Contemporary Advances in Physics—XI
Ionization

By KARL K. DARROW

IONIZATION, in its most general sense, signifies a segregation of positive from negative charge within the volume of a substance which as a whole is (or initially was) electrically neutral. In practice a gas (for instance) is said to be *ionized* if charges of either sign can be extracted from it. Charged particles of both signs, electrons and ions, can be drawn out from a gas in which an electrical discharge is being maintained; in such a condition, therefore, a gas is ionized. Millikan's droplets, floating around in a gas which had recently been irradiated, absorbed charges of either sign out of the gas, which therefore was ionized by the radiation and remained ionized for some time afterward. A negatively-charged electrode immersed in a carefully-screened gas receives very little charge from it; this condition continues if the gas is bombarded with electrons having less than a certain speed; let the speed of the bombarding electrons be increased past this limit, and the electrode begins to receive positive charge—the gas is ionized by the electrons. Dilute electrolytic solutions are evidently in a continual and spontaneous state of ionization.

Observations on positive ions issuing from ionized gases have been interpreted as meaning that all such ions are atoms or molecules bearing charges of which the magnitude is e, or $2e$, or some other small-integer multiple of e; in other words, as meaning that positive ions are atoms or molecules from which one or more electrons have been detached. Generalizing from these to all cases, it is believed that the first stage of ionization, in monatomic gases at least, is the detachment of electrons from atoms. Whether the separated electrons remain free, or attach themselves to other atoms, or become the gathering-agents of clusters of atoms, is an interesting but at present subsidiary question. Ionization in monatomic gases begins by the detachment of electrons from atoms; and the word "ionization" in fact is frequently used to mean this process alone. In diatomic and compounded gases, the nature of the ions observed permits either of two suppositions; the initial process of ionization may be the detachment of electrons from molecules, or the splitting of molecules into fragments each consisting of one or more atoms, some of these fragments having an excess and the others a compensating deficit of electrons. Special experiments must be performed to decide between these suppositions.

While self-sustaining discharges in gases may produce a vast variety of identifiable ions, they are not suitable for revealing the process of producing these ions. By bombarding a gas with electrons of known speed, ions may be produced under very simple and intelligible conditions. It is then found that in order to detach an electron from an atom of a monatomic gas, a definite amount of energy, the *ionizing-energy* of the gas, must be transferred to the atom. The ionizing-energy is not unique; for most kinds of atoms there are several distinct quantities answering to the same definition. Nevertheless there is one particular and outstanding value which is particularly known as *the* ionizing-energy or *ionizing-potential.* It varies periodically from element to element along the Periodic Table, and is therefore ascribed to an outer electron of the atom; indeed it may be described as the *extraction-energy for the outermost or loosest electron.*

Of the other values of ionizing-energy for a given atom, some are lower than the principal ionizing-potential. These, however, are attributed to atoms in abnormal states. The others are greater than the principal ionizing-potential; some of them are very much greater and increase steadily from one element to the next along the Periodic Table, and are therefore ascribed to deeper-lying electrons and may be described as *extraction-energies for inner electrons.*

The spontaneous ionization of radioactive substances is an entirely irregular function of atomic number and is attributed, for this and other reasons, to events occurring in the nuclei.

At this point it is necessary to define some units. In most determinations of ionizing-energies, a stream of electrons originally moving with speeds thought negligibly small is accelerated by a potential-rise and then projected into the gas under examination. Their kinetic energies in ergs are thus given in terms of the *voltage* V of the potential-rise by the equation

$$\text{Kinetic Energy} = eV/300 = 1.591 \cdot 10^{-12}\ V. \qquad (1)$$

It is customary to measure the kinetic energy of an electron by the voltage-rise which gave it, or could have given it, that energy; which is tantamount to employing a unit of energy equal to $1.591.10^{-12}$ erg. This unit may be called the *equivalent volt.*

$$\textit{One equivalent volt} = 1.591 \cdot 10^{-12}\ \textit{erg} \qquad (2)$$

The name, it must be admitted, is neither short nor elegant; at all events it is preferable to the slovenly usage of speaking of an electron as having so many "volts of energy" (!) or a "speed of so many volts" (!!) On the other hand, it seems quite unobjectionable to speak of an

electron having a kinetic energy of one equivalent volt as a "one-volt electron."

The ionizing-energy of an atom is usually given in equivalent volts, whence the name *ionizing-potential.*

Occasionally one meets with a value stated for an ionizing-potential in terms of a unit known as the *wave-number* ("equivalent wave-number" would be better) which amounts to $1.968.10^{-16}$ erg.

Ionization-Potentials

The ionizing-potential of a monatomic gas is usually measured by projecting electrons with controllable kinetic energy K into the gas, and determining the value of K at which current begins to flow into an electrode inserted into the gas and maintained at such a potential that positive ions, but no electrons, can reach it.

This method requires more elaborate apparatus than the outline suggests. The experimenter must guard against an effect which was not suspected by those who first worked with the method. Electrons having kinetic energy less the ionizing-energy of the gas may cause the atoms which they strike to emit radiation. Some of this radiation falls upon the electrode arranged to collect positive ions, and expels electrons from it. The field around the collecting-electrode, being such as to draw positive ions toward it, drives these electrons away; and so there is a continuous current of negative charge out of the electrode into the gas, which is quite indistinguishable from a current of positive charge out of the gas into the electrode. Thus the value of K at which positive charge first seems to flow into the electrode from the gas is the "critical" electron-energy (as the phrase is) not for producing ionization but for producing radiation. The earliest determinations of what were thought to be ionizing-potentials were vitiated by this effect.

