limits to its validity.

Consider a gas, in a state of thermal equilibrium, containing molecules of different kinds. The state of one of these molecules depends upon a certain number of independent parameters, their number

increasing with the complexity of its structure and internal movements. Its energy E is a function of these parameters and can always be represented as the sum of two terms,

$$E = L + V,$$

representing the total kinetic energy and the total potential energy respectively. The potential energy at any given moment depends only on the internal structure and the position of the molecule in the external field of force; it is therefore a function of the " co-ordinates of position " $x_1, x_2, x_3 \dots$ and of them alone. For example, if the molecule may be compared with a material point, its internal potential energy must be zero, and V will be reduced in consequence to the energy originating in the external field (created by the other molecules, by its weight, etc.). The total potential energy will, therefore, depend only upon the three co-ordinates x, y, z of the molecule.

On the other hand the kinetic energy depends upon the velocities, or the differential coefficients $\dot{x}_1, \dot{x}_2, \dot{x}_3 \dots$ of the co-ordinates of position with respect to the time. Its algebraic expression may be modified by replacing $\dot{x}_1, \dot{x}_2 \dots$ by linear combinations of these differential coefficients conveniently chosen, and in mechanics it is shown that this choice can always be made in such a manner as to express L in the form,

$$2L = a_1 \xi_1^2 + a_2 \xi_2^2 + \dots$$

in which $\xi_1, \xi_2 \dots$ are the new " co-ordinates of velocity " and $a_1, a_2 \dots$ are coefficients which may depend upon the co-ordinates of position $x_1, x_2 \dots$

* Mathematically this is nothing more than the well-known property of quadratic forms of being resolved into a sum of squares.

The velocity-co-ordinates so chosen have received the name "momentoids."

If the components of the velocity of the centre of gravity of the molecule are represented by u , v , and w , that part of its kinetic energy due to its translational motion,

$$\frac{1}{2}m(u^2 + v^2 + w^2),$$

may be distinguished, since the three variables, u , v , w may always be chosen as three of the momentoids belonging to the molecule, and L may be expressed in the form,

$$2L = m(u^2 + v^2 + w^2) + a_4\xi_4^2 + \dots \quad (45)$$

Let us now attempt the evaluation of the number of molecules per cm.³ of the kind considered, whose co-ordinates of position lie within the range x_x and $x_1 + dx_1, x_2$ and $x_2 + dx_2 \dots$ and whose momentoids at the same time lie between the limits f 1 and $\xi_1 + d\xi_1, \xi_2$ and $\xi_2 + d\xi_2$, etc. Maxwell and Boltzmann have shown that, if the total number of the molecules in question per cm.³ is n , and their total energy U , the problem has statistically but one solution, subject to the realisation of certain very general hypotheses, such as that of "molecular chaos" (see Art. 2).

To express this solution in a simple fashion, we notice that the number sought is evidently of the form,

$$dn = n f(x_1, x_2 \dots \xi_1, \xi_2 \dots) dx_1 dx_2 \dots d\xi_1 d\xi_2 \dots \quad (46)$$

$f(x_1, x_2 \dots \xi_1, \xi_2 \dots)$ being an unknown function which it is proposed to determine. For brevity we shall write symbolically

$$dn = n f dx d\xi.$$

The result may be given immediately in the form of the following equation,*

$$f(x_1, x_2 \dots \xi_1, \xi_2 \dots) = Ae^{-2hE} = Ae^{-2h(L+V)} \quad (47)$$

in which A and h are constants, the second being the same for every type of molecule contained in the gas. These constants are easily determined by expressing the fact that the total molecular density is n , and the total energy U , leading to the auxiliary equations,

$$\int f dx d\xi = 1 \quad \cdot \quad \cdot \quad \cdot \quad (48)$$

$$\sum \int n E f dx d\xi = U.$$

The first sum is extended over all the molecules of the type considered, and determines the constant A for them. There will be an equation of this kind for each type of molecule. The second sum must be extended over all the different kinds of molecule in the gas, and it determines the constant h ; it gives rise to one equation only. In both cases the integrations should be performed, quite evidently, over all the field of possible variations of $x_1, x_2 \dots$ and of ξ_1, ξ_2

The applications we are about to make of the general law of the distribution of energy expressed by formula (47) will throw much light on its character, which is rather abstract by virtue of its very generality.

34. Equipartition of Kinetic Energy,—If, in the expression for the kinetic energy, only the terms corresponding to the energy of translation (formula

* The principle of the demonstration will be found in the following chapter* Art. 31.

45) are considered, the general equation (47) assumes the form,

$$f = H e^{-h m (u^2 + v^2 + w^2)},$$

in which H no longer depends upon u , v , and w . We arrive once more at the law of the distribution of the velocities of translation due to Maxwell (formula 3). This law is thereby demonstrated for molecules of any structure whatever, mixed with other kinds of molecules, situated in an arbitrary conservative field of force. It only presupposes the gas to be in equilibrium, mechanical and thermal.

As we have seen in Chapter I, the constant h is inversely proportional to the absolute temperature of the gas.

Let us now turn our attention to that part of the kinetic energy of the molecule due to any momentoid ξ_i , that is $\frac{a_i \xi_i^2}{2}$. The mean value of this energy, calculated for all the molecules of the particular type considered contained in one cubic centimetre, is

$$\overline{\frac{a_i \xi_i^2}{2}} = \frac{1}{n} \int \frac{a_i \xi_i^2}{2} dn \quad \cdot \quad \cdot \quad (49)$$

From equation 46

$$dn = n f dx d\xi$$

and consec
$$\overline{\frac{a_i \xi_i^2}{2}} = \frac{1}{n} \int \frac{a_i \xi_i^2}{2} n A e^{-h m} dx d\xi.$$

In the expression for the energy E of the molecule, let us isolate the term corresponding to the momentoid ξ_i , in the form

$$E = \frac{a_i \xi_i^2}{2} + E_1.$$

Then

$$\begin{aligned}\frac{\overline{a_i \xi_i^2}}{2} &= \frac{1}{n} \int n \frac{a_i \xi_i^2}{2} A e^{-2h \left(\frac{a_i^2 \xi_i^2}{2} + E_i \right)} dx d\xi_i \\ &= A \int \frac{a_i \xi_i^2}{2} e^{-h a_i^2 \xi_i^2} e^{-2h E_i} dx d\xi_i\end{aligned}$$

taking the constants n and A outside the integral sign. Since the variables x and ξ_i are independent, and E_x is a function of x only and is independent of ξ_i this integral may be regarded as the product of two integrals, referring to x and ξ_i respectively. From equation (48) also,

$$\int A e^{-2h E} dx d\xi = 1$$

and

$$\begin{aligned}A &= \frac{1}{\int e^{-2h E} dx d\xi} \\ &= \frac{1}{\int e^{-h a_i^2 \xi_i^2} d\xi_i \int e^{-2h E_x} dx}\end{aligned}$$

The mean energy corresponding to the momentoid ξ_i therefore becomes

$$\begin{aligned}\frac{\overline{a_i \xi_i^2}}{2} &= \frac{\int \frac{a_i \xi_i^2}{2} e^{-h a_i^2 \xi_i^2} d\xi_i \int e^{-2h E_x} dx}{\int e^{-h a_i^2 \xi_i^2} d\xi_i \int e^{-2h E_x} dx} \\ &= \frac{\int_{-\infty}^{+\infty} \frac{a_i \xi_i^2}{2} e^{-h a_i^2 \xi_i^2} d\xi_i}{\int_{-\infty}^{+\infty} e^{-h a_i^2 \xi_i^2} d\xi_i}\end{aligned}$$

since ξ_i may assume all values to infinity in the positive or negative directions. The evaluation of this integral is a simple matter, since it is of standard form (see Note I at the end of the book), the final result being

$$\frac{a_i \xi_i^2}{2} = \frac{1}{4h}.$$

Thus the mean kinetic energy belonging to any one of the momentoids of the molecule has the invariable value $\frac{1}{4h}$, independent of the kind of molecule selected, and is a function of the temperature alone. Or again: "there is equipartition of energy between the different momentoids belonging to all the molecules."

Such is the general enunciation of the principle of equipartition of kinetic energy, of which Maxwell's law of distribution appears as a particular case.

25. Application to the Specific Heats of Gases with Poiyatomic Molecules.—The most simple picture we can form of the molecule of a perfect diatomic gas is that of a system of two homogeneous elastic spheres, bound rigidly to one another. This system being one of revolution about the line of centres of the two spheres, collisions will not affect the rotations about this line, but all the other rotations will suffer alterations by collision. Besides the three components of the velocity of translation, therefore, we must introduce two new parameters in order to calculate the total kinetic energy (or rather the part of this energy susceptible to modification by collision); take, for example, the projections of the velocity of rotation on two axes perpendicular to the line of centres. Thus the total number of the momentoids will be 5,

and, by virtue of the principle of equipartition, the kinetic energy of rotation will be, on an average, two-thirds of the energy of translation. This was the experimental result mentioned above (Art. 22) for several diatomic gases.

For a gas with rigid molecules with no axis of revolution, the number of momentoids will obviously be greater by one. The ratio of the energies of rotation and translation will be one, being the equivalent of the results mentioned above for certain triatomic gases.

Finally, if the molecules are no longer rigid, the new degrees of freedom which appear betray themselves by the existence of a new momentoid ; the intramolecular energy, as a consequence of equipartition, tends to increase at the expense of the kinetic energy of translation. The ratio of the two specific heats diminishes and tends towards unity.

In this way we arrive once more at the group of results formulated at the end of Article 22, results which the elementary theory was unable to account for. We shall see in Chapter VI that certain difficulties still remain, however, imposing modifications on the theory. The most important of them arise in the variation of the specific heats with the temperature.

26. Distribution of Density. Formula of Barometric Height.—Let us now turn to an interesting application of the general law of distribution expressed by formula (47). Suppose the gas to be placed in the field of gravity (instead of neglecting it, as we have done implicitly up to the present). The potential energy of a molecule will be, with the exception of a constant term,

$$V = m g z,$$

in which g represents the acceleration due to gravity, and z the ordinate of the molecule reckoned on a vertical axis directed upwards. The number of molecules per cubic centimetre whose ordinates lie between the limits z and $z + dz$ will be, therefore,

$$dn = k e^{-2hmgz} dz$$

where k is a factor which no longer depends on z . The molecular density at an altitude z , and consequently at a pressure p , is, therefore, of the form

$$p = p_0 e^{-2hmg(z-z_0)} \quad . \quad . \quad (50)$$

p_0 being the pressure at the altitude z_0 .

This expresses the well-known formula of barometric height, in a gas at uniform temperature, and, if h is replaced by its known value (18), the formula takes the classical form:

$$p = p_0 e^{-\frac{Mg(z-z_0)}{RT}}$$

M being the molecular weight of the gas.

The interest of this method of demonstration lies in showing that the formula is valid even for a gas which is merely one component of a mixture. Each of the gases distributes itself in height under the influence of gravity as if it were alone, the law of distribution varying more rapidly the greater the molecular weight of the gas.

CHAPTER V

THERMODYNAMICS AND STATISTICAL MECHANICS. ENTROPY AND PROBABILITY

27. First Law of Thermodynamics.—Heat does not exist as such in the form of a distinct kind of energy in the kinetic theory of gases. The process of communicating heat to a gas is simply that of increasing the kinetic and potential energy of its molecules. The enunciation of the principle of the conservation of energy is nothing more than a statement of the purely mechanical theorem of *vis viva*. The classical equation,

$$dQ = dU + pdV \quad \cdot \quad (51)$$

which expresses this theorem in algebraic form, and which connects the small element of heat dQ supplied to one gramme-molecule of the gas, expressed in mechanical units, with the increase of internal energy dU and with the external work pdv , is interpreted without difficulty. It states that the total mechanical energy expended in modifying the state of the gas has been employed, first in increasing the molecular energy in the kinetic or potential form, and again in overcoming the forces of external resistance which act at the surface.

It is a consequence of the arguments put forward in the last chapter (formula 43) that, at constant volume, we may write

$$dQ = dU = C_v dT,$$

and that consequently the internal energy,

$$U = \int C_v dT = \frac{3R}{2} \int (1 + a) dt,$$

is a function of the temperature alone (Joule's Law). In the case of a perfect monatomic gas we have simply (formula 40):

$$U = \frac{3R}{2} T = C_v T \quad \cdot \quad (52)$$

and the internal energy is proportional to the absolute temperature.

It is interesting to consider in a few examples, this interpretation of the transformation of mechanical work into heat from the molecular point of view. The mutual friction between two bodies has the effect of creating differences of kinetic energy between the neighbouring molecules of the two bodies; these differences tend to equalise through the medium of molecular collisions, and, by a progressive transmission to the molecules situated at a greater distance, distributes itself gradually throughout the whole mass. Under these conditions the tangible kinetic energy has become molecular kinetic energy and work has become heat. In the same way, when a liquid is poured into a vessel, the work done by gravity endows the component parts of the liquid with perceptible movements, to which quite definite amounts of kinetic energy must correspond. Little by little the movements become smaller and more irregular; molecular collisions fulfil their function of distributing the kinetic energy at their disposal among the individual molecules. The work done by gravity is thereby converted into heat.

28. The Second Law of Thermodynamics. Entropy of a Perfect Gas.—The molecular theory

of Carnot's principle is much less simple. It has given rise to difficulties which we shall expound at some length, in the illumination of which a path has been opened up leading to a new interpretation of the second law.

Let us examine first of all the case of a perfect monatomic gas, one gramme-molecule of which is submitted to an infinitely small reversible transformation. Equation (51) which expresses the conservation of energy during this transformation may, by virtue of formula (14) which is valid for perfect gases, assume the form,

$$dQ = C_v dT + R p d\left(\frac{T}{p}\right).$$

This expression, which depends upon the two variables p and T and on their differentials, is not in general a complete differential. On the other hand it becomes complete if both its members are divided by T . In fact

$$dS = \frac{dQ}{T} = C_v \frac{dT}{T} + R \left(\frac{dT}{T} - \frac{dp}{p} \right)$$

or, from (41)

$$dS = C_p \frac{dT}{T} - R \frac{dp}{p}.$$

It is obvious that dS is the complete differential of the function

$$S = \int \frac{C_p}{T} dT - R \log p.$$

If T and V are taken as independent variables, it is found in the same way that

$$S = \int \frac{C_v}{T} dT + R \log V.$$

The function S is called the entropy of the gas and the preceding expressions define it, but for the omission of an additive constant. In the case of a perfect monatomic gas, the molecular heat at constant volume is a constant defined by formula (40) ; for such a case, neglecting the additive constant referred to

$$S = C_v \log T + R \log V = R \log (T^{\frac{5}{2}} V) \quad . \quad (53)$$

In conjunction with formula (52), this formula recapitulates the complete thermodynamics of perfect monatomic gases, undergoing a series of reversible changes.

29- Irreversible Phenomena,—If we try to explain by molecular mechanics an irreversible phenomenon, such as the diffusion of two gases into one another or the production of heat by friction, grave difficulties are encountered from the very beginning. Molecular movements are supposed to be subject to the laws of classical mechanics, and, therefore, to be essentially reversible. If, at a given moment, the velocities of all the molecules are imagined to be completely reversed, the gas will retrace exactly all its preceding states in turn. In particular, if we are concerned with a mixture arising from the mutual diffusion of two distinct gases, these gases will separate afresh. Now, common experience shows the impossibility of such a spontaneous separation, which would be in conflict with Carnot's principle, but none the less compatible with the laws of mechanics. In this way the molecular theory of gases seems to have become powerless to explain irreversible phenomena ; further, these phenomena, which appear to a more or less marked degree in all practical transformations of energy, appear to contradict any tentative mechanical explanation at the very **outset**.

Struck by this difficulty, Maxwell made several pertinent remarks upon the subject, which actually contained the solution of the problem in embryo. Carnot's principle had been established by "macroscopic" observations, or observations made upon objects of appreciable size containing a large number of molecules : the quantities which occur in thermodynamics (for example, the temperature and the pressure of a gas) are only defined by a mean state of all the molecules contained in a given volume of finite size. It is in no sense proven that the principle remains valid for "microscopic" phenomena, that is to say, phenomena studied on the molecular scale. It is easy to imagine forms of molecular mechanism leading to results in direct conflict with it.

Suppose, for example, that a mixture of two gases at uniform temperature were placed in two receptacles A and B separated by a partition, and a small agile creature were present, capable of opening or closing a small hole in the partition in a very short space of time and without the expenditure of any work. By appropriate manipulation, this "demon" would be able to allow molecules of the first gas travelling towards the aperture to pass from B into A, and molecules of the second kind from A into B. By such means a separation of the gases would be effected, in contradiction to Carnot's principle. The same "demon" in operation upon a simple gas could, by an arrangement of the same kind, effect a segregation of the more swiftly moving molecules in the vessel A, and the slower ones in B : inequalities of temperature would be created thereby without the expenditure of external work, violating once again the second law of thermodynamics. Now, whatever results this demon may achieve by purely

mechanical means may also be attained by a sequence of suitable molecular encounters with no external interference at all. The conclusion seems inevitable, and in the light of this argument Carnot's principle cannot be applied to changes in a gas, when they are observed in molecular detail.

