It commonly happens that the materials thus obtained are, like the parent compound, explosive, and they are, moreover, very sensitive to light. From a study of their refractive power, it appears that in the aliphatic series the increment of refraction for the triazo-group is 8·91 as compared with 8·93 for bromine; and whilst the atomic dispersion of this halogen is 0·35, that attributable to the triazo-group is 0·36. Moreover, the elevation of boiling point produced by this complex lies between those due to bromine and iodine, whilst the effect on the dissociation constant of an aliphatic acid exceeds that of iodine, but is less than that of bromine. Thus the physical evidence supports those chemical characteristics which classify the triazo-group as a complex radicle having a strong family resemblance to the halogens.

The changes undergone by triazo-compounds may be referred to one of three main types:—

(1) Liberation of two nitrogen atoms in elemental form, leaving the third attached to the carbon which originally carried all three. This is exemplified by triazoantipyrine, which passes spontaneously into a red azo-compound, whilst in triazoacetone, triazocamphor, and triazoacetic acid the change is accelerated by alkali. Sometimes this type of alteration is violently explosive, as in the case of triazoacetic azide.

(2) Unfolding of the three-atom nitrogen ring into a straight chain such as occurs in diazoaminobenzene or in the cycloid tetrazole. Allylazoimide, for instance, a colourless liquid, changes spontaneously into an isomeric solid which no longer contains the triazo-group, whilst hydrazoic acid converts prussic and fulminic acids into tetrazole and hydroxytetrazole respectively.

(3) Complete removal of the triazo-group in the form of hydrazoic acid. The simplest example of this change is found in the behaviour of triazomethylamine derivatives, which liberate hydrozoic acid when treated with cold water; this happens also when triazotised carbon is associated with a halogen, as in the case of triazoethylene dibromide, but more generally this type of decomposition requires the action of alkali.

Although the preparation of chloroazoimide by Raschig (1908) indicates the possibility of producing hexatomic nitrogen by the union of two triazo-groups, this new form of the element has not yet been realised.

A NEW METHOD OF CHEMICAL ANALYSIS.[1]

I HAVE had on several occasions the privilege of bringing before the members of the Royal Institution some of the results of the experiments on the positive rays on which I have been engaged for the last few years. I wish this evening to direct your attention to some applications of these to various chemical problems.

The first application I shall consider is the use of these rays to determine the nature of the gases present in a vacuum tube, to show how they can be used to make a chemical analysis of these gases—an analysis which, as we shall see, will enable us to determine, not merely whether an element, say, for example, oxygen, is present in the tube, but will tell us in what form it occurs, whether, for example, it is present in the atomic as well as the molecular condition, and whether there are allotropic modifications present, such as ozone, O_3, and other still more complex aggregations.

The method is as follows: the positive rays, after passing through a fine tube in the kathode, are exposed simultaneously to magnetic and electric forces, the magnetic field being arranged so as to produce a vertical deflection of the rays, while the electric field produces a horizontal deflection. Thus, if when neither electric nor magnetic fields are present, the rays strike a screen placed at right angles to their direction at a point O, they will, when both electric and magnetic forces are at work, strike it at a point P, where the length of the vertical line PN is equal to the deflection produced by the magnetic field, and the horizontal line ON to that produced by the electric field.

We know from the theory of the action of electric and magnetic fields on moving electrified particles that

$$PN = A\frac{e}{v} \qquad ON = B\frac{e}{mv^2}$$

where A and B are constants depending on the strength of the magnetic and electric fields and the geometrical data of the tube, e is the charge on the particle, m its mass, and v its velocity.

From these relations we see that

$$\frac{m}{e} = \frac{A^2}{B}\,\frac{ON}{PN^2}.$$

When these rays strike against a photographic plate, they affect the plate at the point against which they strike, and thus when the plate is developed we have a permanent record of the deflections of the rays. The methods of taking these photographs and the details of the experiment are described in my paper in *The Philosophical Magazine*, February. The values of A and B can be determined accurately by the methods I have given in previous papers, and hence if we measure on the photographs the values of ON and PN, we can determine the value of m/e. If we wish to compare the values of m/e for two different rays, it is not necessary to determine A and B; all we have to do is to measure the values of ON and PN, and thus the photograph alone gives us the means of comparing the value of m/e.