To avoid or recognize the influence of radiation several schemes have been devised.[1] For example, if two collecting-electrodes are used in alternation, one having a large area and the other being small, much more radiation will fall upon the larger one, and there will be a correspondingly great difference between the currents of negative charge out of the two; but if ions are being formed in the gas, the difference between the numbers of these which find their way to the large and to the small electrode will be much less pronounced. A slender collecting-electrode may record only a very small current due to radiation, but a

[1] For a detailed account of the methods developed up to 1924, consult K. T. Compton and F. L. Mohler: "Critical potentials" (*Bull. Nat. Res. Council,* No. 48).

very large one whenever ionization commences. This scheme has been adopted by K. T. Compton.

Another, and the most common, device for distinguishing ionization from radiation consists in surrounding the collector with a sheath of metal gauze, maintained at a potential slightly (say 3 volts) more negative than the electrode which it screens. Positive ions pass through its meshes to the collector, somewhat slowed down but not driven back. Radiation also passes through the meshes to the collector, but the electrons which it drives out are turned back by the adverse field and reenter the metal whence they came, so that the net result is the same as though they had never come out. Ionization thus produces a current of positive charge into the collector, and radiation none; or radiation may even produce a current of negative charge into the collector, thus accentuating the contrast, for electrons which are ejected from the metal gauze are drawn to the screened electrode. This is the scheme devised by F. S. Goucher.

Another, and possibly the best, method for measuring ionizing-potentials is quite insensitive to radiation. A hot filament is immersed in the gas, which may be supposed to be surrounded by connected metal walls so that its boundaries are all at the same potential. If the efflux of electrons from the filament is so plentiful that it is limited by space-charge,[2] and this condition persists as the potential-difference between walls and filament is raised to the value just sufficing to give to the electrons energy enough to ionize the gas, then at the moment of incipient ionization the space-charge limitation is partially or totally cancelled, and the current increases sharply. This is I. Langmuir's method. It is better to keep the potential-difference between the walls and the filament small and constant, and admit into the gas electrons with controllable energy from another source; when the energy of these auxiliary electrons is raised to attain the ionizing-potential of the gas, the current from the filament suddenly increases. This is the method of G. Hertz[3] and K. H. Kingdon.[4]

Most of the accurate measurements of ionizing-potentials have been made with a collecting-electrode sheathed by a gauze, according to the precept of Goucher. The apparatus is a complicated affair, for the parts already mentioned are by no means all that are required; in some cases the whole interior of the tube appears to be webbed with gauzes. A hot filament (occasionally an illuminated metal plate) is provided as source for electrons, and its potential—or the potential of

[2] See the sixth article of this series (December, 1924).

[3] *ZS. f. Phys.* 18, pp. 307–316 (1923).

[4] *Phys. Rev.* (2) 21, pp. 404–418 (1923).

its negative end—is taken as the zero from which the other potentials are measured. In the sketch (Fig. 1) this is marked F. Close to the source there is a gauze (G_1) maintained at the controllable potential V and thus providing the potential-rise by which the electrons are accelerated. It is clearly desirable that the electrons should move at their

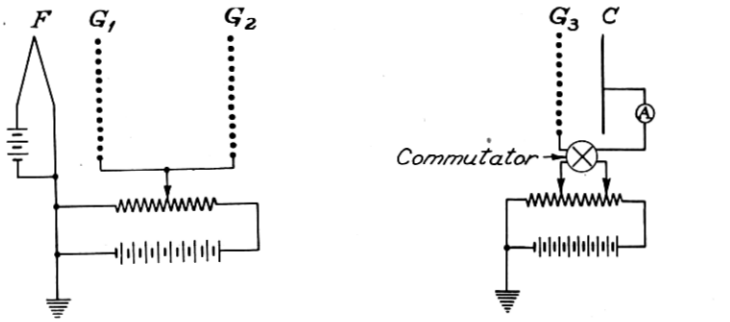

Fig. 1

known maximum speed over as long a path as possible in the gas; consequently a second gauze (G_2) is set up beyond G_1, and maintained at nearly the potential V so that there is a nearly equipotential region between them. (Generally the potential of G_2 is raised a fraction of a volt above V so that there may be a slight impulsion of the ions formed between G_1 and G_2 toward the collector.) Beyond G_2 are the collector C and its protecting gauze G_3, maintained at potentials lower than the filament so that no electrons may reach them. The current of which the sign indicates whether it is due to radiation or ionization, as was explained above, flows through the galvanometer at A.

With such an apparatus as this it seems to be easy enough to measure ionizing-potentials correctly within one or two volts. As soon as greater accuracy is sought after, the real troubles begin. The electrons do not all leave the source with negligible speed; their speeds are distributed over a finite range. The potential to which they climb in passing through the meshes of a gauze is not quite equal to the potential of the gauze-wires themselves. The potential-differences between the different electrodes are not accurately given by voltmeters, for there are contact-potential-differences superposed upon the values indicated. The filament is not an equipotential surface if it is heated by a current, although this difficulty can be overcome if the experimenter thinks it worth the trouble. Electric charges marooned upon the walls of the tube, electrons ejected by radiation from the gauze G_3 and accelerated backwards to G_2 with a final speed higher than the electrons from F

ever attain, are capable of causing false conclusions. The third significant figure in the value of an ionizing-potential is many times harder to attain than the first two; and it is not surprising that many experimenters have chosen to mix some standard gas such as helium into the gases with which they experimented, and to determine the difference between the ionizing-potentials of the standard gas and the other gases, rather than any of them absolutely.