As we shall see a little later, the experimental study of the Brownian Movement and certain other phenomena has fully confirmed this point of view: it seems quite certain that the validity of Carnot's principle ceases when phenomena are studied on a scale sufficiently near that of molecular dimensions. We are still left with the problem of bringing to light the reason which will explain why the principle has never been found at fault in the study of macroscopic or average phenomena.

30. Entropy and Probability.—The merit of clearing up this point is due to Boltzmann. In the thermodynamic study of a gas, the state of the gas depends upon a small number of parameters, such as temperature and pressure, and we only seek relations which define their interdependence. In kinetic considerations we must have a very large number of independent parameters (the co-ordinates and velocity-components of the molecules, etc.) in order to define the state of the gas, and to obtain relations which may be verified practically we determine the average values of certain quantities, extended over a very large number of molecules. Since an exact knowledge of the movements of each molecule is inaccessible to us, it is necessary to resort to the methods of the calculus of probabilities and to construct a statistical mechanics. In particular, it is clear that one and the same state of a gas, perfectly defined from the thermodynamic point of view, may be realised by numerous different combinations

of the molecular parameters, or again, adopting an expression of Gibbs and Boltzmann, corresponding to the same macroscopic state the molecular parameters may assume a very large number of different "complexions." We shall consider the state of a gas as more probable when it may be realised by a greater number of complexions, and we shall take the number w of these complexions as a measure of its probability.*

It is natural to assume that a gas, initially in any state whatever, will develop, if molecular chaos is preserved, towards states which correspond to the greatest number of possible complexions, that is to say, towards the most probable states; it will develop in such a way that w tends towards a maximum. This principle of evolution—and consequently of irreversibility—which was inconceivable from the point of view of ordinary mechanics, becomes essentially reasonable in statistical mechanics.

It seems logical, therefore, to expect some relation between the principle of evolution towards the most probable states and the law of Carnot, according to which the entropy of the gas changes constantly in favour of higher and higher values. To combine these two principles in one, it is sufficient to assume that the entropy S is an increasing function of the probability w ,

$$S=f(w) \quad . \quad . \quad . \quad (54)$$

The form of this function is determined as soon as it is admitted that the total entropy for two independent gases is the sum of their partial entropies, in

* This definition differs a little from that usually adopted in mathematics : instead of defining the probability by the ratio of the number of favourable cases to the total number of possible cases, we measure it simply by the number of favourable cases.

conformity with the principles of classical thermodynamics.

$$S = S_1 + S_2 \quad . \quad . \quad . \quad (55)$$

For if w_1 and w_2 represent the probabilities of the states of the two gases, their independence is expressed, for the system of two gases, by the well-known equality,

$$w = w_1 w_2,$$

so that equation (54), applied to this system, assumes the form,

$$f(w_1 w_2) = f(w_1) + f(w_2).$$

This functional equation is solved without difficulty by differentiating twice, with respect to w_1 and to w_2 . In this way we arrive at the equation,

$$f'(w_1 w_2) + w_1 w_2 f''(w_1 w_2) = 0$$

or

$$f'(w) + w f''(w) = 0,$$

the solution of which is evidently of the form,

$$S = k \log w \quad . \quad . \quad . \quad (56)$$

neglecting an additive constant.

This important relation, established in the first place by Boltzmann for a gas, is nowadays considered as quite general. It relates the entropy of a system to the logarithm of its probability in a very simple manner: these two functions only differ by the universal constant k , the significance of which we shall appreciate a little later. Thanks to this result, the second law of thermodynamics is seen to be statistically true, being applicable only to systems which depend upon a large number of molecular parameters. It must be considered as valid only within the limits imposed by the calculus of probabilities. It is extremely probable that two gases mixed by

diffusion will never separate spontaneously, but nevertheless it is not rigorously certain. The chances of such a separation are merely so very small as to justify the assumption that they are practically non-existent.

31. Boltzmann's H-Theorem.—The general conclusion we have just formulated was not reached all at once. Boltzmann was led to it, and was able to justify it, by the detailed examination of the kinetic properties of a gas, which, for the sake of simplicity, we may regard as perfect and monatomic.

In this case it is possible, not only to calculate completely the probability w , defined as the number of complexions, but to study its variation with the time and to show that it increases constantly in consequence of molecular collisions. It is no longer necessary to assume that the system evolves in the direction of increasing probabilities. It is actually demonstrated. It is further shown that in the stationary state the law of the distribution of velocities is necessarily that of Maxwell. Finally, it is proved that the function of the probability defined by equation (56) agrees exactly with the entropy of thermodynamics when the stationary state is reached, and that without making any appeal to the additive property of entropy expressed by equation (55). In a word, the fundamental equation (56) can be established with a minimum of hypotheses in the case of perfect gases, and therefore seems to be a very plausible generalisation in the other cases.

To proceed, let us consider as in Chapter I, the velocity-points corresponding to the velocities of the n molecules contained in one cm.³ of the gas. The law of the distribution of these velocities will be expressed by an equation analogous to (1):

$$in = F(u, v, w, t)du dv dw = Fdr \quad . \quad (57)$$

The time t has been included explicitly to emphasise that the law of the distribution of velocities may vary with the time, but for simplicity we may assume (cf. Art. 2) that the molecular density remains constant and uniform, and that the law of distribution of velocities is the same at all points in the gas. A comparison with (1) shows that the function f of Chapter I is related to the function F by the relation,

$$F = nf \quad . \quad . \quad . \quad (58)$$

The space in which the velocity-points are plotted is supposed to be split up into equal elements dr or e , the dimensions of which are regarded as fixed once and for all, which we shall consider as sufficiently small to justify our regarding them as playing the part of differentials in our calculations, and at the same time large enough for each one to contain a very large number dn of velocity-points.

Let us assign to each of these different elements of volume a number of the series 1, 2 . . . and let dn_1 dn_2 . . . represent the numbers of points they include respectively. To find the probability of the state of the gas we must calculate the number of possible ways in which dn_1 points may be distributed in the element 1, dn_2 points in the element 2, etc. This number of complexions w must be evaluated, taking into consideration the conditional equation,

$$n = dn_1 + dn_2 + \quad . \quad . \quad . \quad (59)$$

and assuming further that all the volume-elements c represent regions of equal probability for the velocity points ; this latter assumption is really that of the permanence of molecular chaos.

Suppose one of the distributions under consideration to have been realised. Other possible distributions may be obtained from it by permuting the

different velocity-points among themselves. But if the dn_1 velocity-points contained in the element I are permuted among themselves, the $(dn_1)!$ new distributions obtained must not be considered as distinct from the first, since they correspond to the same microscopic state of the gas. The same applies to the $(dn_2)!$ distributions which correspond to the permutations of the velocity-points contained in the element 2, etc. Of the $n!$ distributions obtained by permuting all the velocity-points in every way possible, only those which are not derived by one of the preceding permutations are to be regarded as distinct. Their number is consequently

$$w = \frac{n!}{(dn_1)! (dn_2)! \dots}$$

To transform this expression we shall make use of the approximation formula of Stirling (see Note I), which may be written, for any value of the whole number p which is sufficiently high,

$$\log(p!) = p \log p - p$$

considering equation (59), and using this formula,

$$\log w = -[dn_1 \log (dn_1) + (dn_2) \log dn_2 + \dots] + n \log n.$$

Now, equation (57) provides an expression for dn_i

$$dn = F d\tau.$$

$$\begin{aligned} \text{Sub } \log w &= - \sum F d\tau \log (F d\tau) + n \log n, \\ &= - \sum F \log F d\tau - \sum F \log d\tau \cdot d\tau + n \log n. \end{aligned}$$

Substituting the process of integration for that of

summation in this expression, and substituting n for Fdr in the second term, we get

$$\log w = - \int F \log F d\tau + n \log n + B$$

in which B is an integration constant. We may further simplify this expression by writing

$$\log w = - \int F \log F d\tau + B',$$

B' representing a constant independent of the particular distribution chosen. If we write

$$H = - \int F \log F d\tau \quad . \quad . \quad (60)$$

and ignore the additive constant, we may put

$$\log w = H \quad . \quad . \quad (61)$$

We have thereby gained an expression for the probability of the state of the gas depending only on the law of the actual distribution of velocities.

To ascertain how the probability varies with the time, we are compelled to study the variation δH of the function H . Now

$$\delta H = - \int \delta F (\log F + 1) d\tau \quad . \quad (62)$$

The sign of this variation may be determined by a detailed study of the mechanics of molecular collisions. It is found that, for a gas composed of spherical elastic molecules, it is always positive (or zero in the limit), and consequently that the functions H and w are continuously increasing.

Therefore molecular collisions make the gas change in the direction of the state of maximum probability.

If the stationary state is reached, the expression

(62) must become zero, which provides a condition which we may use to determine the function F ,

$$\int \delta F (\log F + 1) d\tau = 0 \quad . \quad . \quad (63)$$

The variation δF is not arbitrary, since the function F is subject to the two conditions,

$$\int F d\tau = n \quad . \quad . \quad (64)$$

$$\int \frac{1}{2} m(u^2 + v^2 + w^2) F d\tau = U \quad . \quad (65)$$

which express that the total number n and the total energy U of the molecules are definitely fixed. The variation δF is, therefore, subject to the two conditional equations,

$$\int \delta F d\tau = 0 \quad . \quad . \quad (66)$$

$$\int (u^2 + v^2 + w^2) \delta F d\tau = 0 \quad . \quad . \quad (67)$$

which are directly deduced from their predecessors by taking the variation with respect to the time. Following a well-known procedure, we now add the three equations (63), (66) and (67), after multiplying the two latter by undetermined factors λ and μ , finally arriving at the following single equation,

$$\int \delta F [\log F + 1 + \lambda + \mu(u^2 + v^2 + w^2)] d\tau = 0,$$

in which the variation δF is now completely arbitrary.

The necessary and sufficient condition for this equation to be satisfied is therefore

$$\log F + 1 + \lambda + \mu(u^2 + v^2 + w^2) = 0$$

from which we obtain very simply

$$F = Ae^{-b(u^2 + v^2 + w^2)},$$

A and b being constants. In this way we find as the condition of the permanent state the Maxwell law of the distribution of velocities, which is demonstrated thereby. Comparison with (58) and with the formulae of Chapter I shows that we may also write

$$F = nae^{-hmc(u^2 + v^2 + w^2)} = nae^{-hmc^2} \quad \bullet \quad (68)$$

The same line of argument is applicable to any gas whatever. Besides the components u , v , w of the velocity of translation c of the molecule, it is sufficient to introduce all the other parameters which define its state (cf. Art. 23), and to replace the kinetic energy of translation in equation (65) by the total energy of the molecule. We thus derive the general law of distribution (47) and the principle of equipartition studied in Chapter IV, the demonstration of which may now be regarded as complete.

Finally, let us calculate, for the case of a perfect monatomic gas in the stationary state, the H function of Boltzmann which is defined by equation (60) and connected with the probability w by the relation (61). From (68) it is obvious that

$$H = -\log(na) \int F d\tau + hm \int c^2 F d\tau$$

or taking (64) into account and remembering the definition (7) of the mean square velocity C ,

$$H = -n \log(na) + hmnC^2 = -n \left[\log(na) - \frac{3}{2} \right].$$

Finally, from the value of a expressed in (2) and the expression for n as a function of the molecular volume V

$$n = \frac{N}{V}$$

we get

$$H = \frac{N}{V} \log (T^{\frac{1}{3}}V) + \frac{D}{V}$$

in which D is a constant.

If the result is referred, not to unit volume of the gas, but to the molecular volume V , the preceding expression must be multiplied by V , and neglecting an additive constant, we derive the expression

$$H = N \log (T^{\frac{1}{3}}V) ;$$

as usual N represents Avogadro's constant. A comparison of this result with equation (53) shows that the H function of Boltzmann only differs from the entropy S of the gas by a constant factor. In fact

$$S = \frac{R}{N}H = kH = k \log w \quad . \quad . \quad (69)$$

representing by k Avogadro's constant referred to one molecule (Art. 7). The significance of the constant k in equation (56) is established in consequence ; it is often referred to as " Boltzmann's constant."

One important remark remains to be made in conclusion. The relation (69) has been obtained by suppressing certain additive constants which might occur in one of the intermediate equations. We may make the " hypothesis " that these additive constants disappear from the final result: the entropy would therefore be defined " in absolute terms " by the relation (69). This hypothesis, which does not contradict the laws of thermodynamics in any way merely defines them more completely. It was made by Nernst in the first place, in a somewhat different form, and it has led him to some extremely fundamental results in the study of physico-chemical equilibria. The subject cannot be further developed here, without straying far beyond the confines of molecular theory.

CHAPTER VI

THE SPECIFIC HEATS OF SOLIDS THE THEORY OF QUANTA

33. Reconsideration of the Specific Heats of Oases. Difficulties in the Theory.—The theorem of the equipartition of kinetic energy offers an approximate explanation of the numerical values obtained for the specific heats of gases. The considerations advanced in Chapter IV in the study of gases consisting of rigid elastic molecules, whether monatomic or polyatomic, have shown that to be the case.

For all gases, the molecular heat at constant volume C_v is an integral multiple of the same quantity $\frac{R}{2}$ (approximately 1 gramme-calorie), that multiple² being at least 3. It should, therefore, be independent of the temperature, as is known to be the case in the neighbourhood of the ordinary temperature for a large number of gases, and throughout the whole range of temperature for monatomic gases.

At much higher temperatures, however, the molecular heats of polyatomic gases show a very significant increase, easily seen in the numerical tables in Chapter XI (Table V).

To arrive at some explanation of these variations we may suppose that the increase of temperature has the effect of bringing into play new degrees of freedom and consequently new momentoids. Since

each of them must on an average, possess the kinetic energy $\frac{RT}{2}$ per gramme-molecule, a corresponding increase of $\frac{R}{2}$ must appear in the molecular heat at constant volume. Furthermore, we have so far taken no account of the vibrations of atoms within the molecule, that is, of the intramolecular potential energy. We shall see shortly (Art. 33) that this energy again introduces a certain number of terms in the specific heat, each equal to $\frac{R}{2}$. It is, therefore, easy to understand that the molecular heat of certain gases with complex molecules may assume large values at high temperatures (see, for example, the numbers quoted at the end of this volume for carbon dioxide, etc.).

According to the preceding mode of argument, if the new degree of freedom develop at the same temperature in all the molecules, the molecular heat will be discontinuous at this temperature. On the other hand, if they do not appear simultaneously in each molecule, but are subject to chance fluctuations due to molecular collisions, the specific heat will increase progressively as experiment shows. Thus the considerable and continuous increase in the specific heats of polyatomic gases at high temperatures are not irreconcilable with the theorem of equipartition.

Such is not the case at low temperatures however. Measurements made by Nernst and his pupils (Chapter XI, Table V) have shown that for hydrogen and oxygen at low temperatures, the molecular heat at constant volume has a value lower than $\frac{5R}{2}$

(5 calories), and tends towards the limiting value of $\frac{3R}{2}$, valid for monatomic gases. They behave in exactly the same way as they would if the rotational degrees of freedom disappeared by degrees, leaving only those corresponding to translational motion, or if the molecules became more and more like homogeneous elastic spheres in their behaviour. This fact seems to be very difficult to reconcile with the theorem of equipartition. We shall see that a difficulty of the same kind appears in the study of the specific heats of solid bodies.

33. Specific Heats of Solids. Dulong and Petit's Law. — The general law of the distribution of energy expressed by formula (47) is a direct consequence, as we have already seen, of Boltzmann's relation (56). If, as seems likely, this principle may be considered as general and applicable to all states of matter, the law of distribution (47) must be applied to all material systems, and in particular to solid bodies.

Let us consider the molecules of a solid as elastic spheres (monatomic molecules), preserved in mean positions of equilibrium by the influence of neighbouring molecules, but capable of executing small vibrations of frequency ν about these positions of equilibrium. The kinetic energy of a molecule will have the same expression,

$$L = \frac{1}{2}m(u^2 + v^2 + w^2),$$

as that of a molecule of a monatomic gas. The potential energy V , reckoned from the position of equilibrium, is a function of the co-ordinates x, y, z

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of the centre of gravity of the molecule, which may be approximately expressed in the form,

$$V = ax^2 + by^2 + cz^2.*$$

The total energy E or $L + V$ consists, therefore, of a sum of six terms, each of which has the same algebraic form, depending respectively upon the three co-ordinates of position x, y, z and the three momentoids, w, v, w .

The calculation made in Art. 23 to evaluate the mean kinetic energy corresponding to a momentoid is applicable in this case, without modification, to the three terms of the kinetic energy and to the three terms of the potential energy. Each one of them has the same average value $\frac{1}{4h} = \frac{kT}{2}$ as defined previously. Each positional co-ordinate, therefore, makes a contribution to the internal energy exactly equal to that corresponding to each momentoid, with the consequence that the total energy of the molecule is, on an average, twice that of a molecule of a monatomic gas. The internal energy per gramme-molecule of a solid body of the kind considered is, therefore, given by the formula,

$$U = 3RT \quad . \quad . \quad . \quad (70)$$

which takes the place of formula (52), and the molecular heat at constant volume becomes

$$C_v = 3R \quad . \quad . \quad . \quad (71)$$

The molecular heat at constant pressure is very little greater than this, since the body is solid and expands

* In the development of V in series, the terms of the first degree disappear because V is a minimum in the position of equilibrium, and the terms of higher degree than the second disappear because the vibrations are supposed to be very small.

only slightly in consequence. Furthermore, it coincides by hypothesis with the atom, because the molecules are supposed monatomic. The atomic heat of the solid body under consideration should, therefore, have an invariable value near 6 calories ($3R = 5.96$) when measured at constant pressure, as is usually the case. This is the well-known "law of Dulong and Petit," initially obtained empirically, which receives thereby a theoretical foundation. It enables us to think of all simple solid bodies as behaving like a system of monatomic molecules from the thermal point of view.