Since for the same type of carrier m/e is constant, so that whatever may be the velocity $\frac{PN^2}{NO}$ is constant, and therefore the locus of P, *i.e.* the curve traced on the photographic plate by this carrier, is a parabola. The reason we get a curve instead of a point is that the rays are not all moving with the same velocity, and the slower ones suffer greater deflection than the quicker ones. Each type of carrier produces its own line on the plate, and there are as many curves on the plates as there are kinds of carriers; from an inspection of the plates we can find, not merely the number of kinds of carriers, but from the dimensions of the curves we can at once determine the atomic weight of the carrier, and thus determine its nature. This is one of the great advantages of this method. To illustrate this advantage, let us compare the method with that of spectrum analysis. If the spectroscopist observes a line unknown to him in the spectrum of a discharge tube, the most he can deduce without further investigation is that there is some unknown substance present in the tube; and even this would be doubtful, as the new line might be due to some alteration in the conditions of the discharge. But if we observe a new curve in the positive-ray spectrum, all we have to do is to measure the curve, and then we know the atomic weight of the substance which produced it. To take an example, I have photographed the positive-ray spectrum for nitrogen prepared from the atmosphere and that for nitrogen prepared from some nitrogenous compounds, and have found that the former contains a line[1] which is not in the latter, and that the value of m/e for this line is 40 times that for the atom of hydrogen. We thus know that atmospheric nitrogen contains an element of atomic weight 40, which is not present in chemical nitrogen—this element is, of course, argon. We might by ordinary spectrum analysis have found lines in the spectrum of atmospheric nitrogen which are not in the spectrum of chemical nitrogen, and might thus have suspected the presence of another element; but spectrum analysis could not tell us anything about the nature of this element, whereas the positive-ray spectrum at once gives us its atomic weight.

The positive-ray method is even more delicate than that of spectrum analysis, for by it we can detect the presence of quantities of a foreign gas too minute to produce any indication in the spectroscope. I have, for example, often been able to detect the presence of helium by this method when no indication of its presence could be detected by a spectroscope.

Again, when a line in the positive-ray spectrum can be seen, the atomic weight of the carrier which produces it can be determined with great accuracy. Though the method is only a few months old, it is even now sufficiently developed to determine with an accuracy of 1 per

[1] Discourse delivered at the Royal Institution on Friday, April 7, by Sir J. J. Thomson, F.R.S.

[1] As a matter of fact, there is a second, very faint line for which m/e is about twenty times that for the atom of hydrogen. This is probably due to an atom of argon with two electric charges.

© 1911 Nature Publishing Group

cent. the atomic weight of a gaseous substance, without requiring more than 1/100 milligram of the substance. Another very important advantage of this method is that it is not dependent upon the purity of the material; if the material is impure, the impurities merely appear as additional lines in the spectrum, and do not affect the parabola due to the substance under examination, and therefore produce no error in the determination of the atomic weight. The method would seem to be peculiarly suitable for the determination of the atomic weights, not

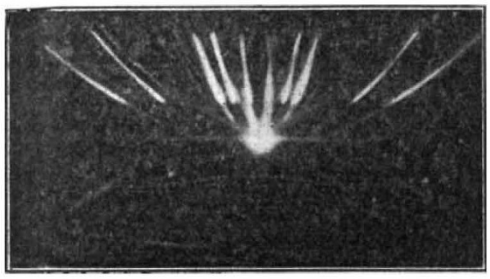

FIG. 1.

merely of the emanation from radio-active substances, but also those of the products into which they disintegrate.

The rays, too, are registered within less than a millionth of a second after their formation, so that when chemical combination or decomposition is occurring in the tube, the method may disclose the existence of intermediate forms which have only a transient existence, as well as of the final product, and may thus enable us to gain a clearer insight into the process of chemical combination.