Before bringing out the numerical values of ionizing-potentials, I must allude to the fact that the quantity measured in these experiments is the kinetic energy possessed by the electrons when they are just able to ionize the atoms, which might not be the same thing as the energy actually transferred to the atoms. A particle of mass m moving with speed u has not only kinetic energy $K = \frac{1}{2}mu^2$ but also momentum mu. If it impinges against a previously-stationary particle of mass M, and momentum is conserved in the impact, then the particles must be in motion after the impact, and some of the initial kinetic energy of the striking particle must be saved, so to speak, to provide for this motion. What is left over is available for ionization or other purposes. Without involving ourselves in the general case, we may note that the most favourable conceivable case for having a large proportion of energy left over, when the striking particle is less massive than the struck one, is that in which the more massive particle has all the momentum after the impact. Suppose therefore that after the impact the striking electron and the liberated electron are both stationary, and the ion of mass M is moving with speed V. Conservation of momentum is expressed by writing:

$$mu = MV. \tag{3}$$

The energy T available for ionization or other purposes is given by:

$$K = \tfrac{1}{2}mu^2 = \tfrac{1}{2}MV^2 + T. \tag{4}$$

so that

$$T = K(1 - m/M). \tag{5}$$

Since the masses of atoms range from 1845 to nearly half a million times the mass of an electron, an electron might spend over 999 promille of its energy in ionizing an atom; and therefore there is no essential impossibility in supposing that the energy possessed by an electron just able to ionize is actually equal, within the uncertainty of measurement, to the ionizing-energy of the atom. This supposition is confirmed by the agreements between observed ionizing-potentials and the theoretical values deduced from spectra by using Bohr's method of interpretation.

If the gas or the electron-stream is extremely dense, positive ions appear when the energy of the bombarding electrons is lower than the ionizing-energy as determined by experiments with more rarefied gas or a scantier stream of electrons. Various reasons are assigned for this in various cases; one fundamental reason is, that an atom struck by an electron having less than the ionizing-energy may be put into abnormal states of some duration, in which it can be ionized by receiving a smaller amount of energy than would ionize it in its normal state.

In Fig. 2 the measured values of ionizing-potential are plotted.[5]

There is a way of expressing these and other yet-to-be-presented facts about ionizing-energies, which at this point will probably seem

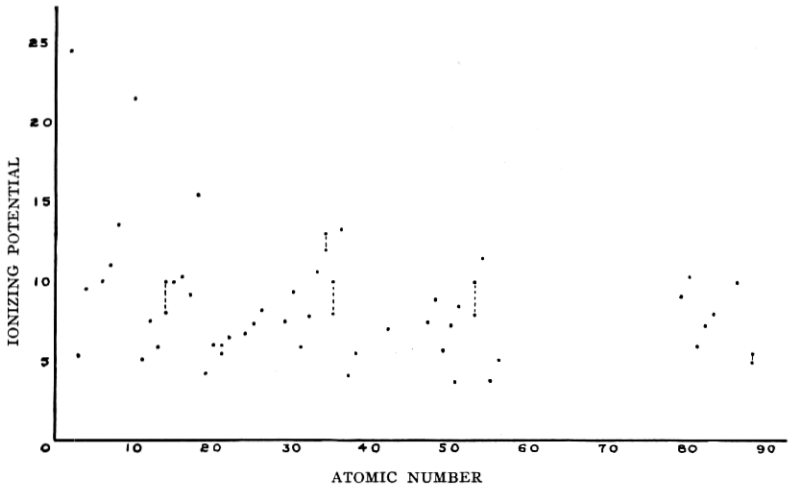

Fig. 2

unnatural but later will be highly convenient. Suppose that by transfer of the ionizing-energy V_0 to an atom it is converted into a system composed of an ion bearing charge $+ e$ and a free electron. This system has potential energy V_0 relatively to the normal state of the atom. The detached electron may wander off and the ion eventually unite itself with another electron. It is convenient, therefore (whether or not it is strictly legitimate) to think of this potential energy V_0 as being associated with the ion alone; and to say that the atom possesses, in addition to its normal state, one or more *states of ionization* or *states of the ionized atom*, each of them characterized by a certain value of po-

[5] I am deeply indebted to Professor F. A. Saunders, who has kept a current catalogue of published values of ionizing-potentials, for enabling me to copy his tabulations.

tential energy. The ionizing-potential of the atom is then, by definition, equal to the potential energy of that state of ionization which differs least in energy from the normal state.

Another way of describing the ionizing-potential is to say that it is the *energy required to detach the loosest electron from the atom.* This involves a picture of an atom as a system of separately-identifiable electrons, "bound" with various degrees of looseness or tightness. Such a picture is so nearly indispensable, that there need be little hesitation about introducing it here. Frequently the term *valence-electron* is used instead of "loosest electron"; there is little in its favour beyond the general inability of physicists to think of a better one.[6]

Detachment of the Loosest Electron by Other Agencies than Electron-Impacts

Other agencies than the blows of electrons are capable of detaching the loosest electron from an atom; but it is very much more difficult to obtain simple and intelligible information about their immediate effects than about those of electron-impacts.

The study of *ionization by radiation* involves a host of new problems. Theoretically the conditions seem simple enough. Radiation of any frequency ν behaves in some respects as though it consisted of streams of particles each having energy $h\nu$ and momentum $h\nu/c$. Since it behaves in this manner in so far as absorption in gases and ejection of electrons from solids are concerned, we should expect it to do likewise in effecting ionization of atoms. If so, radiation should ionize atoms if and only if its frequency ν equals or exceeds a critical or threshold value ν_0, expressed in terms of the ionizing-potentials V_0 of the atoms (measured in equivalent volts) by

$$h\nu_0 = eV_0/300. \tag{6}$$

Projecting light from a spectrum upon a gas, and passing steadily from low to high values of ν, we should expect ionization to commence abruptly at ν_0.