34. Specific Heats at Low Temperatures and the Theory of Quanta.—The preceding theory requires the specific heat of a solid to be independent of the temperature, as in the case of gases. In actual fact, increases are easily verified at high temperatures; we may try to explain them as we did for gases (Art. 32) by the progressive appearance of new independent parameters within the molecule, and consequently of new terms equal to $\frac{RT}{2}$ in the average molecular energy.

These explanations are not valid for variations observed at low temperatures; if one could imagine the specific heat to exceed 6 it certainly could not be imagined below this limit, since the number of parameters belonging to an oscillating molecule cannot fall below this figure. Earlier measurements had already shown that for certain elements at the ordinary temperature (silicon, carbon . . .) the atomic heats were lower than 6. Recent measurements, principally due to Nernst and his pupils, and carried out as low as the temperature of liquid hydrogen, have shown that the specific heats of all solids tend towards zero when the temperature approaches

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absolute zero. Numerical examples are given in Chapter XI (Table VI).

It is concluded from this that the theorem of equipartition cannot be applied without modification at low temperatures, and that a fundamental change is necessary in our conceptions relative to the distribution of energy among the molecules of a solid. The nature of the required modification has been outlined by Einstein, who utilised in this connection a new idea introduced by Planck in the study of radiation, the concept of the element of energy or "quantum."

Planck showed that, to derive by theoretical means the experimental form of the curve for the distribution of energy in the spectrum of a black body (thermal radiation in equilibrium), it was necessary to assume that the radiant energy emitted by a linear atomic oscillator of frequency ν was formed of elements or discontinuous amounts of magnitude $E = h\nu$, h being a universal constant (6.6×10^{-27} C.G.S.).*

Radiant energy must therefore have an atomic structure, like matter itself. The acceptance of this hypothesis entails as a consequence the law of the distribution of radiation known under the name of "Planck's formula," which is found to be in good agreement with experiment.

Generalising Planck's principle, Einstein made the hypothesis that the vibrating atoms of solid bodies behave like Planck's oscillators, from the point of view of energy exchanges. More precisely, considering the component of the vibration of an atom parallel to one of the axes of co-ordinates, the energy

* Planck's constant k must not be confused with the thermal constant k which we have already denned in connection with the equipartition of energy.

corresponding to this component can only vary in discontinuous jumps or multiple quanta of E , whatever the mechanism of exchange (collisions, radiation, etc.).

Let us now attempt to calculate the mean energy corresponding to such a linear vibration. The parameters on which the state of the molecule depends are, as before, the 3 components x, y, z of its centre of gravity and the 3 components u, v, w of its velocity of translation. According to the general law of distribution (47) the number of molecules of the solid whose parameters lie within the limits x and $x + dx \dots u$ and $u + du \dots$ is of the form,

$$dn = Ae^{-2hE} dx dy dz du dv dw.$$

Let us consider separately that part of the total energy E of the molecule which corresponds to the component of the atomic vibration parallel to Ox . It is represented by the expression,

$$E_x = \frac{1}{2}mu^2 + ax^2 \quad . \quad . \quad (72)$$

By integrating the expression for dn for all possible values of the variables y, z, v, w , we obtain the number of molecules whose parameters x and u lie between x and $x + dx$, u and $u + du$, in the form,

$$dn_x = A_x e^{-2hE_x} dx du.$$

To avoid all confusion in notation with Planck's constant h , we shall express the thermal constant h in the preceding equation as a function of the Boltzmann constant k , by means of the relation already demonstrated $\frac{1}{2h} = kT$, giving as result,

$$dn_x = A_x e^{-\frac{E_x}{kT}} dx du \quad . \quad (73)$$

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This expression may now be transformed, keeping the energy E_x as the only variable, in order to determine the number of molecules for which E_x lies within limits bounded by E_x and $E_x + dE_x$. To do this the expression (73) must be integrated by allowing the variables x and u to vary within a region which is defined, according to (72), by the double inequality,

$$E_x < \frac{1}{2} mu^2 + ax^2 < E_x + dE_x.$$

Known mathematical formulae show the result to be of the form,

$$dn_E = B e^{-\frac{E_x}{kT}} dE_x.$$

In accordance with classical conceptions of statistical mechanics we may now assume that all values of the energy E_x are equally possible for the linear vibration considered, and calculate thereby the mean value of the energy E_x by the formula,

$$\bar{E}_x = \frac{\int_0^\infty E_x dn_E}{\int_0^\infty dn_E} \quad . \quad . \quad . \quad (74)$$

arriving at the final result

$$\bar{E}_x = kT$$

which may be deduced from the general theorem of equipartition. For a molecule capable of vibrating parallel to three axes, the number of parameters will be three times as great, and we have, in consequence,

$$\bar{E} = 3kT,$$

a relation which, multiplied by Avogadro's constant N to extend the result to a gramme-atom, brings us once more to formula (70) and the law of Dulong and Petit.

Let us assume, on the contrary, that the energy of the linear oscillation can only increase by quanta of the magnitude $c = h\nu$. The integrals occurring in (74) are then split up into partial integrals, extending from 0 to c , from c to $2c$ In the first the energy E_x has the value 0, in the second the value c In this way we find

$$E_x = \frac{ce^{-\frac{c}{kT}} + 2ce^{-\frac{2c}{kT}} + \dots}{1 + e^{-\frac{c}{kT}} + e^{-\frac{2c}{kT}} + \dots} = \frac{c}{e^{\frac{c}{kT}} - 1}.$$

For a molecule capable of vibrating parallel to the three axes, the mean energy will obviously be three times as great, and therefore equal to

$$\bar{E} = \frac{3c}{e^{\frac{c}{kT}} - 1} = \frac{3h\nu}{e^{\frac{h\nu}{kT}} - 1}. \quad (75)$$

If this result is to refer to a gramme-molecule of the substance, the internal energy of the substance must be

$$U = 3N \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

Such is the formula which must replace formula (70). From it the molecular heat (or atomic heat, since the molecules are monatomic) at constant volume is calculated to be

$$C_v = \frac{dU}{dT} = 3R \frac{e^{\frac{h\nu}{kT}} \cdot \left(\frac{h\nu}{kT}\right)^2}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}. \quad (76)$$

At high temperatures this formula reduces to the form (71). It expresses once again the law of Dulong and Petit, which appears as a limiting law, valid only when the temperature is sufficiently high: it

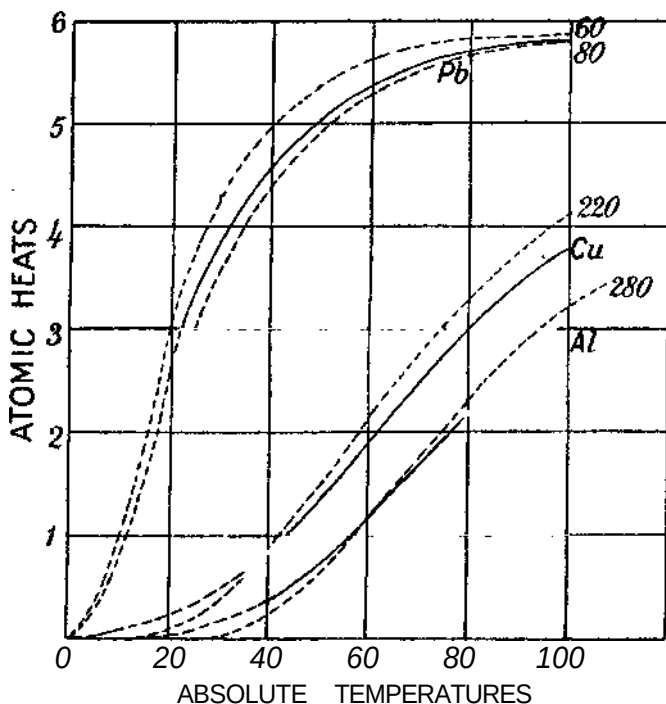


FIG. 2.

appears that, for many simple substances, the ordinary temperature satisfies this condition.

At low temperatures, the form of the curve which represents equation (76) (see Fig. 2) is in complete agreement with that of the experimental curves;

in particular it reproduces the decrease of the atomic heat which tends toward zero as the absolute zero of temperature is approached. The quantitative agreement is quite good, taking the frequency ν of the atomic oscillators to be that deduced from an optical study of the substance.* But, in actual fact, the characteristic frequency of the vibrations of atoms in a solid cannot be considered as limited to one particular value; it must be extended over a complete spectrum. Taking cognisance of this circumstance, Debye has succeeded in perfecting Einstein's calculation, obtaining a formula of the same type, although a little more complicated, which agrees quantitatively with the facts in a highly satisfactory manner.

In conclusion, let us consider the modification which must be introduced in the enunciation of the theorem of the equipartition of energy, in order to account for the preceding results. According to formula (75) every degree of freedom of a molecule must possess a mean energy which, instead of having the value $\frac{kT}{2}$ as a function of the temperature alone, must be expressed in the corrected form,

$$\frac{1}{2} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

This expression reduces to the former if the temperature is high enough, or the characteristic frequency of the atomic oscillation ν sufficiently small.

* The numbers printed on Fig. 2, in the top right-hand corner, beside the dotted curves, represent the numerical values of the parameter $\frac{h\nu}{kT}$, which were chosen to draw the curves according to formula (76). The experimental curves are drawn in thick lines.

In the case of a gas, where intermolecular actions are usually very weak, the characteristic frequency of the molecular vibrations is practically nil, and the theorem of equipartition preserves its usual form. On the other hand the correction becomes necessary for states of matter which are sufficiently condensed and at temperatures so low that T can no longer be regarded as large nor v as small. The theorem of equipartition is no more than a limiting law, analogous to the laws of perfect gases.

CHAPTER VII

BROWNIAN MOVEMENT

35. General Character of the Phenomena.—If small particles in suspension in a liquid are examined under the microscope they are found to be moving rapidly and incessantly in an irregular fashion in all directions ; the smaller the particles, the more lively and noticeable do the movements become. The phenomenon has been given the name of " Brownian Movement " after the English botanist Brown who first discovered it in 1827. From the point of view of molecular theory its importance was not recognised at the time. A long series of researches was necessary to remove all doubt as to its cause, nowadays taken without question to be molecular agitation.

Initially it was natural to suggest an explanation of the phenomenon through the most common physical agencies ; inequalities of temperature, peculiarities of the microscopic preparation, vibrations, chemical action, electrical influences, etc. None of these explanations were satisfactory, in the light of numerous experimental researches on the subject, of which those due to Gouy merit particular attention. Gouy demonstrated the true nature of the phenomenon in very clear fashion: the motion depends only on the size of the particles and **not upon their nature** ; it seems to be eternal, continuing

indefinitely without appreciable diminution or modification. In consequence of his work, there seemed little doubt that particles endowed with Brownian motion behaved just like buoys in a sea of molecules, indicating by their irregular movements the irregularity of molecular collisions : it was proof direct of the existence and movement of molecules.

A great amount of work, theoretical and experimental, carried out more recently, has consolidated this conception by the support of quantitative verification. Before passing to a deeper study of it, however, it is well to remark how clearly the Brownian movement has justified the particular point of view of kinetic hypotheses ; ordinary observations on fluids merely give us some knowledge of their average properties.

A liquid which appears to us to be at rest when we observe it by the coarse means normally at our disposal, really conceals an intense internal agitation which the suspended particles make manifest to us. The mean equilibrium is only apparent, hiding the actual motion.

Similarly the mean temperature appears to be constant to us, although in reality it must necessarily suffer variations or " fluctuations " of a local nature. For example, when a particle animated by the Brownian movement spontaneously rises in spite of its weight, the increase of its potential energy can only occur at the expense of the kinetic energy of the neighbouring molecules, that is to say, at the expense of local cooling. It is obvious that in this case there is a transformation of heat into work without the expenditure of auxiliary work. Carnot's principle will not be satisfied, therefore, if it is confined to a very restricted definition. It must be remembered that theoretical considerations have

already led us to admit that this principle is not necessarily exact for phenomena studied on the molecular scale. It is only valid as a statistical principle, applicable to systems with a very large number of parameters, for which it assumes the nature of a certainty (Chapter V) : we find here the experimental confirmation of this point of view.

36. Theory of the Brownian Movement. Einstein's Formulae.—A theoretical study of the Brownian movement may be made by comparing the particles in suspension in the liquid with bulky molecules of a foreign substance, disseminated among the much smaller molecules of the pure liquid. The laws of motion of these molecules should, therefore, be identical with those which govern the molecules of a dilute solution, and in the final case with those governing the molecules of a gas (see Art. 9). Although the enormous molecular weight of the particles under consideration may change the scale of measurement, they should not affect the fundamental character of the phenomena. In particular, the laws for the distribution of the density and the energy valid for gases should be applicable without essential difference to particles endowed with Brownian motion, if it is assumed that thermal equilibrium is realised. In particular, it should be possible to apply to the particles the formula (50) for the variation of pressure with barometric height, established for a gas occurring in a mixture ; the variation of the molecular density with altitude will merely be much more rapid than in the case of a gas.

The theorem of the equipartition of energy in its classical form may also be applied in a similar manner to the particles, showing thereby that each one of them possesses an average kinetic energy of translation equal to $\frac{3kT}{2}$.

We shall see that experiment has enabled us to verify these two conclusions quantitatively. The first is susceptible to direct experiment. The second one only becomes so through an important intermediate theory due to Einstein, the results of which we shall now consider.

Let x be the component of the displacement of a granule in Brownian motion in a definite direction, which we shall take as the axis of abscissae. At the end of a sufficiently long time the average value of x is evidently zero, because of the supposed irregularity of its movements. Such is not the case, however, with the mean square Δ^2 of x , which will grow with the duration T of the observations, and will be a definite function of T . We shall see that this function may be calculated completely, and that its introduction leads to quantitative relations which may be verified.

With this object, let us imagine that the granules are not uniformly distributed in the liquid, but have a uniform gradient of concentration in the direction of the axis of x . Progressive diffusion will occur parallel to this line (from left to right, say), and, if the permanent state is reached, we may proceed to the calculation of the coefficient of diffusion D . We shall carry out the calculation in two distinct ways.

To, simplify the matter, let us consider the displacements to occur only in the direction of Ox , all the particles suffering the same displacement, equal to the mean square displacement Δ , in the time T . Let n_1 and n_2 be the concentrations of the grains in two sections S_1 and S_2 of a cylinder, whose sides run parallel to Ox , and separated by a distance Δ . The gradient of concentration for the median section will be $\frac{n_1 - n_2}{\Delta}$ and, according to the definition (35)

of the diffusion coefficient D , the surface S will be traversed by a number of grains $D \cdot \frac{n_1 - n_2}{\Delta} \cdot \tau S$ during the period T from S_1 towards S_2 . On the other hand, the movements of the grains having just the same tendency to occur in one direction as in a direction opposite to it, we may assume the grains which cross the surface S from S_1 towards S_2 to be half those which are contained in a cylinder of base S and height A situated beside S_1 , that is $\frac{1}{2}n_1\Delta S$ grains. Similarly those which cross S from S_2 in the direction of S_1 during the time τ must be $\frac{1}{2}n_2\Delta S$ in number. The total flux will be

$$\frac{1}{2}(n_1 - n_2)\Delta S$$

leading to the equation,

$$\frac{1}{2}(n_1 - n_2)\Delta S = D \frac{n_1 - n_2}{\Delta} \tau S$$

$$\text{or} \quad D = \frac{\Delta^2}{2\tau} \quad . \quad . \quad . \quad (77)$$

This formula, obtained by a very simple but imperfect argument, may be checked by more exact calculation.

The same coefficient of diffusion D is related to the viscosity of the liquid. The granules contained in the cylinder defined above are subject as a whole to a tractive force parallel to Ox due to the inequality of the osmotic pressures at its two ends. If p_1 and p_2 represent the values of these pressures in the two sections S_1 and S_2 , the total force acting on the granules within it is $S(p_1 - p_2)$. Assuming the validity of the laws of perfect gases and the theorem of equipartition for the system of granules, the

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Amitotic pressures may be calculated by h^2) and (i8), so that

$$p = \frac{n}{2h} = n \cdot \frac{R}{N} T.$$

The force calculated a moment ago, therefore, takes the form,

$$F = \frac{S}{2h} (n_1 - n_2) = - \frac{SRT}{N} \frac{dn}{dx} \Delta,$$

since the gradient of concentration $-\frac{dn}{dx}$ is supposed to be constant. The total number of particles being $nS\Delta$, the force referring to a single particle is

$$f = - \frac{RT}{N} \cdot \frac{1}{n} \frac{dn}{dx}.$$

Now, a study of the movement of a particle, under the influence of a constant force/, in a viscous liquid has shown that, in the permanent state, the particle moves with a velocity v proportional to the applied force, and defined by an equation of the form

$$f = C v \quad . \quad . \quad . \quad (78)$$

We may, therefore, write

$$C v = - \frac{RT}{N} \frac{1}{n} \frac{dn}{dx}.$$

Further comparison with the definition (37) of the diffusion coefficient D of the particles shows that

$$D = \frac{RT}{NC} \quad . \quad . \quad . \quad (79)$$

The particular case of most importance is that in which the mobile particle is comparable with a

FLUCTUATIONS

mature must occur in a gas in isothermal equilibrium. A charged electrical condenser will show fluctuations in its charge, and a continuous electric current fluctuations in its intensity. We shall see why only a small number of these fluctuations have been brought to light hitherto.

