

INTRODUCTION

The fundamental postulate of the kinetic theory of gases is that of molecular chaos. According to the theory, a quantity of gas consists of a very large number of discrete particles, or molecules, the motion of which is incessant and entirely uncoordinated. In other words, the molecules of a gas do not describe regular orbits, but follow completely random zig-zag paths, each section of the zig-zag being terminated by a collision, either with another molecule or with a wall of the containing vessel. Between collisions, the molecules describe rectilinear paths with uniform velocity; that is, every section of a zig-zag is strictly a straight line.

The velocity of a specific molecule at any instant is unpredictable; but the velocities of the individual molecules are distributed according to statistical laws about a mean value, which is defined precisely by the external conditions. Corresponding to the mean velocity, there exists for a given molecular concentration a perfectly definite mean path between collisions, or mean free path. Thus the existence of the quantities mean velocity, mean free path, and so forth, which serve to characterise a gas under specified conditions, is dependent on the fact that we are dealing with enormous numbers of molecular individuals, to which large numbers alone statistical laws properly apply. It follows, conversely, that the deduction from the behaviour of a gas of the characteristics of the constituent molecules is only possible with the aid of often complicated statistical considerations.

Now suppose that we pierce the wall of a vessel containing a gas, and allow the molecules to effuse through the aperture so formed into an evacuated space (Fig. 1 *a*). Then, provided that the pressure in the containing vessel *A* is not too high, those molecules which happen to approach the dividing wall

between *A* and the evacuated space *B* at the position of the aperture will fly into the space *B*, and will traverse rectilinear paths radiating out from the aperture until they hit the walls. The motion of the molecules in *B* is already no longer chaotic.

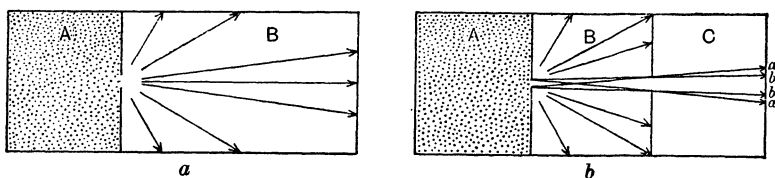


Fig. 1

If now *B* is divided into two compartments, *B* and *C*, by a wall pierced by an aperture (Fig. 1 *b*), only those molecules will enter *C* whose directions of motion lie within the boundaries of the cones defined by the apertures in the walls of *A* and *B*. Moreover, their paths will not intersect, if the aperture in the wall of *A* is sufficiently small to be regarded as a point source: thus the only collisions to which the molecules in *C* will be subject are those arising from the faster molecules overtaking the slower ones which are traversing the same path. But this effect is small, and the molecules in *C* will be for all practical purposes collision free. The selective action of the two diaphragms will, in fact, replace the chaotic motion of the molecules in *A* by a coordinated motion in *C*, where the molecules move in a geometrically defined beam, or ray. It should therefore be possible with the help of such a *molecular ray* to approach the study of molecular properties directly, instead of through the channels of statistical reasoning.

These deductions from gas kinetic theory were brilliantly justified by the pioneer work of Dunoyer.^a A cylindrical glass tube some 20 cm. in length was divided into three compartments by two circular diaphragms of glass. After evacuation, a little redistilled sodium was introduced into the lowest com-

^a Dunoyer, *Compt. rend.* 152, 594, 1911; *Le Radium*, 8, 142, 1911.

INTRODUCTION

3

partment. The sodium was heated to a temperature sufficiently high to vaporise it, when in time there appeared a sharply defined metallic deposit on the upper closed end of the third compartment. The deposit had precisely the size to be expected from the geometry of the apparatus, on the assumption that the sodium atoms describe rectilinear paths between source and deposit. An “umbra” and “penumbra” of the dimensions to be expected if they are defined by the cones *bb* and *aa* (see Fig. 1 *b*) were clearly observable. Objects placed in the path of the beam cast clearly defined “shadows.” With an indifferent vacuum in the tube, the deposit was no longer sharp, but diffuse and ill-defined in outline; which is what one must expect as soon as the mean free path of the sodium atoms is shorter than the distance between source and deposit.