I will now show a few slides prepared from the photographs we have taken of the positive-ray spectra. The first (Fig. 1) is that of nitrogen prepared from air; the measurements of the photograph showed that the atomic weights of the carrier producing these curves were as follows:—

Positive		Negative	
1	H_+	1	H_-
1·99	H_{2+}	11·20	C_-
6·80	N_{++}	15·2	O_-
11·40	C_+	...	
13·95	N_+	...	
28·1	N_{2+}	...	
39	Ar_+	...	
100	Hg_{++}	...	
198	Hg_+	...	

The symbol H_+ denotes that the carrier is an atom of hydrogen with one charge; H_{2+} that it is a molecule of hydrogen with one charge; N_{++} that it is an atom of nitrogen with two charges; and so on.

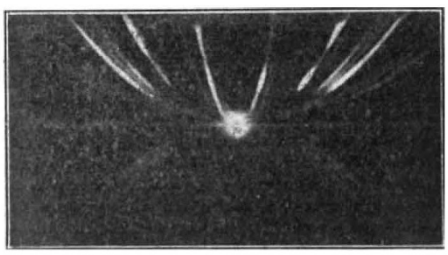

FIG. 2.

With nitrogen from NH_4NO_2 the lines were as follows (the magnetic force was so large that some of the lines corresponding to the lighter particles were thrown off the plate):—

6·1	C_{++}	44·2	CO_{2+}
7·02	N_{++}	65·5	Hg_{+++}?
12·08	C_+	100	Hg_{++}
14·01	N_+	204	Hg_+
27·9	N_{2+}		

The next slide (Fig. 2) is the positive-ray spectrum for CO, and again the magnetic field is so great that the lighter carriers do not appear.

From the measurement of the lines we find that the atomic weight of the carrier is

Positive		Negative
6·00	C_{++}	12 C_-
6·95	N_{++}	16 O_+
7·95	O_{++}	...
12·02	C_+	...
13·9	N_+	...
15·95	O_+	...
28·05	CO_+	...
43	CO_{2+}	...
69·5	Hg_{+++}(?) very faint	...
100	Hg_{++}	..
202	Hg_+	...

The spectrum for CO_2 is represented in Fig. 3; the atomic weights are:—

5·98	C_{++}	43·9	CO_{2+}
8·00	O_{++}	62·5	Hg_{+++}(?) very faint
12·00	C_+	99·6	Hg_{++}
16·00	O_+	200·0	Hg_+
28·02	CO_+		

The spectrum of CH_4, of which a small region with five lines close together is shown in Fig. 4. This is interesting, because the measurement of these lines shows that their atomic weights are 12, 13, 14, and 15, 16, and thus that we have here C, CH, CH_2, CH_3, CH_4. If I am not mistaken, this is the first occasion when the atoms CH, CH_2, CH_3 have been observed in a free state.

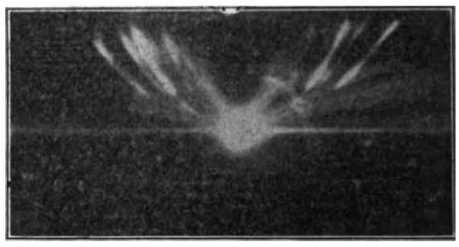

FIG. 3.

The spectrum of the analogous compound chloroform, $CHCl_3$, is represented in Fig. 5. The atomic weights represented in this are:—

1	H_+	18·5	Cl_{++}
1·5	(?)	27·7	CO_+
2	H_{2+}	36	Cl_+
3	(?)	46·5	CCl_+
6	C_{++}	63	(?) faint
8	O_{++}	81	CCl_2
11·9	C_+	102	Hg_{++}
13·7	N_+	201	Hg_+
16	O_+		

The carriers with atomic weights 1·5 and 3 have not been identified. They are of frequent occurrence. I have here two slides, one of SiH_4 (Fig. 6) and the other of the residual gas in the tube, in which they are well marked, though at their best they are only faint lines. In Fig. 7 we have the positive ray spectrum of air, taken under conditions which produce very narrow lines, which can be accurately measured.