The existence of fluctuations contradicts the principle of Carnot in its former rigid enunciation. On the other hand it is in agreement with it when it is regarded as a statistical law, as we have shown in Chapter VI. Since thermodynamic equilibrium, characterised by the maximum value of the entropy, is merely a statistical equilibrium corresponding to the most probable state, the other possible states are not excluded, and states sufficiently near to the equilibrium condition may be reached by the system in accordance with the laws of probability; this is the origin of fluctuations.

41. The General Law of Fluctuations.—The general law of fluctuations has been given by Einstein. It may be derived in the following way:

We have seen that the entropy S of a system is connected with its probability w by Boltzmann's relation (69). If it starts in a state of thermodynamic equilibrium for which the entropy S_0 and the probability w_0 have their maximum values, Boltzmann's relation may be written:

$$S - S_0 = k \log \frac{w}{w_0}$$

or again

$$w = w_0 e^{\frac{S - S_0}{k}} \quad . \quad . \quad . \quad (89)$$

If one of the parameters which define the state of the system assumes the value x_0 in the state

thermodynamic equilibrium, and, the internal energy U remaining constant, if the same parameter takes the value x in the course of its fluctuations, we may admit that this variation will have little noticeable effect on the temperature T . The difference between the available energies ϕ_0 and ϕ for the two values of the parameter x_0 and x_t when the internal energy is constant, is given by the relation,*

$$S - S_0 = \frac{\phi_0 - \phi}{T},$$

which enables us to write formula (89) in the form,

$$w = Ae^{-\frac{\phi - \phi_0}{kT}} \quad . \quad . \quad . \quad (90)$$

in which A is a constant.

Such is the general law of fluctuations ; it expresses the probability $w(x)$ that the available energy shall have a value $\phi(x)$ corresponding to the value x of the parameter, differing from x_0 . It is known that if the change from one state to another can be made in an isothermal and reversible manner, the increase in available energy is equal to the external work U done by the system, with the sign reversed.^f In this case we may, therefore, write

$$w = Ae^{\frac{\tau}{kT}} \quad . \quad . \quad . \quad (91)$$

a relation which, in most cases, makes the calculation of fluctuations a comparatively easy matter.

In general the available energy ϕ is a continuous

Since $\phi \ll U - TS$ (see text-books of thermodynamics),
^f See, for example, Nemst, "Theoretical Chemistry" : Introduction ; or Lewis, "Introduction to Physical Chemistry" vol. ii.

function of the variable x . As it should be a minimum for the state corresponding to thermodynamic equilibrium, we may develop $\phi - \phi_0$ in a power series of $(x - x_0)$, the first term being neglected since $\frac{d\phi}{dx}$ is zero when ϕ is a minimum, and terms higher than the second ignored because of their extreme smallness. In this way

$$\phi - \phi_0 = a(x - x_0)^2$$

where a is a constant quantity. Formula (90), therefore, allows us to calculate the mean value of $\phi - \phi_0$ and gives immediately (by a process precisely analogous to that in Art. 24),

$$\phi - \phi_0 = \frac{kT}{2} = \frac{1}{4h}.$$

We have here a generalisation of the theorem of equipartition. It is obvious that the mean deviation of the available energy in the course of the fluctuations is equal to the mean kinetic energy of a molecule per degree of freedom at the same temperature. The fluctuations are, therefore, very small, and can be demonstrated experimentally in a very small number of cases only.

For example, to get some idea of the spontaneous charge assumed by a condenser whose plates are joined by a conducting wire, or the spontaneous variations of the current in a closed circuit, we may say that the electrostatic energy $\frac{CV^2}{2}$ of the condenser in the first case, and the magnetic energy $\frac{LI^2}{2}$ of the variable current in the second case, have the

mean value $\frac{kT}{2}$. Similarly, any linear oscillator whatever (spring, organ pipe, etc.) will make spontaneous oscillations, whose kinetic energy and potential energy will, on the average, have the same value $\frac{kT}{2}$, and whose total energy will consequently be kT .

42. Fluctuations of Density in a Fluid. Critical Opalescence.—An interesting application of the general theory has been made by Smoluchowski to the fluctuations of density in a fluid. Let us consider a volume element ω of the fluid containing n_0 molecules. The density ρ , and consequently the specific volume $v = \frac{1}{\rho}$ of the fluid, instead of remaining uniform in the element ω , will oscillate about the values ρ_0 and $v_0 = \frac{1}{\rho_0}$ which correspond to uniformity. To find the value of these fluctuations, let p_0 be the pressure corresponding to uniform density, and p the actual pressure. The external work done isothermally in bringing the element to from the mean state of equilibrium to the actual state will be

$$\tau = mn_0 \int_{v_0}^v (p - p_0) dv \quad . \quad . \quad (92)$$

and the probability that the specific volume shall lie between v and $v + dv$ will be, in consequence, according to (91),

$$w(v)dv = Ae^{\frac{\tau}{kT}} dv \quad . \quad . \quad (93)$$

But an obvious development in series by Taylor's theorem gives

$$\int_{v_0}^v (\bar{p} - p_0) dv = \frac{\partial \bar{p}}{\partial v_0} \frac{(v - v_0)^2}{2} + \frac{\partial^2 \bar{p}}{\partial v_0^2} \frac{(v - v_0)^3}{2 \cdot 3} \\ + \frac{\partial^3 \bar{p}}{\partial v_0^3} \frac{(v - v_0)^4}{2 \cdot 3 \cdot 4} + \dots$$

Since $v - v_0$ is very small, we may generally stop short at the first term. If, therefore, γ represents the "condensation" $\frac{v - v_0}{v_0}$, we may write

$$w(\gamma) d\gamma = A e^{-B\gamma^2} d\gamma \quad . \quad . \quad (94)$$

in which

$$B = - \frac{mn_0 v_0^2}{2kT} \frac{\partial \bar{p}}{\partial v_0} = - \frac{\omega N}{2RT} v_0 \frac{\partial \bar{p}}{\partial v_0} \quad . \quad (95)$$

Formula (94) gives the probability that the spontaneous condensation of the fluid in the element co lies between y and $y + dy$. It is easily seen that it obeys the law of chance (see Note |, p. 5).

The constant A is easily determined as a function of B , when it is observed that the integral of $w(\gamma) d\gamma$ taken from $-\infty$ to $+\infty$ should be equal to unity.

The value of A is found thereby to be $\sqrt{\frac{B}{\pi}}$ (see Note I at the end of the volume).

Thus

$$w(\gamma) d\gamma = \sqrt{\frac{B}{\pi}} e^{-B\gamma^2} d\gamma \quad . \quad . \quad (96)$$

Utilising formulae already used in several cases, we may deduce simple expressions for the mean absolute value of the condensation,

$$|\bar{\gamma}| = 2 \int_0^\infty \gamma \sqrt{\frac{B}{\pi}} e^{-B\gamma^2} d\gamma = \frac{1}{\sqrt{\pi B}} \quad . \quad (97)$$

and for the mean square of the condensation,

$$\overline{\gamma^2} = \int_{-\infty}^{+\infty} \gamma^2 \sqrt{\frac{B}{\pi}} e^{-B\gamma^2} d\gamma = \frac{1}{2B}.$$

According to this last result, formula (96) may be written in the form,

$$w(\gamma)d\gamma = \frac{1}{\sqrt{2\pi\overline{\gamma^2}}} e^{-\frac{\gamma^2}{2\overline{\gamma^2}}} d\gamma,$$

in all respects similar to formula (86) for the Brownian movement. This latter is nothing more than the fluctuation of position of a particle in suspension in a liquid.

Formula (96) is valid for any fluid whatever. In the particular case of a perfect gas, the relation (95) gives the value of B immediately as

$$B = \frac{n_0}{2}.$$

Formulae (96) and (97) become

$$w(\gamma)d\gamma = \sqrt{\frac{n_0}{2\pi}} e^{-\frac{n_0\gamma^2}{2}} d\gamma$$

$$|\overline{\gamma}| = \sqrt{\frac{2}{\pi n_0}}.$$

We see that the mean condensation, throughout the fluctuations, differs more and more from zero as the number of molecules becomes smaller. It will be difficult, however, to study experimentally volumes so small that fluctuations of density reach a noticeable magnitude. In a cube whose side is of the order of the wave-length of visible light, the number of molecules under normal conditions will be of the

order 10^9 (see Art. 17), if the density is of the same order as common liquids. The fluctuations of condensation will not exceed one 30,000th of the normal density. For a gas under normal conditions they scarcely reach one thousandth. They remain inappreciable, therefore.

Such is no longer the case at the critical point of the fluid. Formulae (95) and (97) show, in fact, that the mean condensation is the more important the smaller B becomes, that is to say, the greater the compressibility of the fluid, and it is common knowledge that at the critical point the compressibility tends to become infinitely great. According to the classical theory of fluids, at the critical point $\frac{\partial p}{\partial v_0}$ and $\frac{\partial^2 p}{\partial v_0^2}$ are zero. It is formula (91) once more which gives the probability that the condensation lies between y and $y + dy$, but in order to calculate U this time it is necessary to push the development in series to the term containing $\frac{\partial^3 p}{\partial v_0^3}$. In this manner it is found that

$$w(\gamma) d\gamma = A e^{-B_1 \gamma^4} d\gamma,$$

putting

$$B_1 = - \frac{mn_0}{kT} \frac{v_0^3}{2 \cdot 3 \cdot 4} \frac{\partial^3 p}{\partial v_0^3}.$$

The fluid no longer behaving like a perfect gas, the calculation may be continued, for example, by introducing Van der Waals' equation (20). We find thus,

$$B_1 = \frac{9}{64} n_0,$$

which gives as mean of the absolute values of the condensation the value

$$|\bar{\gamma}| = \frac{1.13}{\sqrt{n_0}},$$

independent of the fluid chosen. The application of this result to a cube of liquid whose dimensions are of the same order as the wave-lengths of visible light (a cube containing about 10^9 molecules) now gives for the mean deviations of condensation a number of the order of one-hundredth.

This deviation explains why the medium appears turbid when it is strongly illuminated and observed at right angles to the direction of the incident light. The emission of a bluish light is observed, a phenomenon known by the name of the critical opalescence. From the preceding theory Keesom has been able to deduce theoretically the intensity of the light diffused. The agreement between theory and experiment is quantitative ; their comparison affords a method of calculating still another value for Avogadro's constant, which has been found equal to 75×10^{22} , in satisfactory agreement with those already given.

It is interesting to note that an application of Keesom's calculations to a gas gives a derivation of the formula given by Lord Rayleigh for the intensity of the "blue of the sky," considering it as solar light diffused by the molecules of the air. This phenomenon is thereby related to the general theory of fluctuations.

We shall not lay stress here on the phenomena of fluctuation which have been encountered in the study of radioactive bodies ; fluctuations in the emission of α particles, scintillations in the phosphorescence of a screen struck by these particles, etc. Reference must be made to special works for further information concerning them.

CHAPTER IX

HIGHLY RAREFIED GASES

THE properties of highly rarefied gases present certain remarkable characteristics. We have seen that the mean free path of the molecules of a gas should vary inversely as the pressure ; from the order of one ten-thousandth of a millimetre at ordinary pressures, it may become several centimetres or even several decimetres at very low pressures. In other words, we may realise pressures so low that the mean free path reaches, and even exceeds, the dimensions of the apparatus in which the work is being carried out. It will be particularly easy to attain this result if the gas is contained in a capillary tube or between two plates very close together. The collisions of the molecules with one another then become less numerous than the collisions of the molecules with the solid walls, and if the pressure is sufficiently low, may not occur at all. A profound change in the ordinary properties of gases occurs in consequence ; experimental and theoretical study has led to a series of most interesting conclusions, of which we shall consider the more important.*

43. Experiments on the Flow of Gases through Capillary Tubes.—We have seen that the flow

* There is no question here of electric discharges in highly rarefied gases. The important discoveries made in this field belong to another chapter of molecular physics.

of a gas through a capillary tube at ordinary pressures, satisfies the law of Poiseuille, expressed by formula (28) ; this law provides a means of measuring the viscosity η of the gas. The gas behaves as if it adhered to the walls of the tube (formula 26), and its velocity of flow increases from zero to a maximum value going from the walls towards the axis. The amount lost is proportional, according to formula (28a), not only to the difference of pressure $P_1 - P_2$ between the extremities of the tube, but also to the mean pressure $p = \frac{p_1 + p_2}{2}$ of the gas

flowing. All the consequences of formula (28), deduced from the classical hydrodynamics of viscous fluids, are fully verified by experiment. It is to be remembered that the coefficient of viscosity of the gas, calculated by this formula in agreement with the theory expounded in Chapter III, is independent of the pressure throughout a very wide range, when the range is not too large.

The deviations from formula (28) shown by experiment appear when the mean pressure is so low that the mean free path λ of the molecules is no longer negligible compared with the radius of the tube. The gas behaves as if it no longer adhered to the wall, but glided over it with a definite velocity; there is a discontinuity in velocity at the wall passing from the solid to the gas. We may also say that its behaviour is such that the gaseous layers reach zero velocity, not at the wall of the tube itself, but at a fictitious wall of greater radius ; the delivery, therefore, becomes greater than is predicted by Poiseuille's law. This latter must be replaced by the following:

$$G = \frac{\pi r^4}{8\eta l} (p_1 - p_2) \frac{pM}{RT} \left(1 + \frac{4\lambda}{r}\right) \quad . \quad (98)$$

expressing that the radius r is apparently increased by the small amount ϵ . The experiments of Kundt and Warburg (1875) have confirmed this new law and have furnished numerical values for ϵ which, like the mean free path, vary inversely with the pressure, and which are of the same order of magnitude as the mean free path itself. Another way of looking at the matter is the following: the coefficient of viscosity $-q$ derived from the formula (28), instead of being independent of the pressure in agreement with Maxwell's theory, gradually decreases when the pressure becomes sufficiently low.

The theoretical reason for this change remained obscure until the experimental work of Knudsen (1909) shed a new light upon it. These experiments were carried out at the lowest pressures it was possible to realise. They showed that the law expressed by formula (98) itself needed a supplement; at very low pressures the rate of flow under a given pressure drop, instead of decreasing proportionally to the mean pressure, passes through a minimum, increases again, and finally tends towards a constant limit when the pressure is sufficiently near zero. These results are represented by a curve of the type drawn above (Fig. 3), in which the rectilinear part AB corresponds to the law of Poiseuille, the part BC to the gliding of the gas relative to the wall, and the part DE to a constant rate of flow.

These very curious results show that the conception of the coefficient of viscosity loses all significance at very low pressures, and that flow occurs under the influence of causes which are quite new. It is, in fact, not the mutual collisions of molecules which govern the velocity of discharge, but the collisions with the wall of the tube.

More recent experiments of Gaede (1914), made

with many precautions, relative to the flow of gases between planes with parallel faces very close together (for which the effects considered may be much magnified), have completely confirmed the results of Knudsen.

44. Theory of Molecular Flow.—A partial theory of the observed facts has been given by Knudsen ;

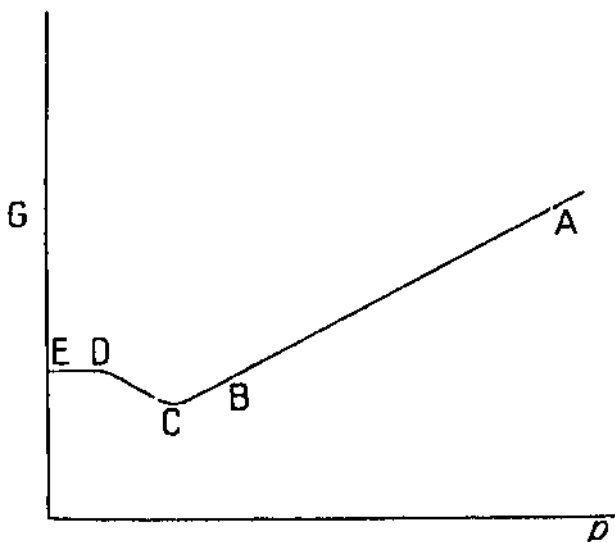


FIG. 3.

it refers to the case of the very lowest pressures, for which the rate of flow G is constant and no longer depends on the mean pressure of the gas (the part DE on the curve). It is the case in which intermolecular collisions no longer come into account. Only the collisions with the wall are of any importance ; the process has changed from one of viscous flow to molecular flow. Subject to those

objections common to all theories using the notion of mean free path, this theory has been improved by Smoluchowski, and seems to be quite satisfactory in all its essential features.