From these beginnings in 1911, an elaborate and increasingly important technique has been developed, chiefly at the hands of Stern and his collaborators.^a The orientation of the work has changed greatly since the time when the experiments were regarded mainly as striking confirmation of the essential accuracy of the conceptions of the dynamical theory of gases. Increasingly wide use has been made of the coordinated character of the motion of the molecules in a beam to investigate directly the properties of the individual molecules; and the molecular ray technique has become a powerful tool in the study of the structure of matter. It is this tool, and some of its applications, which we aim to describe in the following pages.

It should already be sufficiently clear that a molecular ray is a beam of *neutral* molecules, moving *in vacuo* with thermal velocities corresponding to the temperature of the source. The

^a The main body of this work is contained in a series of papers in the *Zeitschrift für Physik*, from 1926 onwards, under the general title “Untersuchungen zur Molekularstrahlmethode aus dem Institut für physikalische Chemie der Hamburgischen Universität” (cited as U. z. M. 1, etc.).

average velocity of the molecules in a molecular ray lies therefore between some 10^4 cm./sec. and 10^5 cm./sec., depending on the molecular species and on the temperature. A molecular ray can in principle be produced from any stable molecular (including atomic) species whatsoever; the range of the method in this direction is limited solely by the technical possibilities. The method is, however, in general ill-adapted to the study of *excited* molecules; this is at once clear when it is recalled that the time of excitation is of the order 10^{-7} to 10^{-8} sec.; the length of path traversed by a molecule, once excited, before it returns to the normal state, is thus only some 10^{-4} to 10^{-2} cm. This was demonstrated purely experimentally by Dunoyer.^a He showed that a sodium beam could be rendered visible by exciting it to emit the resonance radiation; when only a central band was irradiated by the *D*-lines, the boundaries of the luminous portion were seen to be extremely sharp, coinciding as far as could be observed exactly with those of the exciting beam. Although the method is thus not suited to the general study of excited states, the investigation of *metastable* states is within its scope; here the difficulties are the purely technical ones of producing a sufficient concentration of metastable molecules in the source.

A distinction must be drawn between a molecular ray and a *jet* of gas (*Dampfstrahl*). A molecular ray is practically collision free; within a jet there is turbulent motion. It is therefore impossible for a jet to maintain its form for more than a few millimetres of path *in vacuo*. There is no sharp limit separating the conditions for the production of a molecular ray on the one hand, and a gas jet on the other: the one passes continuously over into the other as the pressure in the source is raised.

The technique is concerned with the production of a molecular ray of the maximum possible intensity. It may appear at first sight, when one considers how few are the essential

^a Dunoyer, *Compt. rend.* 157, 1068, 1913; *Le Radium*, 10, 400, 1913.

INTRODUCTION

5

arrangements necessary to the formation of a molecular ray, that the technique should be one of comparative simplicity. It must be remembered, however, that for many purposes beams of very narrow cross section (ca. 0.01 mm.) must be used, and it becomes then a matter of some difficulty to obtain a sufficiently intense beam. Nevertheless, the main details of the production of the rays are now well understood, thanks almost entirely to the work of the Hamburg school.^a

There remains the problem of detection. The most familiar form of detector is of course the primitive cooled target, on which the beam marks in time the imprint of its cross section; the target detector is, however, only semi-quantitative, and by no means of universal application. There are indeed no perfectly general methods of detection of the molecular rays, such as exist for the detection of charged particles of high energy; each molecular species has to be considered on its merits and a suitable detector devised for use with it. Several satisfactory types of quantitative detectors, of more or less limited range of application, have been developed; but the great majority of substances await the advent of suitable metrical devices for their completely successful study. The central problem on the technical side is the problem of detection. (Chapter 1.)