Experimentally, the task of testing this inference has baffled everyone, at least until very recently. In the first place, the values of threshold-frequency ν_0 for various atoms correspond to values of threshold-

[6] The terms "optical electrons" and "series electrons" are sometimes seen; they are derived from theoretical pictures which are in danger of mutation (some people now ascribe most series-spectra to displacements of electrons in groups). The German term "Leuchtelektron" probably sounds better in German than its equivalent "shining electron" would sound in English. It may be remembered that difficulty in choosing a good name for a concept sometimes signifies that the concept is essentially vague and not rooted in Nature.

length λ_0 lying between 504A (helium) and 3184A (caesium); and this is the most troublesome region of the spectrum to deal with, partly because light of wavelengths lying within it is tremendously absorbed by nearly all solids and even gases, and partly because good sources for such light are difficult or impossible to procure. Even in the comparatively accessible zone between 2000A and 3500A it is customary to use the light of the mercury arc, which provides a few widely-spaced bright spectrum-lines; as though in determining ionizing-potentials by electron-impacts one had to use electrons of certain distinct and widely-spaced energy-values, and could not refine the measurements by adjusting the accelerating voltage to intermediate values *ad libitum*. In measuring ionizing-potentials by electron-impacts there is a secondary difficulty due to radiation from struck atoms falling upon the collector; here the difficulty becomes a primary one, since the primary radiation itself is competent to produce this effect. The effect is most vicious with alkali-metal vapours, as they deposit themselves over all the solid surfaces of the apparatus in films excessively liable to pour out electrons when stimulated by light or warmth; yet these are the only elements for which λ_0 lies above 2500A.

Several experimenters have minimized the undesired effects of the radiation by projecting a narrow beam of light across a jet of alkali-metal vapor boiling up out of a narrow channel in the main tube. The beam struck nothing except the jet and beyond it a "trap" in which presumably it was totally absorbed and no part was scattered. The jet passed onward, near to an electrode negatively charged to receive positive ions. With potassium vapors, for which λ_0 should be 2856A, R. C. Williamson found ionization commencing somewhere between 3100A and 2800A; H. Samuel thought that it commences between 2804A and 2893A; E. Lawrence concluded that it begins at 2610A.[7] P. D. Foote and F. L. Mohler[8] detected the positive ions by their effect in annulling the space-charge limitations upon the current from a hot filament, after the fashion of the last-mentioned method of determining ionization-potentials. Their result was somewhat unexpected; they found ionization in caesium vapor at wavelengths even greater than the threshold-wavelength. This is attributed to the same cause as brings about a lowering of the apparent ionizing-potential when dense

[7] *Phys. Rev.* (2) 27, pp. 37–51 (1926); 26, pp. 197–207 (1925).

[8] E. O. Lawrence, *Phil. Mag.* 50, pp. 345–359 (1925); R. C. Williamson, *Phys. Rev.* 21, pp. 107 (1923); H. Samuel, *ZS. f. Phys.* 29, pp. 209–213 (1924); and prior literature cited in the first two. In all of the cited experiments the vapor had freshly issued from condensed potassium, and may have contained a large proportion of molecular aggregates, to which Lawrence attributes the difference between his observed threshold-wavelength and the calculated ν_0. Cf. also G. F. Rouse and G. W. Giddings, *Proc. Nat. Acad. Sci.* 11, pp. 514–177 (1925).

streams of bombarding electrons are used: that is to say, it occurs because light of less than the threshold frequency puts some of the atoms into abnormal states, in which less energy is required to ionize them than in the normal state.

The study of *ionization by positive ions* is also very troublesome. This is partly because there are no such convenient sources for controllable positive ions as there are for electrons. The ions emerging from hot filaments are generally not all of one kind. If ions of a particular sort, hydrogen ions for instance (these would give the most valuable information of any) are produced by bombarding the proper kind of gas by electrons having a suitable ionizing-energy, they cannot be used for ionizing except in the same tube and therefore upon the same gas; further, it is necessary to keep the bombarding electrons out of the region where the positive ions are meant to ionize, by an elaborate system of gauzes and opposing potentials. If the collecting electrode is maintained at a positive potential so as to receive electrons produced by the ionization, it receives also the electrons which are knocked out of the walls of the tube by positive ions which strike them. It is scarcely surprising, then, that the published data are scanty and not always concordant.[9]

The considerations about conservation of momentum during impacts, mentioned in dealing with ionization by electrons, show that we should hardly expect a positive ion to be able to ionize unless it has much more energy than must be transferred to the atom to detach the loosest electron from it; twice as much, if the ion is of the same mass as the atom.

Identification of Ions Produced by Electron-Impacts

The methods hitherto described for detecting the onset of ionization in a gas show when free positive charges appear in a gas, but give no further information about them. The methods employed by J. J. Thomson and F. W. Aston reveal the charge-to-mass ratios of ions occurring in a gas carrying a self-maintaining discharge, but give very little information about the precise conditions necessary to produce them. A combination of methods of these two kinds was first effected by H. D. Smyth.[10]

One of the tubes employed by Smyth is sketched in Fig. 3. Electrons from the filament F are accelerated through the potential-rise V_1 to the

[9] For work published up to 1922 see the review and bibliography by A. J. Saxton, *Phil. Mag.* 44, pp. 809–823 (1922). See also J. T. Tate, *Phys. Rev.* (2) 23, pp. 293–294 (1924).