The principal difficulty encountered in this connection, as in all questions involving collisions against a wall, is relative to the nature of the exchanges of velocity which take place between the molecules and the wall. In what direction will the molecules rebound and what will be their mean velocity after the collision? If the gas is at rest and if, as in the actual case, the temperature is uniform, one is tempted to assume that the law of distribution of velocities, before and after the collision, is the law of Maxwell. If the gas is in motion the law of Maxwell can only serve as a first approximation, with which we must be content. As for the directions of the velocities after collision, we shall consider them, with Knudsen, as distributed with an equal probability in all directions. In fact, we shall assume that the collisions have the effect of diffusing the molecules at random, as if the wall absorbed them to eject them afresh without sending them in any privileged directed (such as the direction of regular reflection). This hypothesis, which seems to be verified by its consequences, is expressed, as in the case of the complete diffusion of light, by the "cosine law"; the number of molecules ejected by an element of the wall in a direction which makes an angle θ with the normal to the element is proportional to $\cos \theta$.*

To apply these principles to the study of the flow

* This is probably true only at sufficiently high temperatures. At low temperatures, the proportion of molecules absorbed by the walls and not diffused becomes more and more important: a true condensation of the gas then occurs. This is what happens in Langmuir's diffusion pump which will be described later.

of a highly rarefied gas in a capillary tube, let us first calculate the amount of momentum transferred to unit surface of the wall in unit time. We have seen that the number of molecules which will strike this element in one second is given by the relation (9):

$$\nu = \frac{nC}{\sqrt{6\pi}}$$

in which n represents the molecular density and C the mean square velocity. The quantity of momentum parallel to the axis of the tube, transmitted by the collision of the molecules to the element considered will therefore be

$$B = nu \frac{nC}{\sqrt{6\pi}}$$

in which u is the mean velocity of the molecules parallel to the wall at the moment of the collisions, or taking the formulae (7), (12), and (15) into account,

$$B = up \sqrt{\frac{M}{2\pi RT}} \cdot \cdot \cdot (99)$$

If the molecules are equally diffused in all directions by collisions, the wall will not receive any other momentum, and if the intermolecular collisions may be neglected, the velocity u may be considered as the velocity of the whole gas parallel to the wall.

In consequence of this the total mass of gas delivered per second will be

$$G = \pi r^2 \rho u = \frac{\pi r^2 \rho}{p} \sqrt{\frac{2\pi RT}{M}} B = \pi r^2 \sqrt{\frac{2\pi M}{RT}} B \quad (100)$$

To transform this expression, we must find some other method of calculating the momentum B . To

this end let us consider a portion of the capillary tube of length l , putting p_1 and p_2 as the pressures of the gas at each end (the pressure gradient being regarded as uniform). The total force exerted by the gas on this part of the tube is evidently

$$\pi r^2(p_1 - p_2).$$

If it is referred to one square centimetre of the lateral surface $2\pi rl$ of the tube, a force is obtained which should be identical with the momentum B per unit surface.

$$B = \frac{r}{2} \cdot \frac{p_1 - p_2}{l}.$$

Introduced in equation (100) this value gives

$$G = \frac{\pi r^3}{l} \sqrt{\frac{\pi M}{2RT}} (p_1 - p_2) \quad \cdot \quad (101)$$

A more rigorous calculation leads to formulae identical with (99) and (101) except for a numerical factor in the neighbourhood of unity—equal to $\frac{8}{3\pi}$ according to Knudsen—which must be introduced in the second term of these equations.

45. Experimental Verification. The Molecular Manometer.—It should be noticed in the first place that the formula (101) is in good qualitative agreement with the results obtained by Knudsen at very low pressures. The amount discharged under a given fall of head, which, in the Poiseuille regime, is proportional to the mean pressure, should become independent of the pressure at pressures which are sufficiently low to secure the validity of formula (101); this is the phenomenon of the constant limit of discharge discovered by Knudsen. On the other hand, in conformity with the relation (101) it is easily

verified that the limiting rate of flow is proportional to the third power of the diameter of the tube, and not to the fourth power as in the Poiseuille region. Finally, the nature of the gas no longer comes into consideration through the coefficient of viscosity η , but only through the molecular weight M ; the limiting rate of discharge is proportional to the square root of M .

The relation (101), which represents the laws of the limiting flow very satisfactorily, appears to agree very well in absolute value. An a priori calculation of the limiting discharge rate may be made with a very satisfactory accuracy.

When a given volume is evacuated by means of a pump with a high rate of discharge, the tube which connects the apparatus to be evacuated with the pump itself offers a certain resistance to the passage of the gas which, for sufficiently low pressures, may be deduced from formula (101). This resistance is proportional to $\frac{l}{r^4}$, and the connecting tube should be

chosen such that the limiting discharge corresponding to it shall be comparable with that of the pump; if this is neglected all the advantages of rapidity afforded by modern pumps are lost completely. For use with very rapid pumps (see Art. 50) it is advisable to select pipe systems for evacuation of a diameter which is, at first glance, surprising; with a Gaede molecular pump, for instance, a vacuum tube of 1 metre should have an internal diameter of 20 millimetres at least; according to formula (101) the increase in diameter is much more important than the diminution in length.

Formula (99) may be used for the measurement of very low pressures, equal to, or less than, a few thousandths of a millimetre of mercury; for such

pressures the MacLeod gauge no longer provides very sure results, because of the vapour pressure of the mercury which is superposed on that of the residual gas. For greater generality we shall write the formula in the form,

$$B = K\omega p \sqrt{\frac{M}{RT}} \quad . \quad (102)$$

in which K is a constant. Dushman's molecular manometer, which utilises this formula, comprises : 1st, a horizontal disc suspended by a quartz fibre whose constant of torsion is C , carrying a mirror intended to measure the angle through which it has turned; 2nd, a disc parallel to the first, situated a few millimetres below it, and given a constant velocity of rotation, of a known magnitude which is sufficiently high, about an axis in prolongation of the suspending fibre. If the whole apparatus is placed in a highly rarefied gas,* that is if the above formula is applicable, it is possible to calculate the total moment of the molecular forces exerted by the movable disc on the fixed disc. The formula (102), in fact, expresses the force exerted by unit surface of the mobile disc, taken at a point where the linear velocity is u , on the fixed system suspended by the quartz fibre. If ω is the angular velocity of the movable disc, and r is the distance of a point on this disc from the axis of rotation, the sum of the momenta of the molecular forces will be, therefore,

$$H = \int_0^r . K\omega r p \sqrt{\frac{M}{RT}} 2\pi r dr = \frac{K\pi r^4 \omega p}{2} \sqrt{\frac{M}{RT}}.$$

* The rotation of the lower disc in the vacuum is obtained by the action of a magnetic field turning a magnet fixed to the disc.

The upper disc turns through an angle α defined by the equation,

$$C\alpha = \frac{K\pi r^4 \omega p}{2} \sqrt{\frac{M}{RT}}.$$

This relation permits the measurement of the pressure p by the angle of rotation α , subject to the constancy of rotation of the lower disc. In principle, it necessitates a calibration, but perhaps there would be no great difficulty in obtaining a value for the constant K sufficiently exact to transform the apparatus into an absolute manometer. The sensitivity depends on the velocity of rotation of the lower disc and is proportional to it; it may be used to measure a pressure of a thousand millionth of a millimetre of mercury.*

46. Effusion of Gases.—This is the name given to the progressive passage of a gas through a small opening cut in a thin wall in the envelope which encloses the gas. If the pressure of the gas is high enough for the mean free path of the molecules to be considered small with respect to the size of the aperture, effusion will occur according to laws predicted by hydrodynamics and confirmed by experiment; it forms a gaseous jet which is ejected into the external space, and the volume discharged at constant pressure varies inversely as the square root of the density of the gas (Graham's law). If the pressure of discharge exceeds the back-pressure from the outside by a sufficient amount, this latter does not enter into consideration, and the rate of flow is simply proportional to the pressure of discharge.

* At higher pressures the same arrangement may be used for measuring the coefficient of viscosity of the gas in absolute measure; the method is capable of very great precision.

When the pressures on each side of the aperture diminish so much that the mean free path of the molecules becomes comparable with the dimensions of the aperture, the laws of the discharge are completely altered. The formulae of classical hydrodynamics become powerless to explain them, and the gaseous jet disappears. On the other hand, the kinetic theory enables us to account for the facts, at least at pressures so low that the mean paths are much greater than the diameter of the opening ; this is the case of molecular effusion, again studied by Knudsen, where intermolecular collisions only play a negligible part.

Let us recall the fact that the number of the molecules which strike unit surface of the wall in unit time is given by the formula (9):

$$\nu = \frac{nC}{\sqrt{6\pi}}.$$

If the element of the wall struck is removed, the molecules will traverse the opening so formed. Similarly, a number of molecules,

$$\nu' = \frac{n'C}{\sqrt{6\pi}},$$

will pass in the opposite direction in one second, calling n the molecular density in the external space. The total quantity discharged per second across an element of surface S will therefore be

$$G = \frac{CS}{\sqrt{6\pi}} (p - p'),$$

p and p' being the absolute densities of the two gaseous masses. According to formulae (13) and (15) we may also write

$$G = (p - p') S \sqrt{\frac{M}{2\pi RT}}$$

introducing the pressures p and p' . This formula, verified quantitatively by Knudsen, shows that the mass discharged is now proportional to the difference of pressure and to the square root of the molecular weight M . The volume discharged varies inversely as $\sqrt{M}$, as for high pressures. The result is a law equivalent to that of Graham, although the nature of the flow is entirely different.

The preceding results may be applied to the measurement of the maximum pressures of the vapours of certain liquids of very low volatility. For example, the maximum pressure of mercury vapour at ordinary temperatures may be measured by making it effuse through a small opening in a space which is practically a complete vacuum, where it is condensed by cold. The determination of the mass effused permits the calculation of p by the above formula, since p' is zero. In this way results are obtained in good agreement with older and more direct measurements, although the pressures measured are only of the order of a thousandth of a millimetre of mercury.

47. Radiometric Phenomena. Crookes' Radiometer.—Up to the present we have always considered highly rarefied gases at uniform temperature. If inequalities of temperature are created in the gas, thermal conductivity comes into play, which has already been studied in Chapter III. Further, if the pressure is very low the ordinary laws of conductivity are profoundly modified, and certain new phenomena are encountered which we shall now describe.

The best-known consists in the appearance of forces called "radiometric." The apparatus known by the name of the Crookes' radiometer (1870) is made up of a glass vessel of highly rarefied gas, con-

taining an easily movable mill-wheel with mica vanes. These vanes are blackened on one of their faces. It is sufficient to illuminate the mill-wheel even feebly, to make it turn in such a direction that the blackened faces of the vanes appear to be repelled by the radiation. In sunlight the rotation is extremely rapid.

The radiometric forces which provoke the movement are due to a phenomenon of thermal conductivity in the gas ; but, owing to the rarefaction, it is not the ordinary law of conductivity, with its characteristic coefficient, which comes into play. The mean free path has become of the same order as the dimensions of the vessel and we can no longer speak of a well-defined coefficient of conductivity; the conductivity has assumed a molecular character. Here, then, is the principle of the explanation. The blackened faces of the vanes are more strongly heated by the radiation than their opposite faces. The molecules which strike them, therefore, carry away, on the average, a greater momentum, and this effect is not compensated by the intermolecular collisions, whose number has become negligible. The reaction resulting from its influence on the vanes produces their rotation.

For a given apparatus, the effect of radiation should evidently be greatest for a certain pressure ; if the pressure is too high, collisions between the molecules tend to equalise the exchanges of momentum between the gas and the two faces of the vanes. If it is too low, the number of collisions with the vanes is insufficient to set them in motion. By choosing the gas and its pressure conveniently, and suspending the illuminated surface by a very delicate torsion fibre, it has been possible to convert the Crookes* radiometer to an extremely sensitive

instrument for measuring radiant energy (Nichols). We shall go no further here into its applications.

48. Knudsen's Absolute Manometer.—A careful quantitative study of radiometric phenomena has been made by Knudsen. In principle, it consists in suspending a thin flat plate vertically to a torsion balance and bringing near to it another similar plate parallel to the first and at a higher temperature. If the pressure is so low that the mean free path of the molecules exceeds the distance between the plates, the radiometric forces preponderate, and the heated surface exerts an apparent repulsion on the cold surface. By theoretical means the law of this repulsion may be established.

Let T_x and T_2 be the absolute temperatures of the two parallel surfaces A_x and A_2 , the second being supposed at the same temperature as the envelope containing the rarefied gas. In the state of equilibrium there are n_1 molecules per cm^3 between the surfaces possessing a velocity-component directed from A_1 towards A_2 and n_2 molecules per cm^3 possessing a velocity component directed from A_2 towards A_1 . We shall suppose the velocities of each of these groups of molecules to be distributed according to Maxwell's law. The first class possesses a mean square velocity C_1 greater than the mean square velocity C_2 of the second, since, at the moment of their collisions with A_1 they have at least partially equalised their temperature with that of A_1 . In the stationary state, the numbers of collisions per cm^3 per second suffered by each of the two surfaces are necessarily identical, which, according to formula (9), introduces the relation,

$$n_1 C_1 = n_2 C_2$$

On the other hand, unit surface perpendicular to the

surfaces and situated at the edge of the field which separates them should, on the whole, be crossed by zero mass. If, then, we put n as the molecular density in the external space (where we suppose the mean square velocity equal to C_2), we have

$$n_1 C_1 + n_2 C_2 = n C_2$$

and consequently,

$$n_1 C_1 = n_2 C_2 = \frac{n C_2}{2}.$$

Formula (n) shows from this that the excess of the pressure between the surfaces over the pressure exerted on the other face of the plate A_2 is

$$F = \frac{m}{3} (n_1 C_1^2 + n_2 C_2^2 - n C_2^2) = -\frac{mn C_2^2}{6} \left(\frac{C_1}{C_2} - 1 \right).$$

Finally, assume—and this is the most doubtful hypothesis—that, at the moment of collision, the molecules reach temperature equilibrium with the surfaces A_1 and A_2 , or with the walls of the envelope. We may then write

$$\frac{C_1^2}{C_2^2} = \frac{T_1}{T_2},$$

and

$$F = \frac{p}{2} \left(\sqrt{\frac{T_1}{T_2}} - 1 \right) \quad \cdot \quad \cdot \quad (T03)$$

The repulsive force F as well as the two temperatures T_1 and T_2 being given by experiment, formula (103) gives an expression for the pressure p inside the apparatus in absolute terms; hence the name of absolute manometer which Knudsen gave to it.

Formula (103) seems to be verified quantitatively at the lowest pressures in the different apparatus used

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by Knudsen. The sensitivity may be improved considerably by increasing the ratio $\frac{T_1}{T_2}$ sufficiently; it is sufficient to permit the measurement of pressures of the order of a thousandth of an atmosphere. It seems more prudent, however, to make several reservations on the absolute value of the pressure coefficient in equation (103). The hypothesis made concerning the equalisation of temperature between the moving molecules and the walls they encounter certainly has no general validity. The molecules which rebound into space from a solid wall will normally assume a mean temperature different from that of the wall. It is necessary to introduce a partition coefficient which seriously complicates the theory ; but we can deal no further with this rather delicate question.

49. Thermal Conductivity at very Low Pressures.—The same difficulties present themselves in the measurement of thermal conductivity at very low pressures (Smoluchowski, Knudsen . . .) the interpretation of which has given rise to numerous discussions. We shall merely note that the phenomena present characteristics in all respects similar to those we have met in the measurement of viscosity.

According to Maxwell's theory, valid for ordinary pressures, the coefficient of conductivity, like that of viscosity, should be independent of the pressure (formula 34). That is verified experimentally when the pressure is not too low. If it becomes very small, the coefficient of conductivity diminishes with the pressure, and the phenomenon is similar to that of the gliding over the wall in the study of viscosity. This time we are concerned **with a sudden change in temperature at the wall. The gas in the vicinity of the wall has a temperature different from the wall** itself

(the difference has reached y° in certain experiments), such that the temperature gradient in the gas is smaller than that calculated between the walls themselves. Such is the cause of the apparent diminution in conductivity.

In reality the very idea of coefficient of conductivity loses all precise significance, just as in the case of the coefficient of viscosity. Intermolecular collision having ceased to play any appreciable part compared with collisions with the wall, the theory must be re-established on entirely new foundations.

The attempts which have been made in this direction do not so far seem quite satisfactory ; if it is permissible to assume as a general law that molecules striking a wall are diffused by it in all directions, there is no certain indication of the magnitude and distribution of velocities after collision. This is the difficulty already noted in the case of the absolute manometer.

Without loitering unduly, we may consider an interesting comment due to Knudsen, which has led him to some ingenious experiments. If two vessels A and B, joined by a narrow tube, are at different temperatures T_x and T_a thermodynamic equilibrium corresponds, if the rarefaction of the gas is not too great, to equality of pressure between the two vessels; that is, in a notation similar to that of the preceding paragraph, to the equation,

$$n_1 C_1^2 = n_2 C_2^2.$$

On the other hand if the rarefaction is very great, such that the passage of the gas through the tube can only occur by means of molecular flow, equilibrium corresponds to the new condition,

$$n_1 C_1 = n_2 C_2.$$

which states that the mass of gas which crosses any section whatever is zero in the stationary state. In consequence, the pressures in A and B are no longer identical. If they are represented by p_1 and p_2 we have, from the last equation,

$$\frac{p_1}{p_2} = \frac{C_1}{C_2} = \sqrt{\frac{T_1}{T_2}}.$$

This consequence may be tested experimentally. By local heating at the end of one of a number of fine capillary tubes arranged in series or porous plugs separating the vessels where the gas is highly rarefied, it has been possible to produce pressure differences reaching several millimetres of mercury. If the heating effect is moderately small and the pressure is everywhere very low, the formula obtained is verified quantitatively.