The most immediate use of a perfected technique of molecular rays lies in the direct experimental study of gases. Here much has already been accomplished. The central law of the kinetic theory of gases, the Maxwell Law of Distribution of Velocities, has been directly confirmed. An elegant method of measuring the mean free path has been developed. A wide field of study, that of intermolecular scattering, has been opened up, and important information about the nature of

^a The fundamental principles of the production of intense molecular beams of narrow cross section were laid down in 1926 by Stern (*Z. Physik*, 39, 751, 1926. U. z. M. 1).

molecular fields may be expected to accrue from future investigations in this direction. On the technical side, it has been found possible to produce molecular beams of sensibly uniform velocity, which should prove extremely valuable for many applications of the molecular ray method (Chapter 2). It should be possible to observe directly the dissociation of diatomic molecules by means of the velocity selectors which are used to produce beams of uniform velocity (Chapter 7).

Intensive study of the mechanism of collision and condensation of molecules at solid surfaces has been made possible by the advances in vacuum technique which have been made during the last twenty years. The ability to confine the impinging molecules within the definite limits of a directed beam is clearly often of great value, and the molecular ray method has already yielded results of fundamental importance in the investigation of the scattering and reflection of molecules at solid surfaces.

The most recent work in this field has been largely guided, and considerably clarified, by the recognition of the wave nature of matter. It will be recalled that de Broglie^a suggested that just as light displayed a dual character, undulatory and corpuscular, so matter should likewise be regarded as possessing a dual character, corpuscular and undulatory. It was known that the momentum of a light quant, frequency ν , wavelength λ , could be expressed as

$$\frac{h\nu}{c} = \frac{h}{\lambda},$$

where c is the velocity of light, and h is Planck's constant. de Broglie put forward the hypothesis that the momentum mv of a moving particle could be written

$$mv = \frac{h}{\lambda},$$

where λ is the wavelength of the plane wave which represents

^a de Broglie, *Phil. Mag.* **47**, 446, 1924.

the rectilinear motion of the particle. He supported the hypothesis by a fine mathematical analysis.

The hypothesis was brilliantly confirmed, for the electron, by Davisson and Germer in America, and by G. P. Thomson in this country; and electron diffraction has become an intensively cultivated field of research.^a It is in some ways surprising that the effect was not discovered earlier, purely experimentally; but when it is remembered that the de Broglie wavelength for electrons of say 25,000 volts energy is only 0.75×10^{-9} cm., it is clear that only a lucky chance could have disclosed the existence of such short waves without the guidance of theory.

Now it is an essential feature of de Broglie's theory that the rectilinear motion of *every* moving mass can be represented by a plane wave. Thus the de Broglie wavelength of for example hydrogen at 0° C. is of the order

$$\lambda = \frac{h}{mv} \sim \frac{6.54 \times 10^{-27}}{3.3 \times 10^{-24} \cdot 1.7 \times 10^5} \sim 1.2 \times 10^{-8} \text{ cm.},$$

that is, of the same order as that of X rays. For heavier elements and higher temperatures the de Broglie wavelength of the molecules becomes extremely short, and difficult of observation. Attention has therefore been confined hitherto chiefly to the lightest gases.

It has been found that certain of the conditions for the specular reflection of a molecular ray at a solid surface appear to be just those for the reflection of light from a matt surface (Chapter 3); and further, that beams of hydrogen, helium, and atomic hydrogen reflected from the cleavage surface of a crystal are split up into diffraction patterns, which have precisely the characteristics demanded of the reflection of plane waves of the predicted de Broglie wavelength from the lattice formed by the regularly spaced ions in the crystal face (Chapter 4).

^a For references to the literature, see G. P. Thomson, *Wave Mechanics of Free Electrons*, New York, 1930.

On a more prosaic level, the study of metal films deposited on solid surfaces from molecular beams has given a better insight into the process of the formation and growth of condensates, and an indication of the conditions under which they may adequately be observed (Chapter 3).