[10] *Proc. Roy. Soc.* A102, pp. 283–293 (1922–23); A104, pp. 121–134 (1923); *Phys. Rev.* (2) 25, pp. 452–468 (1925) and references there given.

gauze E_1, and then turned back by an adverse potential-fall V_2 before they reach the partition E_2 pierced by the slit S_2. Positive ions produced by the electrons in the region between E_1 and E_2 are drawn

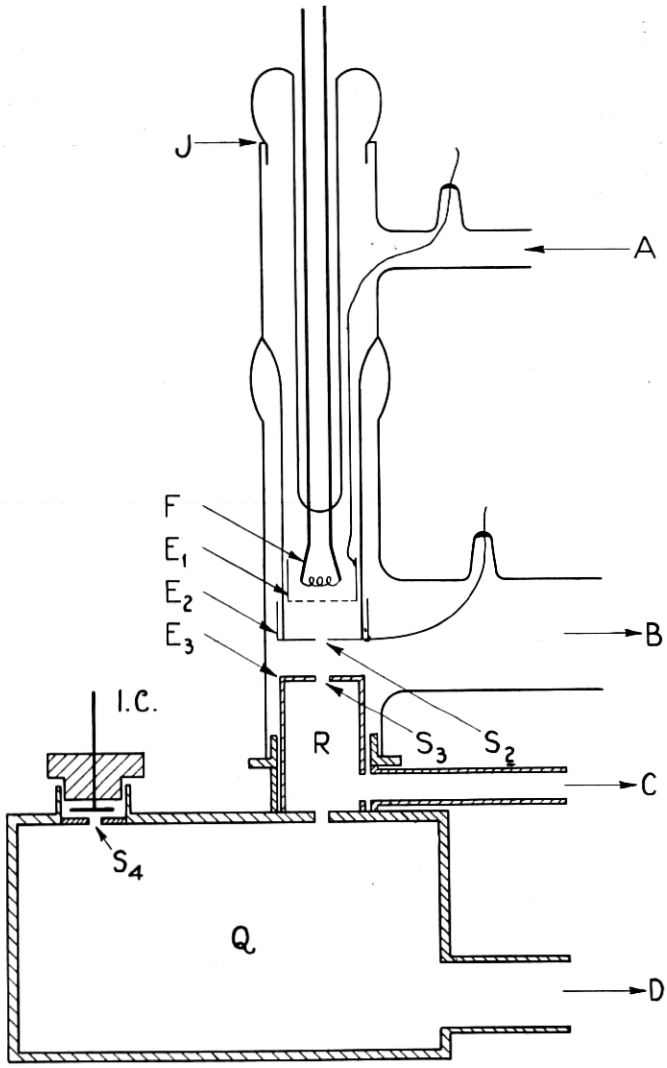

Fig. 3

toward E_2; some of them emerge through S_2, and encounter an additional potential-fall V_3 which draws them to the partition E_3. Those which pass through the slit S_3 are now ready, after passing through the

field-free region R, to be swung around in semi-circular arcs by a magnetic field H applied normally to the plane of the paper over the region Q; thus they arrive at the ion-collector behind the slit S_4. The major experimental difficulty consists in maintaining simultaneously a gas-density between F and E_2 high enough to afford plenty of ions, and a gas-density in R and Q low enough so that the ion-stream is not dispersed. This is effected by feeding in the gas through A and applying powerful pumps to draw it out through B, C and D.

Varying H and plotting against it the current into the ion-collector, one obtains a curve with peaks, such as the one in Fig. 4. This is, how-

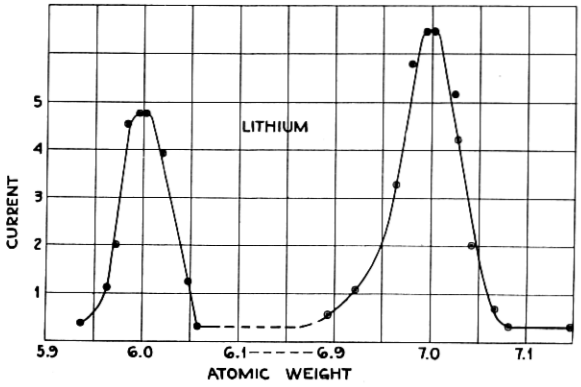

Fig. 4

ever, a curve obtained by Dempster with ions issuing from a hot filament. The charge-to-mass ratio for the kind of ion producing each peak is calculated from the accelerating-voltages, the deflecting field, and the diameter of the circular arc through which they swing.

The use of this method in determining ionizing-potentials may be illustrated from the work of H. A. Barton on argon.[11] Observing at values of V_1 superior to some 50 volts a two-peaked curve with the M/E values of the corresponding ions standing in the ratio 2:1; and observing at values of V_1 inferior to some 40 volts only one of these peaks, the one with the greater value of M/E; he inferred that this peak was due to A^+ ions and the other to A^{++} ions. Plotting the heights of these peaks or the areas under them as functions of V_1 he obtained curves such as those shown in Fig. 5. From many such curves as these he deduced that the energy of electrons just able to produce doubly-ionized argon atoms exceeds that of electrons just able to produce

[11] *Phys. Rev.* (2) 25, pp. 469–483 (1925).

singly-ionized argon atoms by 30 equivalent volts.[12] In the same manner, Smyth concluded that the energy of electrons just able to produce doubly-charged mercury ions exceeds by about 9 equivalent volts that of electrons just able to produce singly-charged mercury ions. The method, however, has been used chiefly for studying diatomic gases, and therefore will be mentioned in another section.