Let us now consider some of the results brought to light by these photographs. In the first place, they show that a gas through which an electric discharge is passing is a much more complex thing than a collection of molecules all equal to each other. Even an elementary gas becomes in these circumstances a mixture of a great many different substances. Thus, to take oxygen as an example, the photographs show that when a current of electricity passes through it, we may have present simultaneously oxygen in the following states:—

© 1911 Nature Publishing Group

(1) Ordinary molecular oxygen, O_2.
(2) Neutral atoms of oxygen, O.
(3) Atoms of oxygen with 1 positive charge, O_+.
(4) Atoms of oxygen with 2 positive charges, O_{++}.
(5) Atoms of oxygen with 1 negative charge, O_-.
(6) Molecules of oxygen with 1 positive charge, O_{2+}.
(7) Ozone with a positive charge, O_{3+}.
(8) O_6 with a positive charge, O_6.

And, in addition, there are free negative corpuscles. Thus in the elementary gas there are at least nine (the list has no claim to be exhaustive) separate substances present when the discharge passes through it. Each of these substances has almost certainly different properties, possibly a characteristic spectrum. If we took any other gas we should find that the same thing would be true: thus in hydrogen we have H, H_2, H_+, H_-, H_{2+}, even if we do not ascribe to hydrogen the lines giving $m/e = 1{\cdot}5$ or 3. In nitrogen we have N, N_2, N_+, N_{++}, N_{2+}, carbon occurs as C_+, C_{++}, C_-, chlorine as Cl, Cl_2 Cl_+, Cl_{++}, and Cl_-, mercury as Hg, Hg_+, Hg_{++}, and probably as Hg_{+++}, as there is a very persistent line for which m/e is about 66.

Thus, whenever the electric current passes through a gas, and probably whenever a gas is ionised, the gas becomes a mixture of many different substances. We can thus readily understand why in the spectra of many elements many of the lines may be grouped together so as to form different series—the principal series, the first coordinate series, and so on—and the spectrum of the discharge tube regarded as the superposition of a number of different spectra the relative intensities of which may be subject to very great variations. This, indeed, is just

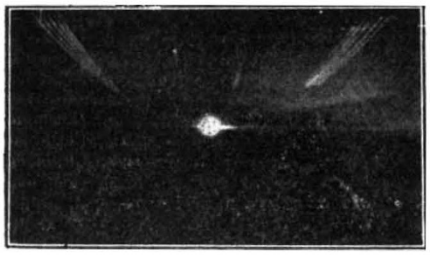

FIG. 4.

what would happen if some or all of the substances which are present when the gas is in the ionised state gave rise to different spectra.

Another feature which I think is of great interest from the point of view of the theory of chemical combination is the occurrence of particles with negative charges. Let us consider for a moment how these are formed. They are formed after the particles have passed through the kathode; the path between the kathode and the photographic plate contains abundance of corpuscles produced by the ionisation of the gas; a neutral particle, after passing through the kathode, picks up a negative corpuscle, and so becomes negatively charged. For this to occur, the attraction between the corpuscle and the neutral particle must be exceedingly strong, for it is not a question of a particle at rest attracting to itself a negatively electrified corpuscle sauntering about in its neighbourhood. In our case the neutral particle is rushing past the corpuscle with a velocity of the order of 10^8 cm. per sec. In order that the particle may in these circumstances be able to drag the corpuscle along with it, the attraction between the two must be so great that to move a corpuscle against this attraction from the surface of the particle away to an infinite distance must require an amount of work of the same order as that required to communicate to the corpuscle a velocity of 10^8 cm. per sec.; this is equal to the work required to move the atomic charge against a potential difference of about 3 volts, and is therefore comparable with the work required to dissociate some of the most stable chemical compounds.

The fact, then, that some particles get negatively charged shows that in the neutral state these particles have an exceedingly strong affinity for a negatively electrified particle, while the absence of a particular particle from the negative side shows that its affinity is much less, but does not imply that it vanishes altogether. From what we have said, it should follow that the more slowly the neutral particles are moving relatively to the corpuscles, the more easily will the negatively electrified systems be formed. This is confirmed in a very striking way by our experiments, for when the discharge is passing very easily through the tube, and the velocity of the neutral particles is relatively small, the number of negatively electrified particles is very much increased; indeed, in some cases the brightness of the part of the photograph corresponding to the negative particles is as great as that corresponding to the positive, whereas when the discharge is passing with great difficulty, and the velocity of the neutral particles is very high, the negative part is very faint compared with the positive.

