THURSDAY, FEBRUARY 7, 1895.

ARGON.

THE scene in the theatre of the University of London on Thursday last was in many respects unique. It will certainly be historical. It was unique in that the Royal Society had formally invited members of two other scientific bodies to attend the meeting, and had left the comparative seclusion of Burlington House to meet, in Burlington Gardens, an audience numbering at least eight hundred. It was the first of a series of discussion meetings to which, we suppose, similar invitations will be issued; but it will be long before the same eagerness to obtain a ticket is displayed—long before those who gain admission, will listen to so much worth hearing.

The previous history of the subject to be "discussed" is known to most of our readers. Lord Rayleigh has for some years been engaged on one of the most difficult of physical measurements, namely, the determination of the densities of some of the more permanent gases. In the case of nitrogen, he was confronted with the fact that if obtained from chemical compounds, it was about one half per cent. lighter than if extracted from the atmosphere. This result he published in the spring of last year, and the cause of the discrepancy was a subject of general conversation in scientific circles. Lord Rayleigh himself discussed it with some of his chemical friends. Prof. Ramsay was interested, and since last Thursday he has confided to an interviewer some details as to the part he played in solving the problem. It appears that he asked Lord Rayleigh's permission to investigate the matter, that using a chemical method he succeeded in separating a heavier constituent from atmospheric nitrogen, and that on writing to Lord Rayleigh, he learned that he, too, had achieved the same result by a process of "sparking."

The fact of the discovery was announced in a semi-public way at the meeting of the British Association at Oxford. Of course it attracted great attention, and curiosity was further stimulated by the silence of the discoverers during the five succeeding months. Towards the end of last year it was announced that they would give their results to the world in January. On Thursday last the promise was fulfilled, and all that is known of "Argon" was told to all.

Three papers were read, which showed that the period of silence had been devoted to strenuous work. It was proved beyond possibility of doubt or question that the atmosphere contains a hitherto unknown constituent. It has been separated from the air by atmolysis, by red-hot magnesium, and by "sparking." Its density has been determined to be about 19·7. It is very soluble in water, and it has been proved that the nitrogen extracted from rain-water is twice as rich in argon as that which exists in the air.

Mr. Crookes has found that the new substance has two spectra, marked by red and blue lines respectively. Both he and Prof. Schuster certify that the principal lines are identical in the case of two specimens obtained by different methods. The properties at very low temperatures have been determined by Prof. K. Olszewski, of Cracow. The critical temperature is $-121°$ C., the critical pressure 50·6 atmospheres. The liquid boils under a pressure of 740·5m.m. at $-186°·9$, having at the boiling point a density of about 1·5. The melting point is about $-189°·6$, and it has been frozen into a white solid resembling ice. Last, but not least, the ratio of the specific heats of the gas is approximately 1·66, and all attempts to induce it to enter into chemical combination with other substances have up to the present entirely failed.

After this torrent of well-established facts, it cannot reasonably be doubted that Lord Rayleigh and Prof. Ramsay have really discovered a substance, which, though existing in enormous quantity, has hitherto defied detection. Lord Rayleigh's work first showed that there was something to explain; the patience and masterly skill which he displayed throughout years devoted to weary weighings, must command universal admiration. As has been well said, the result is "the triumph of the last place of decimals," that is, of work done so well that the worker knew that he could not be wrong. Prof. Ramsay, too, is to be congratulated in that when this preliminary stage had been accomplished, his energy and skill enabled him to take such a share in the hunt after the unknown cause of the difficulty, that he rightly ranks as a co-discoverer of the new gas.

In scientific investigations, however, the answer to one question always suggests others, and interest in a discovery quickly precipitates into interest in its results. Seldom have a series of facts and figures raised more important issues. The ratio of the specific heats is 1·66, which points to the conclusion that the substance is monatomic. If it is monatomic, it must be an element or a mixture of elements. If it is a single element, its atomic weight must be about 40, and in that case no place is ready for it in Mendeléeff's table. The easiest way out of the difficulty is to suppose that argon is a mixture, and the authors point out that there is evidence for and against this view; "for, owing to Mr. Crookes observations of the dual character of its spectrum; against, because of Prof. Olszewski's statement that it has a definite melting point, a definite boiling point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance, the former is not known with certainty to be characteristic of a mixture." The question is to be further investigated, but at present the authors conclude that the balance of evidence is in favour of simplicity.

On this hypothesis a very awkward question is no doubt raised. The periodic classification of the elements cannot, and ought not, to be abandoned at the first challenge, and till further evidence is forthcoming a heavy strain is thrown on the link of the chain of argument which connects the ratio of the specific heats with the monatomicity of the gas.