50. The Molecular Pump and the Diffusion Pump.—Gaede has made an interesting application of the properties of highly rarefied gases. He has constructed a molecular pump capable of realising a very high vacuum in a very short time. The principle is as follows :

A movable cylinder rotates very rapidly about its axis in a fixed cylindrical envelope very near to the moving surface. At two points A and B of the envelope apertures are cut leading to tubes, one of which is in communication with the apparatus to be evacuated, the other with a volume already evacuated as a preliminary to a few tenths of a millimetre. The rotation of the internal cylinder takes place from A towards B. As long as the velocity of the movable cylinders is sufficiently low to be negligible compared with molecular velocities, the molecules which issue from the tube A and those coming from the tube B tend to exchange their momentum in-

dependently of the motion of the cylinder, and there is no pressure drop along the circumference of the two cylinders. On the contrary, if the linear velocity at the periphery becomes comparable to the velocity of the molecules (several hundred metres per second), and if at the same time the pressure is so low that the collisions with the wall play an essential role, the molecules coming from A are directed towards B by their rebound from the moving drum, while those coming from B are retarded in their journey towards A. Between A and B, therefore, a molecular pressure drop is established, analogous to that existing in high vacua between the ends of a capillary tube through which a gas is flowing; here, however, it is the movement of the walls which creates the pressure drop, not the pressure drop which tends to produce motion in the walls.

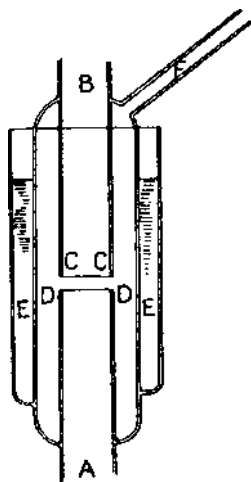


FIG. 4.

The efficiency of this principle is demonstrated by experiment. The apparatus can obtain vacua of one millionth of one millimetre of mercury. It works even if the gas contains a vapour, for example water vapour, drawn in with the gas. Finally, its rapidity is remarkable; it is, of course, a function of the preliminary evacuation. The vacuum tubes, according to a note made earlier, should be sufficiently wide to utilise the pumping power of the pump to the best advantage.

The Gaede diffusion pump and the Langmuir

condensation pump are equally interesting applications of the properties of highly rarefied gases. In the first (Fig. 4), a stream of mercury vapour, obtained by boiling the metal at low pressure, traverses the tube AB. The vessel to be evacuated is put in communication with DD which surrounds AB at F; EE is a jacket of cold water intended to condense the

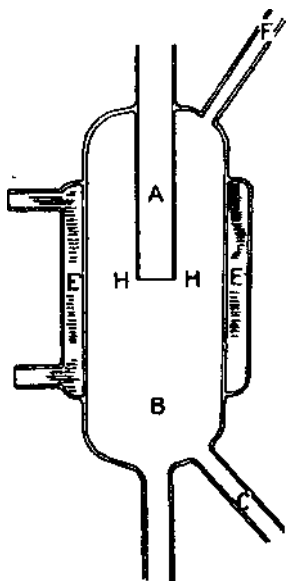


FIG. 5.

vapour. The slit CC serves to draw in air by the stream of vapour. The diffusion of air across the slit is not hindered by the escape of vapour since the latter condenses on the cold wall.

In the second (Fig. 5) the stream of mercury vapour issues from A and condenses on the wall of the tube B, cooled by the water jacket EE. The vessel

to be evacuated is connected at F, and the gas is drawn through C into a vacuum produced by an auxiliary pump. An advantage of this pump over the former is that the gas withdrawn flows in the same direction as the stream of mercury vapour, and is not compelled to overcome the resistance of this stream.

The efficiency of these pumps, particularly the second one, is surprising. For the latter the discharge is several litres per second. The vacuum reached is only limited by the quality of the preliminary vacuum, which should be, at the most, a few tenths of a millimetre of mercury. To get rid of the residual mercury vapour, a vessel interposed between the apparatus to be evacuated and the pump is immersed in carbon dioxide snow or liquid air. The speed of working is two or three times greater than that of Gaede's rotational molecular pump. According to Langmuir, the whole efficiency of the arrangement is accounted for by the following consideration : if the stream of mercury vapour coming from A is not immediately cooled in HH, the molecules of mercury, rebounding from the walls of the tube B (that is, evaporating instantly) will tend, partially at any rate, to reascend towards F by diffuse reflection, thereby preventing, to some extent, the exit of the gas molecules to be withdrawn. On the other hand, condensation in H has the effect of leaving a clear path to the molecules of the gas, which are then drawn out by the influence of the stream of vapour coming from A.

CHAPTER X

THE WIDTH OF SPECTRUM LINES

51. Visibility of Interference Fringes.—Suppose the particular wave-length A_0 of the radiation emitted by the particles of a luminous gas to be the same for all the particles. Neglecting the movements of the particles, the light emitted will be strictly monochromatic and the interference fringes which the source is capable of producing will be perfectly clear, whatever may be the difference of path. On the other hand, if the radiations emitted are not accurately homogeneous—and we shall see that the movements of the particles are quite sufficient to change this homogeneity—the light emitted, examined by a spectroscope, will no longer give an infinitely narrow line,* but a line of appreciable width. Hence the visibility of the interference fringes will depend upon the difference of path. Just as in the foregoing limiting case, when the difference of path is small, the visibility will diminish as the path difference increases, by virtue of the progressive encroachment of the fringe-systems produced by different parts of the line employed. For a sufficiently great difference of path, the minima and the maxima of intensity will ultimately become confused, and

* Neglecting, of course, any diffraction effects produced by the spectroscope.

the visibility will be zero. It is clear that the law of decrease of the visibility depends upon the law of distribution of luminous intensity in the line used, and an experimental study of the visibility will give some information about this law and consequently about the cause which gives the line a definite width. If this cause is molecular movement, we shall thereby possess an indirect means of studying the movement.

We shall first recall the principal results relating to the visibility of the fringes. We shall proceed to the calculation of the distribution of intensity in a line, which may be deduced from the kinetic theory of gases. Finally, we shall compare the results of the theory with experimental fact.

If two monochromatic radiations of the same frequency ν and the same amplitude a , with a phase-difference θ , are allowed to interfere the resultant vibration may be represented by

$$a \cos \phi + a \cos (\phi + \theta) = 2a \cos \frac{\theta}{2} \cos \left(\phi + \frac{\theta}{2} \right)$$

in which ϕ represents the phase of the first radiation. The resultant intensity is

$$I = 4a^2 \cos^2 \frac{\theta}{2} = 4a^2 \cos^2 \frac{\pi \delta}{V} \nu \quad . \quad (104)$$

where δ is the difference in path of the two interfering rays and V is the velocity of light. Under these conditions the minima of intensity, which are obtained for differences of path which are odd multiples of the semi-wave-length,

$$\lambda_0 = \frac{V}{\nu}$$

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are accurately zero, and the visibility of the fringes is independent of the difference of path.

On the other hand, if the radiation used is not strictly monochromatic, the line must be divided into very narrow portions, each corresponding to a very small range of frequencies $d\nu$. For each of these portions, the intensity of the interference fringes will be given by an expression analogous to (104) in which a^2 will become a function of the frequency ν . The total resultant intensity of the observed fringes will be, therefore,

$$\int I d\nu = 4 \int a^2 \cos^2 \frac{\pi \delta \nu}{V} \delta \nu . \quad (105)$$

The result obtained, and consequently the visibility of the fringes, will depend upon the expression of a^2 as a function of ν .

Let us consider the simple case—the interest of which will be apparent later—of a line of finite width but uniform intensity, comprising radiations from a frequency ν_1 to a frequency ν_2 . The middle of the line corresponds to the frequency ν_0 and the wave-length λ_0 . If λ_1 and λ_2 are the wave-lengths corresponding to the two edges, the width of the line is $\nu_2 - \nu_1$ in the scale of frequencies, and $\lambda_1 - \lambda_2 = 2\epsilon$ in that of wave-lengths. These two widths are also related to one another by the relation,

$$\frac{\nu_1 - \nu_2}{\nu_0} = \frac{2\epsilon}{\lambda_0} . \quad (106)$$

to the second order of accuracy.

In this particular case, the evaluation of the integral occurring in (105) is obvious, since a^2 is constant. It is easily found that

$$\int I d\nu = 2a^2(\nu_2 - \nu_1) \left[1 + \frac{\sin \frac{\pi\delta}{V}(\nu_2 - \nu_1)}{\frac{\pi\delta}{V}(\nu_2 - \nu_1)} \cos \frac{2\pi\delta}{V}\nu_0 \right]$$

If the line is so narrow that the width $\nu_2 - \nu_1$ may be treated as indefinitely small, the formula obtained, as is seen immediately, degenerates once more into the formula (104); the visibility is independent of the difference of path S .

In the contrary case, the factor

$$a = \frac{\sin \frac{\pi\delta}{V}(\nu_2 - \nu_1)}{\frac{\pi\delta}{V}(\nu_2 - \nu_1)} \quad . \quad . \quad (107)$$

can no longer be equal to one, and it is that which governs the visibility of the fringes. As long as the difference of path is only a small number of wave-lengths, in other words as long as the order of interference.

$$p = \frac{\delta}{\lambda_0},$$

is a sufficiently small integral number, the factor a may be equated to unity, and the visibility is as good as if the line were infinitely fine; the minima of intensity are perfectly black. If, on the contrary, the order of interference p increases so much that, in the expression for a , the argument of the sine becomes equal to π , the intensity of the fringes becomes uniform, which is the same as saying they disappear completely. In the interval, for any particular order of interference, the ratio of the intensity of a minimum to that of a maximum is

$$\frac{I_2}{I_1} = \frac{1 - a}{1 + a} \quad . \quad . \quad (108)$$

From that we conclude that

$$\alpha = \frac{I_1 - I_2}{I_1 + I_2}.$$

This expression is the one chosen conventionally by Michelson as a measure of the visibility of the fringes. It decreases from 1 to 0 when the order of interference increases from 0 to the critical value defined above.

52. Theory of the Width of Spectrum Lines.—

Let us consider the molecules of a luminous source as elastic spheres, and let us assume the radiations emitted by each of them to have the same frequency, which we shall call their characteristic frequency. Two principal causes will intervene to give the line a certain width:

i. The wave-trains emitted will be limited by the mutual collisions of the molecules which will change every moment in phase and amplitude according to the laws of chance. Decomposing the vibration emitted by a Fourier series, we shall arrive at a distribution of intensity which will no longer be strictly monochromatic. This cause of the widening of the lines is the more important when the free paths of the molecules are smaller, that is to say, when the pressure is higher. In Geissler tubes with rarefied gases, the mean paths are large enough to justify us in neglecting this effect. We shall, therefore, take no account of it in our considerations.*

2. Another cause of the widening of the line, which exists at all pressures, is the actual motion of the molecules. It is this phenomenon which will occupy our attention more closely.

* At the very low pressures which exist in Geissler tubes, the mean separation of the molecules is large enough for us to neglect also the action produced by the electric field of the molecules in the vibrations emitted by the others (Stark effect).

It is known that a monochromatic radiation emitted by a source in motion apparently changes in frequency if the source approaches towards or recedes from the observer. If u represents the velocity of the source, counted positive if it moves towards the observer, the modified frequency is

$$\nu = \nu_0 \left(1 + \frac{u}{V} \right) \quad \cdot \quad (109)$$

We can also say that the relative variation of the wave-length is $\frac{u}{V}$ to the second order of accuracy.

This is the Doppler-Fizeau principle, which has been verified directly in acoustics as well as in optics.

Now, the molecules of a luminous gas take part in its thermal motion; those which approach the observer appear to emit a radiation of wave-length lower than that of the characteristic wave-length, those which recede a radiation of greater wave-length, and finally those which move at right-angles to the line of sight emit the characteristic wave-length unchanged.

Let us calculate the width of the line which should be produced. If all the particles have the same velocity v , the width, evaluated in the scale of frequencies, will be, according to (109),

$$\nu_2 - \nu_1 = 2 \frac{\nu_0 v}{V}.$$

In the scale of wave-lengths the semi-width ϵ will be given by

$$\frac{\epsilon}{\lambda_0} = \frac{v}{V}$$

according to (106). Further, the widened line will have a uniform intensity sharply defined at the

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edges, since the distribution of molecular velocities is the same in all directions.

The results of Art. 51 are, therefore, directly applicable. The visibility a of the fringes (equation 107) here takes the form

$$a = \frac{\sin 2\pi p \frac{v}{V}}{2\pi p \frac{v}{V}}.$$

To fix the ideas, assume with Lord Rayleigh, that the limit of visibility is reached when the ratio of a minimum to a maximum is $\frac{J_2}{J_1} = 0.95$. From (108),

the visibility a then takes the value $0.025 = \frac{1}{40}$.

This value is so nearly zero that the argument of the sine in formula (107) is practically equal to n , which leads to an expression for the order of interference p corresponding to the limit of visibility

$$p = \frac{V}{2v} = 0.5 \frac{\lambda_0}{\epsilon}.$$

If it is remembered now that the mean velocity of the molecules v is related to the temperature and the molecular weight by the relations (8a) and (15), we may write

$$v = \sqrt{\frac{8RT}{\pi M}}.$$

The width of the line is therefore defined by the relation

$$\frac{\epsilon}{\lambda_0} = A \sqrt{\frac{T}{M}}. \quad (110)$$

in which A is the constant

$$A = \frac{1}{V} \sqrt{\frac{8R}{\pi}} = 4.85 \times 10^{-7}.$$

The limiting order of interference is consequently

$$p = 1.03 \times 10^6 \sqrt{\frac{M}{T}}.$$

Following Lord Rayleigh, we may improve the theory by no longer assuming the velocities of the luminous particles to be equal to their mean velocity v , but distributed about it following Maxwell's law of distribution. The velocity components of a particle perpendicular to the line of sight will play no part. The particles whose velocity component in the line of sight lies between u and $u + du$ are, according to formula (5),

$$dn_1 = n \sqrt{\frac{hm}{\pi}} e^{-hmu^2} du$$

per cubic centimetre. To the range of velocity du corresponds an interval of frequency dv , such that if in equation (105) u is taken as independent variable, we must write

$$a^2 dv = b e^{-hmu^2} du = b e^{-\frac{4u^2}{\pi v^2}} du \quad : \quad (112)$$

using formula (8) and putting b as a constant. The distribution of intensity in the fringes is then given by (105) and (109) as

$$\int I dv = 4b \int_{-\infty}^{+\infty} \cos^2 \left[\frac{\pi \delta \nu_0}{V} \left(1 + \frac{u}{V} \right) \right] e^{-\frac{4u^2}{\pi v^2}} du.$$

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The calculation is easily carried out, remembering that

$$2 \cos^2 \left[\frac{\pi \delta \nu_0}{V} \left(1 + \frac{u}{V} \right) \right] = 1 + \cos \left[\frac{2\pi \delta \nu_0}{V} \left(1 + \frac{u}{V} \right) \right]$$

$$= 1 + \cos \frac{2\pi \delta \nu_0}{V} \cos \frac{2\pi \delta \nu_0 u}{V^2} - \sin \frac{2\pi \delta \nu_0}{V} \sin \frac{2\pi \delta \nu_0 u}{V^2}.$$

The last term which contains an odd function of u , gives an integral zero. The two first are well-known integrals (see Note I at the end of the book), and we are led finally to the result

$$\int I d\nu = \pi b v \left[1 + e^{-\pi \left(\frac{\pi p v}{2V} \right)^2} \cos \frac{2\pi \delta \nu_0}{V} \right].$$

Henceforth the argument may be continued as in the case, studied in the previous paragraph, of a line with a uniform distribution of intensity. As long as the order of interference p remains low, the exponential term may be regarded as unity, and we fall back to the case of the optimum visibility, equal to unity. If the order of interference has any value whatever, the visibility, by analogy with the case already studied, is

$$a = e^{-\pi \left(\frac{\pi p v}{2V} \right)^2} \quad . \quad . \quad . \quad (113)$$

The order of interference corresponding to the limiting visibility, for which the fringes seem to disappear, depend on the value assumed for the visibility at this moment. Lord Rayleigh made the calculation assuming $a = \frac{1}{40}$ thereby finding

$$p = 0.690 \frac{V}{v} = 1.42 \times 10^4 \sqrt{\frac{M}{T}} \quad (114)$$

Fabry and Buisson assumed $\alpha = \frac{1}{16}$ as limit of visibility, which leads to the limiting order of interference

$$p = 1.22 \times 10^3 \sqrt{\frac{M}{T}} \quad . \quad . \quad (115)$$

The comparison of Lord Rayleigh's result with formula (in), obtained on the hypothesis of a line with uniform distribution of intensity, and for the same limiting visibility, shows the modification produced by the introduction of Maxwell's law for the distribution of velocities. As in all analogous cases, it only involves the numerical coefficient in the final formula.