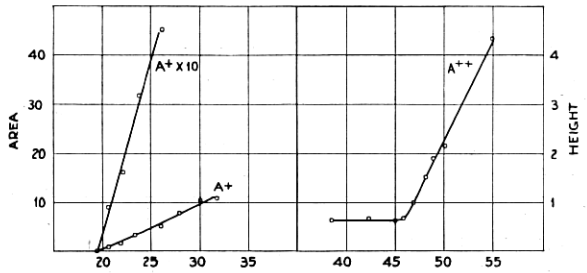

Fig. 5

Ionization of Molecular Gases [13]

The experiments of Thomson and Aston upon the ions proceeding from self-sustaining discharges in molecular gases show that these comprise individual atoms and also molecules of various sorts, each deprived of one or occasionally of more than one electron. Not all of these, however, are produced by the direct and simple agency of a single electron-impact against a normal molecule; some of them result from encounters of ions originally produced in the discharge with molecules which they meet in the gas, either in that region where the discharge is being maintained or in the channel through which they pass to reach the analyzing fields. This stands out very clearly in such experiments as one performed by A. J. Dempster, who projected 800-volt electrons into hydrogen gas and determined the relative abundance of the ions H^+, H_2^+ and H_3^+ arriving at his collecting-electrode after passing through a certain distance in the gas. At a gas-pressure amounting to .01 mm. Hg, the H_3^+ ion was the most plentiful of all and the other two not far behind; at .0017 mm. Hg both the H^+ and H_3^+ ions were definitely less abundant than H_2^+, and below .0005 mm. the H_2^+ ion

[12] Actually he obtained 17.3 volts for the one critical potential, 47.4 for the other, and assumed that the difference between 17.3 and the accepted value of 15.2 for the first ionizing-potential of argon is due to contact potentials and other influences affecting each of the observed critical potentials equally.

[13] For a general bibliography of this subject see T. R. Hogness & E. G. Lunn, *Phys. Rev.* (2) 26, pp. 44–55, 786–793 (1925); also V. Kondratjeff, *ZS. f. Phys.* 22, pp. 1–8 (1924) and 31, pp. 535–541 (1925).

was left almost alone upon the scene. These results signify that an 800-volt electron operates ionization in hydrogen by detaching an electron from a molecule; other kinds of ions appearing in the gas are due to subsequent adventures of these ions.

The method of H. D. Smyth is suitable for investigations into this question. In apparatus such as his, hydrogen bombarded by (say) 40-volt electrons is found to contain all three ions H^+, H_2^+ and H_3^+; but as the density of hydrogen is reduced, the first and the last of these ions become less abundant and finally insignificant by comparison with the ion H_2^+. As the bombarding-voltage is reduced towards the value (about 16) at which ionization commences, all three kinds of ions become less plentiful; but with high densities and sufficiently sensitive apparatus it is found that H_3^+ makes its appearance as early as H_2^+, and there is no reason not to suppose the same about H^+. In hydrogen, therefore, and also in nitrogen, it is agreed that an electron-impact against a molecule results, if in any sort of ionization at all, in the detachment of an electron from the molecule, not (for instance) in a dissociation into one ionized atom and another atom ionized or neutral. Dissociation and new sorts of association may result from the further adventures of this molecule-ion in the gas. In certain compound gases[14] of which the molecules consist of two or more atoms of different kinds, there is reason to expect the contrary: that is, that an electron-impact against a molecule would result directly in splitting it into a positively-charged atom (or group of atoms) and a negatively-charged atom (or group of atoms). Certain experiments indicate this: in $ZnCl_2$ vapor, for instance, Cl atoms bearing an extra electron and ZnCl molecules minus an electron are found as soon as ionization commences; but the question can hardly be deemed settled until comparative measurements are made at various gas-densities.

From these experiments it follows that a measurement of the energy just sufficient to produce ions in a molecular gas, while interesting in itself, can hardly be interpreted without additional data regarding the nature of the ions produced. There are other difficulties in determining ionizing-potentials in such gases; for instance the likelihood that the hot filament will itself dissociate the gas. The published determinations are frequently contradictory; the various published values for the ionizing-potentials of hydrogen, for instance, form one of the most discouraging sets of irreconcilable data to be found in physics.

According to thermochemical measurements the "heat of dissociation" of hydrogen, in other words the energy-difference between a system of two free H atoms and an H_2 molecule, amounts to 3.5 equivalent

[14] Those designated by chemists as heteropolar.

volts. One would expect to be able to dissociate hydrogen by bombarding the gas with 3.5 volt electrons; yet nothing of the sort happens. This is an instance of the frequently-occurring observation that a particle or a quantum may have abundant energy to produce a particular effect and yet be quite unable to produce it. One would expect also that the minimum energy required to convert an H_2 molecule into an H^+ ion and an H atom and a free electron would exceed by 3.5 equivalent volts the ionizing-energy of an H atom, yet the difference appears to be less, which is strange.