The most intensive application of the molecular ray technique to a particular problem has lain until recently in the investigation of the magnetic and electric properties of molecules. The method, which was initiated by the classic experiments of Stern and Gerlach in 1922, depends on the fact that a beam of atoms or molecules which possess a magnetic or electric moment suffers a deviation when shot through an inhomogeneous magnetic or electric field. The extent and character of the deviation can be used to evaluate the magnitude of the moment, and to yield valuable information about the energy states of the molecules constituting the beam (Chapters 5 and 6). The method is of peculiar value in that it serves to measure directly the effect of the field on isolated molecules; the standard susceptibility and dielectric constant measurements, on the other hand, must take account not only of the macroscopic interaction between the field and the magnetic or electric medium, but also of the interaction of the molecules with each other.

The spectroscopic method is that most closely allied to the method of molecular rays. The splitting of spectral lines in a magnetic field (Zeeman effect) or in an electric field (Stark effect) has, as is well known, yielded an enormous mass of data concerning the magnetic and electric properties of atoms and molecules. At the present stage of the technique, the deflection method is indeed, in the majority of cases, closely dependent on spectroscopic theory for an interpretation of its results. However, it actually surpasses the optical method in *sensitivity*; the reason is essentially that it is very much easier to produce high inhomogeneities than strong fields. Thus on the electrical side, the deflection method is often applicable

INTRODUCTION

9

in cases where the corresponding Stark effect is too small to be measurable; on the magnetic side, the use of a modified form of the original Stern-Gerlach arrangement should make possible the detection of magnetic moments which are ten or even a hundred times smaller than those detectable in the Zeeman effect with the most refined optical technique.

A new field has recently been opened up in the study of the dissociation of metallic vapours by means of the magnetic deflection method. If the atoms are magnetic, the molecules non-magnetic, and a mixed molecular-atomic beam is shot through an inhomogeneous magnetic field, the molecules go straight on unaffected by the field; the atoms are deflected right and left of the undeviated molecule beam. Actual physical separation of the atoms and molecules can in this way be effected, and their numbers can be counted by appropriate devices. The method has already yielded results of great elegance (Chapter 7).

Other applications, which have thus far received but little development, are also included in Chapter 7. We have summarised here only the main lines of advance, in order that a general idea of the scope and importance of the molecular ray method may be gained at the outset. But the technique is advancing rapidly, and an application which is now obscure may at any time assume quite another perspective. One may, however, hazard the guess that in the next few years the most important advances will come from a study of the wave nature of molecular beams, both in its fundamental aspects and in its application to the investigation of surfaces and the mechanism of adsorption; while the possibility of working with beams of sensibly uniform velocity should make possible of attack many hitherto intractable problems, not least in connection with the deflection method of studying the magnetic and electric properties of molecules.

Chapter 1

THE PRODUCTION AND MEASUREMENT OF MOLECULAR RAYS^a

We have seen that an apparatus for the production of a molecular ray consists, schematically, of a vessel divided into three compartments by two diaphragms. The three compartments may be termed the source, the collimator chamber, and the observation chamber; the last named contains the detector.

The *source* may take any one of three forms, according to the nature of the substance under examination. (1) It may be a small oven, into which a limited quantity of the substance is introduced, to be vaporised after evacuation of the apparatus. (2) It may be simply a tube communicating through a capillary with a gas reservoir, from which the gas is drawn into the apparatus by pumps. (3) In certain special cases, it may be the surface of a molten solid or heated filament.

The *collimator chamber* is so called, in very loose analogy with optics, because its function is to form an approximately parallel beam of molecules. The technical problem in the design of the collimator chamber is the elimination of *alien molecules*, that is, those molecules which issue from the source aperture in directions other than the narrow range selected by the second or *image aperture*.

The design of the *observation chamber* naturally varies according to the specific purpose of the experiment. The common feature of all arrangements is the *detector*. The design of suit-

^a The essence of this chapter is contained in three important papers from the Laboratory of Physical Chemistry at Hamburg: "Zur Methode der Molekularstrahlen, I", Stern, *Z. Physik.* 39, 751, 1926 (U. z. M. 1); "Zur Methode der Molekularstrahlen, II", Knauer and Stern, *ibid.* 764 (U. z. M. 2); "Intensitätsmessungen an Molekularstrahlen von Gasen", Knauer and Stern, *ibid.* 53, 766, 1929 (U. z. M. 10).