In conclusion, it should be noticed that, in the case actually studied, the width of the spectrum line can no longer be defined with precision. According to (112) and (109), the distribution of intensity in the line is given by the relation

$$a^2 = a_0^2 e^{-\frac{4x^2}{\pi v^2}}$$

in which a_0 represents a constant. We may introduce into this formula the intensities i and i_0 , which are proportional to the squares of the amplitudes. On the other hand, if λ_0 represents the wave-length corresponding to the centre of the line, and $\lambda_0 + x$ the wave-length corresponding to any point in the line, the application of the Doppler principle gives, as we already know,

$$\frac{x}{\lambda_0} = \frac{v}{V}.$$

The law of distribution of intensities as a function of the wave-length is then of the form

$$i = i_0 e^{-Kx^2} \quad . \quad . \quad (116)$$

putting

$$K = \frac{4V^2}{\pi\lambda_0^2\nu^2}.$$

The curve representing formula (116) has the bell-shaped form given by figure (6). Its shape is completely defined by a knowledge of the coefficient K . We may conventionally define the width of the line as the difference $2e$ between the abscissae of the two points C and D for which the intensity is half the maximum intensity i_0 . It is easily deduced that

$$\frac{e}{\lambda_0} = 0.74 \frac{\nu}{V} = 2.58 \times 10^{-7} \sqrt{\frac{T}{M}}.$$

in place of the relation (no) which was valid for a uniform line.

53. Experiments of Fabry and Buisson.—The experiments of Michelson had already brought forward some interesting developments of the theory. Here, however, we shall only note the more complete and more recent results of Fabry and Buisson, which have facilitated the test of certain consequences of the kinetic hypothesis with remarkable precision.

The apparatus used is an interferometer with half-silvered plates, whose distance may be increased to several decimetres. The order of interference may be increased until the fringes cease to be visible, and the limiting order of interference may be directly determined in this way. The luminous source was a Geissler tube immersed in a liquid bath of known temperature. The gases studied so far have been the rare monatomic gases of the atmosphere (helium, neon, krypton) and also certain common gases such as hydrogen.

The results obtained may be summarised, for the

first gases, in the following table, in which are tabulated the order of interference observed at the ordinary temperature, the orders of interference calculated by the theoretical formula (115), and finally those observed when the Geissler tube is plunged in liquid air, and the ratio of these last numbers to the former.

Gas.	Atomic Weight.	Wave-length.	Ordinary Temperature.		Liquid Air p' Observed.	p'/p
			p Observed.	p Calculated.		
Helium	4	5876	144,000	144,000	241,000	1.66
Neon	20	5852	324,000	321,000	515,000	1.6
Krypton	83	5570	600,000	597,000	950,000	1.58

The test is completely satisfactory, assuming the luminous gas to be at the temperature of the surrounding bath in each case, and the mass of the vibrating particle to be the mass of the atom.

Analogous results are obtained in the case of hydrogen, the mass of the vibrating particle being once again that of the atom, which is here distinct from that of the molecule.

The lines considered then appear to be of atomic origin in all the cases studied. Further, it does not seem necessary to produce a temperature of incandescence or luminescence in any way different from that of the Geissler tube itself, as one is often tempted to do.

If the variation of the visibility with temperature occurred strictly in accordance with theory, that is inversely as the square root of the absolute temperature, the numbers in the last column of the table above should have the same value 1.73. The small differences observed may be due to a temperature in the interior of the tube slightly higher than the external temperature.

On the whole the results appear to be in good agreement with theory. The experiments have, furthermore, brought to light luminous sources which are very nearly monochromatic; the line of wave-length 5570 angströms, belonging to krypton, will give orders of interference in the neighbourhood of one million when the tube is immersed in liquid air. The limit of visibility is reached for a dif-

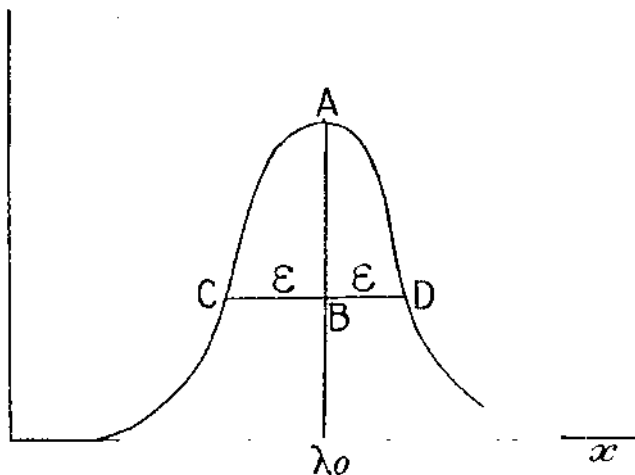


FIG. 6.

ference of path of 53 centimetres, the greatest that has been observed up to the present.

Before concluding, we must sound a note of warning. According to the table given above the quantitative agreement between experiment and formula (115) is within one per cent. It is not legitimate, however, to conclude from that fact that Maxwell's law of distribution, upon which the deduction of formula (115) is based, is verified to the same degree of accuracy. It must not be forgotten that formula

(115) further supposes the limiting visibility to be —.

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A comparison with Lord Rayleigh's result, given by formula (114), and obtained by assuming another limit of visibility, shows that the numerical coefficient in the relation we have attempted to verify cannot be considered as known with an accuracy greater than 10 per cent.

It would be interesting, and no doubt possible, to complete the test by a detailed photometric study of the variation of visibility with the order of interference, which would enable a complete test of the law of variation (113) to be made. In other words, instead of being satisfied with verifying whether the curve in Fig. 6 stops short at the distance of its maximum predicted by theory, we should endeavour to determine the detail of its form experimentally. We should obtain thereby a very interesting verification of Maxwell's law of the distribution of velocities, valid not in a relative fashion, but in absolute terms.

CHAPTER XI

MOLECULAR CONSTANTS. NUMERICAL TABLES

IN this chapter we shall summarise the numerical results obtained in the domain of molecular physics, supplementing them with tables of figures bearing upon questions studied in the preceding chapters.

54. Avogadro's Constant (or Loschmidt's Constant).—This constant N (the number of molecules per gramme-molecule) was first of all determined through the intermediary of Van der Waals' equation (Chapter II). As explained in Art. 17 the two equations (19) and (22) are used, being written:

$$b = \frac{2}{3} \pi \sigma^3 N$$

$$l = \frac{V}{\sqrt{2\pi\sigma^2 N}}$$

V being the molecular volume.

At one and the same time we get the desired number N and the molecular diameter a . The calculation, carried out for argon,* has given

$$N = 62 \times 10$$

$$a = 2.85 \times 10^{-8} \text{ cm.}$$

* A monatomic gas to which the formulae are more strictly applicable.

The constant N has been determined since by a large number of accurate and concordant methods.

i. Experiments based on the study of emulsions and the Brownian movement (Chap. VII) have furnished several independent values for N . We may recall the figures due to Perrin :

Distribution of granules vertically	68.3×10^{22}
Translational motion	68.8
Rotational motion	6 5
Diffusion	6 9

2. The Brownian movement in gases, and particularly the motion of a spherical particle, electrically charged, in an electric field, has also led to accurate measurements. The mean of the results of Millikan and Fletcher (p. 106),

$$N = 60.6 \times 10^{22}$$

is certainly lower than Perrin's figures, although the cause of the discrepancy is not completely elucidated.

3. Certain phenomena having their origin in the irregular distribution of the molecules enable us to determine the value of N . We may mention

(a) the critical opalescence (see Art. 42) which has given the value 75×10^{22} .

(b) the blue of the sky (Lord Rayleigh's formula) which has given the figure 60×10^{22} .

4. The study of the α rays of radioactive bodies has produced four distinct methods of measuring N . First of all the total positive charge of the particles emitted during a certain time may be determined. It is then sufficient to count them in order to deduce their individual charge e and consequently the number N of them contained in one gramme-molecule. The total charge is measured by a Faraday cylinder.

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The particles may be counted by making use of their power of ionising gases and counting the number of kicks registered on an electrometer suitably mounted and exposed to the radiation (Rutherford and Geiger), or by counting the number of scintillations registered on a phosphorescent screen bombarded by the rays (Regener). The figures derived are :

$$\begin{array}{l} 62 \times 10^{22} \text{ (Rutherford and Geiger)} \\ 60.5 \times 10^{22} \text{ (Regener).} \end{array}$$

The measurement of the total charge carried by the particles may be replaced by the measurement of the total mass of helium produced ; it is known, indeed, that the α -particles are charged helium atoms. In this manner we find

$$\begin{array}{l} 63 \times 10^{22} \text{ (Rutherford and Boltwood)} \\ 65 \times 10^{22} \text{ (Madame Currie).} \end{array}$$

Furthermore, it has been possible to measure the time at the end of which the radioactivity of the radium falls to half its initial value. This period is about 1585 years. The value of N resulting from it is

$$71 \times 10^{22}.$$

Finally, the heat liberated by the radium has permitted the calculation of the total kinetic energy of the α -particles ejected and consequently their number. The result is

$$62 \times 10^{22}.$$

5. The study of the distribution of energy in the spectrum of a black body (Planck) has furnished the figure,

$$60.6 \times 10^{22}.$$

Formulae of distribution verified by experiment, such as formula (75) of Art. 34, involve Boltzmann's

constant k , and consequently Avogadro's constant. The same equation (75) shows that Planck's constant h , known as the quantum of action, playing a fundamental role in the theory of quanta, may be determined simultaneously with N .

As the most probable value of N we shall take the number,

$$N = 60.64 \times 10^{23},$$

which is the mean of the best determinations, and which is certainly accurate within a few per cent. It is probable that this fundamental constant will soon be known with an accuracy of the order of a thousandth.

55. The Principal Molecular Constants.—Assuming the constant for perfect gases, referred to one gramme-molecule to be

$$R = 8.32 \times 10^7 \text{ C.G.S.}$$

the gas constant for one molecule (Boltzmann's constant) is found to be

$$k = \frac{R}{N} = 12.8 \times 10^{-17}.$$

Further, assuming the molecular volume under normal conditions to be 22,400 cm.³ the molecular density of all perfect gases under normal conditions is found to be

$$n = \frac{N}{22400} = 2.90 \times 10^{19}.$$

The kinetic energy of a molecule at 0°C. is (formula 16):

$$\frac{mC^2}{2} = \frac{3}{2} k \times 273 = 5.24 \times 10^{-14} \text{ ergs.}$$

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The increase of this energy per degree centigrade is (formula 16) :

$$\alpha = \frac{3}{2}k = 18.2 \times 10^{-17} \text{ ergs.}$$

The masses of the atoms and the molecules are obtained by dividing the corresponding atomic or molecular weight by Avogadro's constant.

The molecular weights M of several gases and the masses m of the corresponding molecules are contained in the following table :

Gas.	M .	$m \times 10^{24}$ gr.
Hydrogen, H_2 .	2.016	3.1
Oxygen, O_2	32.00	49.2
Nitrogen, N_2 .	28.02	43.1
Argon, Ar	39.88	61.3
Helium, He	3.99	6.1
Carbon Monoxide, CO	28.00	43.1
Carbon Dioxide, CO_2	44.00	67.7
Water Vapour, H_2O .	18.02	27.7

In the following table we have, for the same gases, the mean square velocity C of the molecules at $0^\circ C$, evaluated from formula (na), the mean velocity v

Gas.	$C \times 10^{-2}$ cm./sec.	$v \times 10^{-2}$ cm./sec.	$\eta \times 10^6$	$l \times 10^8$ cm.	$\sigma \times 10^8$ cm.
H_2	1838	1693	84	11.07	2.88
O_2	461	425	190	13.8	2.40
N_2	493	454	167	6.278.93	3.570.97
Ar	413	380	211	8.405.89	8.153.78
He	1307	1204	187	6.218.86	3.462.88
CO	493	454	166	76.0717.45	7.902.11
CO_2	393	362	137	5.858.88	3.838.29
H_2O	615	566	90	5.493.85	8.834.0
Air	485	447	171	8.45	—
				5.92	

deduced from formula (8a), the coefficient of viscosity 77 measured experimentally at 0°C , the mean free path under normal conditions deduced from formula (29a) the values of the coefficient of viscosity, and, finally, the molecular diameter calculated from formula (22).

The number of collisions per centimetre of path suffered by a molecule are calculated from formula (23). They are the reciprocals of the figures in the last column but one.

The duration of the mean free paths are deduced from the formula (24) by dividing the mean free paths l by the average velocities v . In this way the following table is obtained as complement to the foregoing:

Gas.	$v \times 10$	$\tau \times 10^{19}$ sec.
Hydrogen, H_2	63.3	0.97
Oxygen, O_2	112	2.10
Nitrogen, N_2	119	1.85
Argon, Ar	113	2.33
Helium, He	40	2.06
Carbon Monoxide, CO	120	1.84
Carbon Dioxide, CO_2	182	1.51
Air	118	1.89

56. Electronic Constants. — It is interesting to complete the preceding tables with a few constants which are connected with them, and which appear constantly in modern molecular theories of electricity.

In Art. 39 we have already noted that Avogadro's constant is connected very intimately with the value of the atom of electricity or electron, the existence of which has been recognised in a very large number of physical phenomena. This elementary charge is

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that which is carried by all monovalent ions in electrolysis. It is identical with that of all gaseous ions and all particles composing cathode rays, the β rays of radium, etc.

We know that a monovalent gramme-ion transports a quantity of electricity equal to 96,500 coulombs in electrolysis. This number F is often known by the name of Faraday's constant. It is obviously related to the Avogadro constant N and the elementary charge e by the relation,

$$F = Ne.$$

If N is taken to have the value 60.6×10^{22} assumed before, we get

$$e = \frac{F}{N} = 4.774 \times 10^{-10} \text{ electrostatic units.}$$

Several of the determinations of N which have already been considered are really determinations of c , a process which, according to the expression just formulated, amounts to precisely the same thing.

The negatively charged particles which constitute the Cathode rays possess this charge. Their mass, however, is much smaller than that of the lightest atoms, and they represent the ultimate unit of matter, which occurs in the constitution of all atoms. They are called electrons or corpuscles. Experiment has permitted us to determine accurately, by several methods which agree at least within one per cent.

the ratio $\frac{e}{m}$ of the charge to the mass of a corpuscle.

The number obtained is

$$\frac{e}{m} = 1.766 \times 10^7 \text{ electromagnetic units.}$$

By comparison with the value of e , the mass of an electron is calculated to be

$$m = 8.4 \times 10^{-28} \text{ grammes.}$$

Referring to the first table above, we see that this mass is a fraction $1/1845$ of that of the lightest atom, the atom of hydrogen.

In conclusion, we append the value of the quantum of action h (Planck), deduced from a study of radiation or specific heats.

$$h = 6.6 \times 10^{-27} \text{ C.G.S. units (erg-secs.).}$$

57. Numerical Constants Concerning the Kinetic Theory.—The following tables summarise a number of constants measured experimentally which serve to confirm the various theories expounded previously.

TABLE I

VARIATION OF THE COEFFICIENT OF VISCOSITY OF GASES WITH PRESSURE (KUNDT AND WARBURG)

1. AIR AT PRESSURES LOWER THAN ONE ATMOSPHERE

Pressure in mm. of Mercury.	Coefficient of Viscosity at 15°.
0.63	0.000161
1.53	0.000170
2.4	0.000174
20.5	0.000179
380	0.000179
750	0.000178

2. CARBON DIOXIDE AT HIGH PRESSURES

Pressure in Atmospheres.	Coefficient of Viscosity at 32.6°.
60.3	0.000189
69.9	0.000214
74.6	0.000241
76.6	0.000273
77.2	0.000315
77.6	0.000367
78.2	0.000426
80.7	0.000496
88.5	0.000575
107.3	0.000678

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TABLE II

VARIATION OF COEFFICIENT OF VISCOSITY OF NITROGEN WITH TEMPERATURE (BESTELMEYER)

Temperature ° C.	$\frac{\eta}{\eta_{17}}$ Observed.	$\frac{\eta}{\eta_{17}}$ Calculated (Sutherland's formula).
- 190.63°	0.3204	0.3144
- 78.56°	0.7207	0.7207
+ 98.4°	1.2064	1.2045
+ 300.4°	1.6279	1.6283

TABLE III

RELATION BETWEEN THE COEFFICIENT OF VISCOSITY, THE COEFFICIENT OF THERMAL CONDUCTIVITY AND THE SPECIFIC HEAT AT CONSTANT VOLUME. (FORMULA 34a: EUCKEN)

TEMPERATURE 0°

Gas.	$k \times 10^7$.	$\eta \times 10^7$.	C_v .	B Observed.	B Calculated.
He	3360	1876	0.746	2.40	2.52
Ar	390	2102	0.0745	2.49	
H ₂	3970	850	2.38	1.965	1.90
N ₂	566	1676	0.177	1.905	
O ₂	570	1922	0.155	1.913	
CO	542.5	1672	0.177	1.835	
NO	555	1794	0.1655	1.870	
CO ₂	337	1380	0.1500	1.628	1.43
H ₂ O	(429)	1006	0.342	1.25	
NH ₃	513.5	926	0.388	1.43	