Detachment of Tightly-bound Electrons from Atoms

We will now consider the most direct and striking evidence for the statement that each atom (apart from those of the lightest elements) possesses several distinct ionizing energies—several distinct "states of ionization." This fact is taken to mean that each atom possesses several or many electrons which are *bound*, as the phrase is, with different degrees of firmness or tightness; that the ionizing-energies of the atom are, so to speak, the *extraction-energies* of these various electrons; to each electron there corresponds a certain extraction-energy, the amount of energy which must be imparted to the atom to extract that electron, the energy-difference between the normal state of the atom and that particular "state of ionization" which involves the absence of that particular electron. I shall frequently use the language of this interpretation, which is extremely convenient and likely to remain so. Nevertheless it is desirable to remember that the quantities actually observed are energy-differences between various states of the atom, or energy-values of various states of the atom referred to the energy-value of the normal state as zero. These energy-values are the data of experience; most other assertions about the states of ionization are speculative.[15]

Conceive a layer of atoms of an element possessing several different values of ionizing-energy W_1, W_2, W_3 and so forth; in other words, atoms which are capable of several states of ionization of which the energy-values exceed that of the normal state by W_1, W_2, W_3 and so forth. Suppose that a beam of radiation of frequency ν, so chosen that the product $h\nu$ exceeds all of the ionizing-energies, falls upon the layer. Such a beam is absorbed as though it consisted of individual particles of energy $h\nu$, each of which is either completely absorbed or totally ignored by the layer of matter upon which it falls. Consider an atom which ab-

[15] In some cases, although not in any which will be discussed in this section, it is found necessary to suppose that several distinct states of ionization correspond to the absence of a particular electron, which is somewhat of a strain upon the picture.

sorbs the amount $h\nu$ of energy from the beam. Through this absorption, an electron is detached from the atom. If however the electrons were merely separated from the atom and left stationary beside it, the energy of the system (ion plus electron) would by definition have been augmented merely by W_i. This quantity is (by our supposition) less than $h\nu$. However the entire energy $h\nu$ has been absorbed; the difference $(h\nu - W_i)$ is likewise transferred to the ion-plus-electron system, in the form of kinetic energy of the liberated electron. The electron flies away with speed V_i determined by the relation

$$\tfrac{1}{2}m V_i^2 = h\nu - W_i. \tag{7}$$

The foregoing paragraph contains several interlocking assumptions, which if they are all true lead to this conclusion: *When a beam of radiation of frequency ν falls upon a layer of atoms having ionizing-energies W_1, W_2, . . . W_i . . . , electrons of various speeds spring out of the layer,*

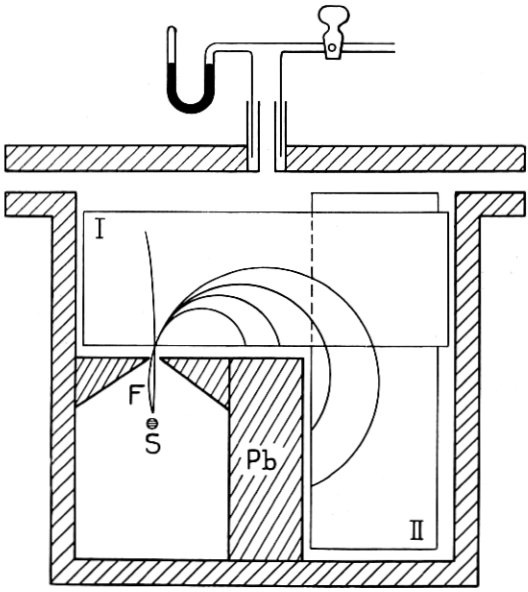

Fig. 6

there being for each value of W, a corresponding group of electrons of which the speed is given in terms of W by equation (7).

Suppose that one irradiates a metal with high-frequency radiation, and by a system of slits confines his experimentation to electrons projected in directions nearly normal to the metal surface, and applies a

magnetic field in a direction parallel to the surface. Then we have the situation which occurs in measuring the speeds and charge-to-mass ratios of electrons and ions by the method of electric acceleration followed by magnetic deflection. The only differences are, that in the present case the speeds v with which the electrons enter into the magnetic field are imparted to them not by an imposed electric field but by

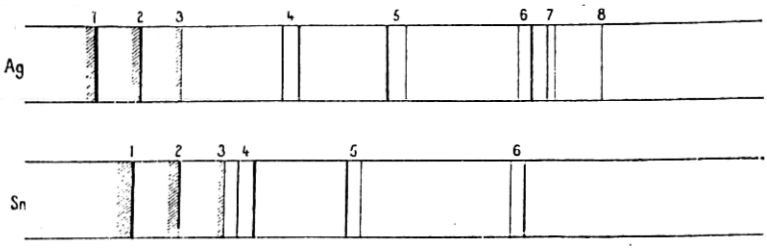

Fig. 7

the radiation which released them; and that the experimenter takes the value of e/m for granted and computes the values of v from the magnetic deflections alone. The electrons are swept around in circular arcs, of which the radii yield their speeds.

The apparatus by which such experiments are performed is of the type shown in Fig. 6. At S there is a long narrow rod or tube of the

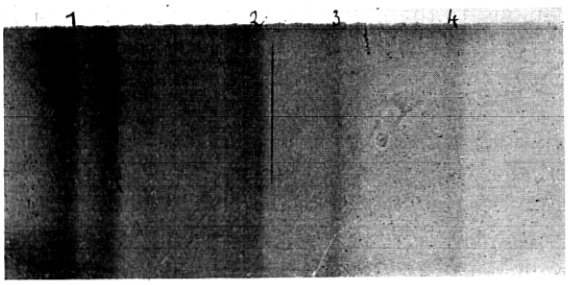

Fig. 8

material to be tested; it is irradiated by X-rays proceeding from a source beyond the diagram to the left. A magnetic field, directed normally to the plane of the paper, sweeps the emerging electrons around in circular arcs, some of which pass through the slit. The appearance of films laid along the top of the block Pb, normal to the plane of the paper, is shown by Figs. 8 and 9. They suggest spectra; and though the lines are signatures of special electron-speeds rather than of special

radiation-frequencies, the difference between these is not so radical as once it seemed, and we may without hesitation call them by some such name as *electronic spectra*.