The particles which have been observed on the negative side are the hydrogen atom, the carbon atom, the oxygen atom, and the chlorine atom. The presence of oxygen and chlorine atoms might, perhaps, have been expected, as these are universally regarded as strong electro-negative elements, *i.e.* as elements which have a strong affinity for negative electricity. The presence of the hydrogen atom is more remarkable, for hydrogen is generally considered to be a strongly electro-positive element, yet on these photographs we find it more persistently on the negative side than any other particle; often when no other line on the negative side is strong enough to be detected, the line corresponding to the hydrogen atom is distinctly visible. This is all the more remarkable, because the hydrogen atom, being the lightest of all the particles, is moving with the greatest

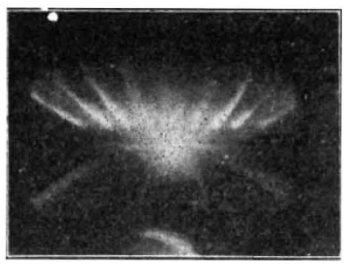

FIG. 5.

velocity relatively to the corpuscles, and therefore would, other circumstances being the same, be the least likely to capture them. The heavier the particle, the slower is its velocity, and the greater chance it has of capturing the corpuscles; the fact that heavy complicated particles are conspicuous by their absence on the negative side shows that the attraction of these for the corpuscles must be exceedingly small compared with that exerted by a neutral atom of hydrogen. It will be seen that the atom of carbon, also regarded as an electro-positive element, is also conspicuous on the negative side.

On looking at the list of the particles which occur on the negative side, we are struck by the fact that they are all atoms: there is not a molecule among them. Thus, although the curve corresponding to the negatively electrified hydrogen atom occurs on every plate, there is not a single plate which shows a trace of a curve corresponding to a negatively electrified hydrogen molecule, although that corresponding to the positively electrified molecule is always present, and on some of the plates is stronger than that due to the positive hydrogen atom. Again, on some plates the positive oxygen molecule shows stronger than the oxygen atom, but on the negative side only the atom is visible.

Thus neutral atoms, but not neutral molecules, can exert on the negative corpuscles those enormous attractions which, under the conditions of these experiments, are required to bind the corpuscles to these rapidly moving particles. We may compare this result with the properties ascribed by chemists to bodies when in the nascent condition, *i.e.* when they have only recently been liberated from chemical combination, and when they are likely to be partly in the atomic state, for atoms, as we have seen.

© 1911 Nature Publishing Group

exert forces on electric charges in their neighbourhood vastly greater than those exerted by molecules.

We may compare the forces exerted by a neutral atom on the corpuscles with those exerted by an unelectrified piece of metal on a charged body in its neighbourhood. In consequence of electrostatic induction, the charge and the metal will attract each other. This attraction is dependent on the electricity in the metal being able to move under the electric forces exerted by the charge, and to rearrange itself in such a way that if the charge is positive, the negative electricity in the metal moves to the part of the metal nearest to the charge, while the positive electricity moves to the part remote from the charge. The force between the metal and the charge depends on the freedom of the electricity to move about in the metal under the action of the electric field. If the metal is replaced by a substance of high specific inductive capacity, like sulphur, in which the electricity has an appreciable amount of freedom, though not so great as in a metal, the attraction, though still appreciable, is very much less than it was with the metal. A very simple experiment will illustrate this point. I have on this cardboard disc, which is suspended from a long string, a number of magnets such as are used for compasses; if I mount the magnets on pivots, so that they are free to turn round, the system of magnets is strongly attracted when another magnet is brought near it; if, however, I take the magnets off their pivots, so that they are no longer free to turn, the magnet exerts very little attraction upon them.

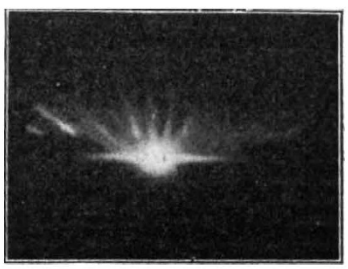

FIG. 6.