TABLE IV

SPECIFIC HEATS OF GASES

It is remembered that in calories

$$\frac{3}{2}R = 2.97 \quad \frac{5}{2}R = 4.95 \quad \frac{7}{2}R = 6.93$$

The following table comprises molecular heats :—

Gas.	C_p		C_v		C_p/C_v	
	Temp. Centig.	Value.	Temp. Centig.	Value.	Temp. Centig.	Value.
Ar	20-90	4.908	0	2.97	—	1.667
He	—	—	0	2.976	—	1.652
Kr	—	—	—	—	—	1.666
Hg	—	—	—	—	310	1.666
H ₂	16	6.860	0	4.80	16	1.407
N ₂	20	6.983	0	4.95	20	1.400
O ₂	20	6.980	0	4.95	20	1.399
CO	18	7.006	0	4.95	18	1.398
H ₂ O	100	7.84	100	5.94	100	1.32
NH ₃	0	8.65	0	6.47	0	1.336
N ₂ O	—	—	0	6.93	0	1.324
CH ₄	—	—	0	6.49	19	1.313
CO ₂	20	8.889	0	6.60	25	1.300
C ₂ H ₄	20	—	0	8.21	0	1.25

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TABLE V

VARIATION WITH TEMPERATURE OF THE MOLECULAR HEATS OF GASES AT CONSTANT VOLUME

(Temperatures in degrees Centigrade)

I. HIGH TEMPERATURES (NERNST)

Temperature.	Ar.	H ₂ .	N ₂ , O ₂ , CO.
0	2.97	4.80	4.95
100	2.97	4.83	4.98
300	2.97	5.08	5.22
500	2.97	5.25	5.40
1200	2.97	5.85	6.05
2000	2.97	6.55	6.75

CARBON DIOXIDE

Temperature.	C _v .	Temperature.	C _v .
18	7.09	1314	9.84
200	7.48	1611	9.98
650	8.60	1839	10.28
1000	9.33	2210	10.47

2. Low TEMPERATURES (NERNST)

HYDROGEN

Temperature.	C _v .	Temperature.	C _v .
- 238	2.98	- 188	3.21
- 233	2.98	- 173	3.41
- 228	3.00	- 163	3.62
- 208	3.04	- 76.5	4.39
- 203	3.10	0	4.80
- 193	3.14		

TABLE VI

SPECIFIC HEATS OF SOLIDS AT LOW TEMPERATURES.
SEE CURVES IN FIG. II. ART. 34

NERNST:

1. ALUMINIUM

Absolute Temperature.	C_p Observed.	C_v Calculated.
32.4	0.25	0.23
35.1	0.33	0.31
83.0	2.42	2.41
86.0	2.52	2.52
88.3	2.62	2.61
137	3.97	3.99
235	5.32	5.15
331	5.82	5.52
433	6.10	5.70
555	6.48	5.80

2. COPPER

Absolute Temperature.	C_p Observed.	C_v Calculated.
23.5	0.22	0.15
27.7	0.32	0.31
33.4	0.54	0.59
87.0	3.33	3.35
88.0	3.38	3.37
137	4.57	4.60
234	5.59	5.42
323	5.90	5.66
450	6.096	5.81

TABLE VI--(continued).

3. DIAMOND

Absolute Temperature.	C_p Observed.	C_v Calculated.
30	0.000	0.000
42	0.000	0.000
88	0.03	0.006
92	0.03	0.009
205	0.62	0.62
222	0.76	0.78
232	0.86	0.87
243	0.95	0.97
262	1.14	1.16
284	1.35	1.37
306	1.58	1.59
331	1.84	1.82
358	2.12	2.07
413	2.66	2.53
1169	5.45	5.19

NOTE I

MATHEMATICAL FORMULA USEFUL IN THE KINETIC THEORY

I. See Jordan, " Cours D'Analyse," II, pp. 162 and 163 ; or Preston, " Theory of heat," 3rd Edition, Art. 373.

$$\int_0^{\infty} e^{-au^2} du = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$\int_0^{\infty} e^{-au^2} u du = \frac{1}{2a}$$

$$\int_0^{\infty} e^{-au^2} u^2 du = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$$

$$\int_0^{\infty} e^{-au^2} u^3 du = \frac{1}{2a^2}$$

$$\int_0^{\infty} e^{-au^2} u^4 du = \frac{3}{8} \sqrt{\frac{\pi}{a^5}}$$

These formulæ are particular cases of the general formulæ

$$\int_0^{\infty} e^{-au^2} u^{2k} du = \frac{1 \cdot 3 \cdot \dots \cdot (2k+1)}{2^{k+1}} \sqrt{\frac{\pi}{a^{2k+1}}}$$

$$\int_0^{\infty} e^{-au^2} u^{2k+1} du = \frac{k!}{2a^{k+1}}$$

In Chapter X, Art. 52, we have used the formula

$$\int e^{-a^2 u^2} \cos 2ru \, du = \frac{\sqrt{\pi}}{2a} e^{-\frac{r^2}{a^2}}.$$

2. STIRLING'S FORMULA

(See Goursat, "Cours D'Analyse," I, p. 291; and *Nature*, March 24, 1923, p. 397.)

When the integer p is very large, we may write

$$p! = \sqrt{2\pi p} \left(\frac{p}{e}\right)^p$$

or with very nearly the same accuracy for taking the logarithm (cf. Art. 31),

$$p! = \left(\frac{p}{e}\right)^p.$$

3. DIRICHLET INTEGRALS

(See Jordan, "Cours D'Analyse," II, p. 190; or Williamson, "Integral Calculus," p. 320.)

The multiple integral

$$I = \int dx_1 dx_2 dx_3 \dots dx_n \quad (n \text{ is even})$$

extended over a range in which

$$x_1^2 + x_2^2 + \dots + x_n^2 \ll R^2$$

has the value

$$I = \frac{\pi^{\frac{n}{2}} R^n}{\left(\frac{n}{2}\right)!}.$$

NOTE II

MEAN FREE PATHS OF CLAUSIUS AND MAXWELL

The formula $l = \frac{l}{n\pi\sigma^2} \frac{v}{r}$ (i)

in Art. 14 expresses the mean free path of a molecule as a function of the velocity v , supposed to be common to all the molecules, and of the average distance between molecules.

Following Clausius we shall see how it is possible to calculate r .

For the purpose of argument it will be convenient to assume that the molecule, whose mean relative velocity with respect to the others we wish to find, is endowed with a velocity c_x different from the velocity c_2 common to the other molecules. Starting from an arbitrarily selected origin O (see figure 7), if two vectors are drawn representative of the velocity c_x of the first molecule and the velocity c_2 of one of the others, and θ represents the angle between the two vectors, the relative velocity r_2 of the two molecules will be given by the expression

$$r_2 = \sqrt{c_1^2 + c_2^2 - 2c_1c_2 \cos \theta}.$$

The vector Oc_x remains fixed. On the other hand the velocities c_2 are supposed to be distributed uniformly in all directions. In other words, all the possible values of the angle θ which lie within θ and n are equally probable. If, then, 11_2 designates the total number of molecules of velocity c_{2f} the number of them whose velocities make an angle within the limits θ and $\theta + d\theta$ with c_x is (cf. the first note in Art. 17)

$$\frac{n_2}{2} \sin \theta d\theta.$$

The mean relative velocity we require is, therefore,

$$r = \int_0^\pi \frac{r_2 \sin \theta d\theta}{2} = \frac{1}{2} \int_0^\pi \sqrt{c_1^2 + c_2^2 - 2c_1c_2 \cos \theta} \sin \theta d\theta$$

or

$$r = \frac{1}{6c_1c_2} \left[(c_1^2 + c_2^2 - 2c_1c_2 \cos \theta)^{\frac{3}{2}} \right]_0^\pi$$

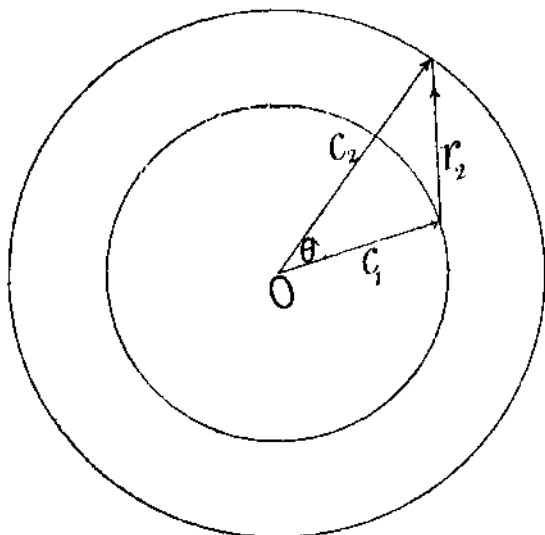


FIG. 7.

The relative velocity is always positive. Introducing the limits of integration 0 and π in the expression $(c_1^2 + c_2^2 - 2c_1c_2 \cos \theta)^{\frac{3}{2}}$ we must decide whether c_x is greater or less than c . If $c_1 > c_2$ we find

$$r = \frac{3c_1^2 + c_2^2}{3c_1} \quad . \quad . \quad . \quad (2)$$

and if $c_1 < c_2$

$$r = \frac{3c_2^2 + c_1^2}{3c_2} \quad (3)$$

If $c_1 = c_2 = v$ we arrive at the initial hypothesis, and the two expressions derived obviously coincide. Their common value is

$$r = \frac{4}{3}v.$$

Formula (1) therefore gives Clausius' mean free path as

$$l = \frac{3}{4\pi n\sigma^2}.$$

To derive Maxwell's mean free path (formula 22 of the text) we must introduce the law of distribution of velocities about the mean velocity. In formula (i) v then represents the mean velocity and r must be replaced by the average value r of all relative velocities. This latter average must now be calculated.

For brevity let us refer to all the molecules whose velocities lie between c_2 and $c_2 + dc_2$ as molecules of class A. The expressions (2) and (3) above give the mean relative velocity r of a particular molecule of velocity c_x with reference to the molecules of class A. To determine the average of r , it must be multiplied by the probability of existence of the class A, which is given in formula (6) of the text as

$$4\sqrt{\frac{h^3 m^3}{\pi}} e^{-hmc_x^2} c_2^2 dc_2,$$

and then integrated with respect to c_z from 0 to ∞ . To effect the calculation, it is important to observe that r will not have the same expression throughout

the whole field of integration, and it will be necessary to use formula (2) or formula (3) according as c_x is greater or less than c_2 . In this fashion we find the mean relative velocity r_1 of a molecule of definite velocity c_1 with respect to all the others—

$$r_1 = 4 \sqrt{\frac{h^3 m^3}{\pi}} \left[\int_0^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} c_2^2 e^{-hmc_2^2} dc_2 + \int_{c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} c_2^2 e^{-hmc_2^2} dc_2 \right].$$

To derive the average r of the relative velocities, the average with reference to c_2 must still be calculated. For this purpose r_1 must be multiplied by the probability that the velocity of a molecule should lie between c_1 and $c_1 + dc_1$ which is

$$4 \sqrt{\frac{h^3 m^3}{\pi}} e^{-hmc_1^2} c_1^2 dc_1,$$

and integrated with respect to c_1 from 0 to ∞ . It is easily found that

$$\bar{r} = 16 \frac{h^3 m^3}{\pi} (J_1 + J_2),$$

in which J_1 and J_2 have the following values :

$$J_1 = \int_0^{\infty} c_1^2 e^{-hmc_1^2} dc_1 \int_0^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} c_2^2 e^{-hmc_2^2} dc_2,$$

$$J_2 = \int_0^{\infty} c_1^2 e^{-hmc_1^2} dc_1 \int_{c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} c_2^2 e^{-hmc_2^2} dc_2.$$

The evaluation of J_2 is immediately obvious ; the integrations with respect to c_2 are elementary ; those

with respect to c_1 follow directly from the formulæ of Note I. We find

$$J_2 = \frac{I}{8\sqrt{2}} \left(\frac{\pi}{h^2 m^2} \right)^{\frac{1}{2}}.$$

To evaluate J_t we notice that c_x varies from 0 to ∞ , and that c_a must remain less than c_v . If the order of these integrations is reversed, c_2 must then vary from 0 to ∞ and c_x must remain greater than c_2 . We may, therefore, write

$$J_1 = \int_0^\infty c_2^2 e^{-hmc_2^2} dc_2 \int_{c_1}^\infty \frac{3c_1^2 + c_2^2}{3c_1} c_1^2 e^{-hmc_1^2} dc_1.$$

This definite integral is now identical with J_2 , except for the notation, since we pass from one to the other by exchanging the letters c_x and c_2 . We have then

$$J_1 = J_2,$$

and consequently

$$\bar{v} = \frac{4}{\sqrt{2\pi h m}}.$$

Referring to formula (8) of the text, which gives the mean absolute velocity v of all the molecules, we see that

$$\bar{v} = v\sqrt{2}.$$

Formula (i), as expressed at the beginning of this note, therefore, gives the mean free path of Maxwell as

$$l = \frac{I}{\sqrt{2\pi n \sigma^2}}.$$

NOTE III

THE PROPERTIES OF THIN FILMS OF SOLID OR LIQUID. THE EXPERIMENTS OF DEVAUX

In many cases, the study of thin films of solid or liquid matter has led to interesting proofs of its molecular structure. We shall limit ourselves here to a few examples.

In the first place it has been shown that the physical constants of their films of pure substances begin to change their value below a certain thickness, demonstrating thereby the preponderance of intermolecular actions over external forces, as in the case of surface tension in capillarity.

For instance, the resistance of a metal in thin films (silver) changes progressively when its thickness diminishes below 50μ (Vincent). The properties of the light reflected from a thin metallic mirror begin to change for thicknesses of the same order.

It is interesting to determine the thickness of metal which is necessary to modify the properties of a subjacent metallic surface to an appreciable extent. The contact electromotive force between a metal and an electrolyte begins to vary when the metal is covered with layers of another metal having a thickness of i to 5μ .

The black spots on soap bubbles have thicknesses of the order of 6μ for the first, and 12μ for the second. The existence of several other black spots has been confirmed, whose thickness appears to increase in arithmetical progression. The whole surface of the bubble appears also to have a lamellar structure, the units of which are about 5μ in thickness (Perrin). Beyond all doubt that is the order of magnitude of

the distance to which forces of intermolecular cohesion extend.

In this way layers of matter only a few millimicrons in thickness may be realised; and at such thicknesses, the influence of intermolecular attractions makes itself manifest quite appreciably ; it is evidence that we are approaching the molecular diameter.

Among the experiments in capillarity performed in this field, the most remarkable, perhaps, are those of Devaux, who appears to have reached the molecular diameters themselves.

It is well known that if a little camphor is scattered on clean water, it is animated with rapid and irregular motions of gyration (Lord Rayleigh). This agitation, due to a local and non-symmetrical alteration in the surface-tension of the water, is completely stopped if the surface of the water is covered with an extremely thin film of oil. The thickness required is very small, but nevertheless thinner films may be produced which are inactive with respect to the gyration of the camphor. Devaux has taken up the study of this phenomenon, and has succeeded in carrying it a long way.

If the surface of the water is covered with a trace of sodium oleate or olive oil, it spreads out in an invisible black film, but with clear boundaries. It may be rendered visible by sprinkling the liquid with talc, and by blowing gently on the surface, the talc, instead of sinking to the bottom of the tank, remains attached to the surface of the oil-drops or sticks to their edges. In spite of their very minute thickness, which is no longer sufficient for them to show interference colours, the drops have a certain cohesion. The use of solutions of known strength of oil in benzene (of which only one or two drops are used)

enables us to determine the thickness from the limiting surface of the film of oil; for sodium oleate this is in the neighbourhood of $1\text{--}10\mu$. Such a film has no action on the gyration of camphor, which proves that it does not alter the surface tension of the water.

Having formed a film of this kind on one side of a tank, if a strip of paper is placed on the surface and carefully moved in such a manner as to decrease the surface of the film of oil or to increase its thickness, it may be shown, by camphor or talc, that the surface tension remains almost invariable and equal to that of pure water till the very moment when the calculated thickness becomes about $i \cdot 30/x/z$. At this instant, and almost without transition, the surface tension falls suddenly and becomes almost that of soapy water; the movement of the camphor stops immediately. The limit may be measured with very considerable accuracy.

If we try to increase the thickness further, it increases almost imperceptibly, and forms lenticular drops on the surface of the water, being more or less voluminous and floating on the surface. This phenomenon is exactly that which first appears on putting a drop of oil on clean water. Before the spreading has assumed its limiting value, we pass in the opposite direction through all the preceding phases; black spots bounded by brilliant droplets, and then a uniform and invisible spot.

Analogous experiments have been made on solids like paraffin, employed in solution in benzene. After spreading from the drop, the benzene evaporates immediately, and a layer is obtained having a thickness of the order of 1μ which maintains all the cohesion of a solid; it moves as a single piece on the surface of the water, and may even be broken into irregular fragments.

A knowledge of the molecular weights of the body studied, combined with Avogadro's constant, allows us to calculate with some accuracy the mean diameter of a molecule. In this way we find for sodium oleate, the number 1.13μ which agrees quite well with the limiting thickness of the films observed. It seems, therefore, that the thinnest films realised in the experiments of Devaux are composed of a single layer of molecules ; up to the moment when the gyration of the camphor ceases, the film remains monomolecular, but with molecules more or less displaced from one another. For the first time we have attained thereby the molecular dimensions themselves by direct experiment.

In a more recent research Labrouste has made several interesting additions to the work of Devaux. In particular he has been able to observe, by means of a simple optical arrangement, a real and progressive fusion of certain monomolecular solid films under the influence of a rise in temperature.

TRANSLATOR'S NOTE

Further references to more recent work dealing with this subject are given in the Bibliography at the end of the book.

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