On the other hand, the conclusion that if the ratio of the specific heats is 1·66 the gas can be diatomic, is directly contrary to all analogy. Merely to say that mercury is monatomic, that Kundt found that the ratio of the specific heats is one and two-thirds, and that therefore a similar relation must hold for argon, is to understate the case. Taking the very outside values, no diatomic gas has a ratio greater than about 1·42; and to place among these a substance for which the ratio is 1·66, would be entirely opposed to all the other indications of a theory which, though admittedly only approximate, nevertheless in all other cases accords fairly with the conceptions of the chemist. The behaviour of mercury vapour suggests that there are two classes of phenomena which occur within the molecule—a coarser group with which the ordinary mechanical theory of gases is concerned, and a more refined type detected by the spectroscope. It is the former, and not the latter, which are of the same order as the chemical facts which lead to conclusions as to the number of atoms in the molecule.

Thus, in the case of mercury vapour, the mechanical theory of gases ignores the vibrations, whether mechanical or electrical, which produce the spectrum, and gives the precise value of the ratio of the specific heats which corresponds to three degrees of freedom. Whether we frame a mental picture of a Boscovitch point, or are content with the more usual contradictory image of a smooth sphere, perfectly elastic, and yet incapable of internal vibrations, is for the present purpose comparatively unimportant. It is impossible to connect the conception of three degrees of freedom with anything that does not behave as one single thing, incapable of being set in rotation, and incapable of internal vibration. That such a thing may have structure is not denied. It is only affirmed that as far as the phenomena under investigation are concerned, structure is not recognisable. It is not denied that it may be subject to internal changes. It is only affirmed that these changes are of different order from the causes which affect the behaviour of the molecule in what may be called the pressure-producing machinery of a gas. Where the ordinary dynamical theory stops, there, and there precisely, chemical analysis stops also. The chemical facts which prove that mercury is monatomic have nothing to do with its spectrum. The arguments used would be valid if it had no spectrum at all. Analysis recognises no structure in the indivisible molecule of mercury. In chemistry, and in the approximate theory of gases, "monatomic" means—in this case, at all events—the same thing.

Next take the case of the diatomic gases.

The results of the dynamical theory can be most easily represented if we suppose the atoms to be smooth spheres, which may, if it is desired, be regarded as mere geometrical surfaces surrounding Boscovitch centres.

The theory shows that unless the two atoms when united can be fairly represented by a single point or a single smooth sphere, the ratio of the specific heats ought not to be greater, but may be less, than 1·4. This value would correspond to the case of two smooth spheres the surfaces of which were maintained in contact, or to two points maintained at a certain fixed distance apart, but otherwise free. Smaller values would indicate greater internal freedom.

The gases may be divided into two classes, viz. firstly, O_2, N_2, H_2, CO, NO and HCl, and secondly, Cl_2, Br_2 and I_2. The mean of the ratios of the specific heats for the first six is, according to Masson,[1] 1·399. The corresponding figure deduced from Regnault's experiments is 1·410. The highest value obtained from Regnault is 1·42 in the case of HCl, but Masson's value for the same gas is only 1·392, the mean being 1·406. In the cases of Cl_2, Br_2 and I_2 the values are lower, lying between 1·293 and 1·323. The larger values thus in some cases slightly exceed, but are in all cases very close to, the limit fixed by the theory on the assumption that the dual character of the molecule can be recognised by it. The smaller values fall well within the limit.

The ratio of the specific heats has not been directly determined for many substances, but it can be calculated by well-known formulæ for all gases of which the specific heat at constant pressure is known, and though the values thus obtained are only approximate, they are sufficient to prove that the molecules of the more complex gases have always more than the minimum number of degrees of freedom which are consistent with the idea of their being built of smooth spheres constrained to remain in contact, and equal in number to the number of atoms within the molecule. Whereas, if argon is a diatomic substance, the molecule has fewer degrees of freedom than the theory indicates, and is thus the single exception to a universal rule. In that event it is not too much to say that the result will indicate a connection between its atoms of a kind absolutely different from that in any other known substance. In all other cases the approximate dynamical theory is in close agreement with the view that molecular structures made up of the union of two or more like or unlike things, have a more or less irregular form, and are capable of rotation. If argon is not monatomic, this rule will for the first time be broken. Quite apart from the absolute validity of the theoretical grounds on which it is based, and regarded only as suggested and not as completely justified by theory, it is nevertheless an empirical generalisation which up to the present has stood every test.

It is not sufficient to explain the difficulty by saying that the bonds between the constituents of the argon molecules must be very strong, for we have already assumed that the tie which unites the centres of the hydrogen or oxygen atoms is proof against the collisions which occur in the gas—*i.e.* is or the purposes of the approximate theory infinitely strong. It is further necessary that the molecule must be incapable of rotation, that the two points must coincide, or the two spheres be crushed out of shape, so that the surface is spherical. Such violent assumptions would be quite unjustifiable unless we are driven to them by facts which cannot be disputed. Until it is directly proved that argon is diatomic, we must agree with the discoverers that the weight of evidence is in favour of the molecule being indivisible. Whether in the future other and more convincing evidence will be adduced on the other side, the future alone can show. The courts of science are always open, and every litigant has an unrestricted right of moving for a writ of error.

[1] See K. Strecker, *Wied. Ann.* 13, 1881, p. 41.