A view of chemical combination which I gave some time ago in *The Philosophical Magazine*, and also in my "Corpuscular Theory of Matter," suggests that there is a very close analogy between the causes at work in the experiment we have just made and those which produce the difference between the behaviour of atoms and molecules. On that theory the atom was supposed to consist of a large number of corpuscles arranged inside a sphere of positive electricity, the corpuscles arranging themselves so as to be in equilibrium under their mutual repulsion and the attraction of the positive electricity. The configuration depends on the number of corpuscles, and the stiffness and stability of the system also change as the number changes. For some particular numbers of corpuscles the system is very rigid, and any movement of the corpuscles would be strongly resisted; since the movement of electricity inside the atom is brought about by the movement of the corpuscles, the electricity could only move with great difficulty inside these atoms, and they would therefore not be able to exert more than feeble forces on electrical charges outside the atom: they would therefore not enter readily into combination with other atoms. We may ascribe such a constitution as this to the atoms of the inert gases, helium, argon, and neon. A system with one, two, or three more corpuscles than the system we have just described would not be nearly so stable, and there would be a tendency to discard the extra corpuscles from the atom so that it might return to the more stable form. We may roughly picture to ourselves the atom with one extra corpuscle as consisting of a number of fixed corpuscles plus one which is free to move about; the freedom of this corpuscle would enable the electricity in the atom to move about, and would endow the atom with the property of attracting any electrical charges which might be near it. If there were two corpuscles in the atom more than the number required for the most stable form, we can picture the atom as having two corpuscles free and the rest fixed. Similarly, if we had more than two extra corpuscles. Thus we may regard the atom as possessing 0, 1, 2, 3 corpuscles which are able to move about with more or less facility, and the free corpuscles will give to the atom the power of exerting attractions on electrical charges to an extent which depends on both the number of corpuscles and the freedom with which they can move about. On the theory to which I have alluded, the number of these "free" corpuscles determines the valency of the atom.

Now let us suppose that two such atoms come into such close connection that the corpuscles in the one exert considerable forces on those in the other. The system consisting of the two atoms will rearrange itself so as to get into a more stable form, if necessary, corpuscles passing from one atom to the other to enable it to do so. The greater stability, however, implies a loss of mobility; the free corpuscles have become parts of a more stable system, and have therefore lost to a greater or less extent their mobility. But with the mobility of the corpuscles goes their power of exerting forces on electrical charges, and thus the combination of the atoms diminishes to a great extent the attractions they exert outside them. Speaking generally, we may say that on this view the combination of atoms to form molecules, either of compounds or elements, fixes corpuscles which were previously mobile and converts the atoms from conductors of electricity into insulators with a small specific induction capacity.

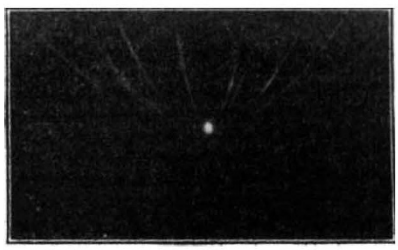

FIG. 7.

I have brought these illustrations before you with the object of showing that we have now methods which are capable of dealing with much smaller quantities of matter than the methods now used by chemists, methods which are capable of detecting transient phases in the processes of chemical combination, and I am hopeful may be of service in throwing light on one of the most interesting and mysterious problems in either physics or chemistry—the nature of chemical combination.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

EDINBURGH.—Mr. A. D. Darbishire has been appointed to the newly instituted lectureship in genetics, and will deliver a course of six lectures on heredity during the summer session, the course to be free to all matriculated students. Dr. W. G. Smith has been reappointed Combe lecturer in psychology. The executive committee of the Chiene portrait fund has resolved to hand to the University the balance of the fund (a sum of from 310*l.* to 320*l.*) for the foundation of a bronze medal, to be called the "Chiene medal in surgery."

M. TISSOT, an assistant in the Paris Museum of Natural History, has been appointed professor of physiology in the museum.

DR. D. FRASER HARRIS, lecturer on physiology in the University of Birmingham, has been appointed the Thompson lecturer in natural science for 1911–12 at the United Free Church College, Aberdeen.

SIR J. CAMERON LAMB, C.B., C.M.G., has been appointed to represent the Royal Society of Arts at the forthcoming

© 1911 Nature Publishing Group