Each line in such a spectrum is produced by electrons of a definite extraction-energy, extracted by radiation of a definite frequency. Continuing with the policy of referring to electrons with a definite extraction-energy as being definitely individualized within the atom, I will designate the electrons of greatest extraction-energy for any particular kind of atom as the K electrons; those of next greatest extraction-energy as the L electrons, and then the M and N electrons in due order. (Later it will be necessary to subdivide these classes, but for the moment this may be avoided.) At other times I shall speak of these elec-

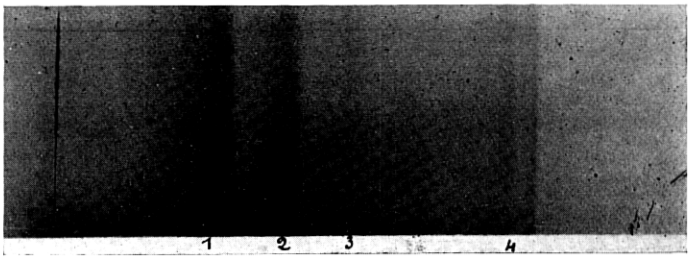

Fig. 9

trons as belonging to the K level, the L level, and so forth; still other terms in use are the K shell and the L shell, or the K ring and the L ring. In a given electronic spectrum we may expect to find a set of lines due to K, L, M and other electrons, for each frequency represented in the incident radiation; unless there are some of these frequencies for which the quantum energy $h\nu$ is less than the extraction-energies of some of the electron-groups, in which case there will be no corresponding lines.

An ideally simple electronic spectrum would be produced by a single radiation-frequency; but this is impracticable, for even if one were to eliminate from the stream of X-rays proceeding out of an X-ray tube all but one frequency, the irradiated atoms would themselves supply others.[16] As in the mass-spectra upon Aston's plates, this unavoidable complexity is actually an advantage; it helps in identifying the several lines.

In Figs. 8 and 9, photographs taken in the manner already mentioned, there appears the electronic spectrum due to silver atoms irra-

[16] These are in fact especially efficient in ejecting electrons, as they originate within the atom-layer itself.

diated by the characteristic X-rays of tungsten.[17] To guard against the possibility that the photographs may lose in clearness by the process of reproduction, I will base the explanation upon the uppermost of the sketches in Fig. 7, which is abstracted by de Broglie from similar pictures. The electron-speeds corresponding to the lines increase from left to right. The irradiating X-rays consist of four characteristic frequencies from the X-ray spectrum of tungsten; in order of decreasing frequency they are known as $K\gamma$, $K\beta$, and the two members of the $K\alpha$ doublet. The four lines marked 4 and 5 in the electronic spectrum are made by electrons extracted by these four radiations from a single level —the K level of the silver atoms. The two following doublets, marked 6 and 7, are made by electrons extracted by the $K\alpha$ frequencies from two other levels of the silver atom, the L and M levels respectively. Line 8 is due to $K\beta$ extracting electrons from the L level. At the other end of the spectrum, the three lines 1, 2, 3 are due to electrons ejected from the L and the M levels by two of the X-ray frequencies characteristic of silver, which the irradiating X-rays stimulate some of the silver atoms to emit. The rays responsible for these particular lines are the so-called $K\alpha$ and $K\beta$ rays of silver, which are so related to one another (as will be stressed in a later passage) that the electrons extracted by the former from the M level have very nearly the same energy as the electrons extracted by the latter from the L level, so that the two frequencies acting on the two groups of electrons produce three (instead of four) distinct lines of the electronic spectrum.

Reverting now to the photographs: in Fig. 8 the pairs of lines marked 4, 3, and 2 are those designated respectively as 6, 5 and 4 in the sketch and in the foregoing explanation, while the lines to the left are those produced by characteristic X-rays of silver acting upon silver atoms. On a larger scale, this latter region of the spectrum is shown in Fig. 9; here the lines are marked by the same numerals as in the sketch; the pair at 4 is due to K-electrons extracted by the two $K\alpha$ rays of tungsten, the line 3 is due to M-electrons extracted by the $K\beta$ radiation of silver, the line 2 results jointly from L-electrons extracted by the $K\beta$ radiation of silver and M-electrons expelled by the $K\alpha$-radiation of silver, while the line 1 is due to L-electrons ejected by the $K\alpha$-rays of silver.

The resemblance and the differences between electronic spectra of elements not far apart in the Procession are illustrated by the two sketches in Fig. 7, the lower relating to tin (atomic number 50) and the upper to silver (atomic number 47) irradiated by the same frequencies.

[17] I am greatly indebted to M. de Broglie for sending me the negatives of these admirable pictures, as well as that of Fig. 10.

Since the extraction-energy of each named class of electrons increases along the periodic table, the lines designated as 4, 5 and 6 in the electronic spectrum of silver reappear in that of tin, displaced in the direction of diminishing electron-speeds, that is, to the left. But, as to the lines 1, 2, and 3, both the extraction-energies of the electrons and the frequencies of the rays responsible for these alter as one passes from silver to tin, and the net result of the double alteration is that the lines are displaced to the right.

The energy-values of the various states of ionization of an atom—or, in terms of the customary picture, the extraction-energies of the various classes of electrons within the atom,—may be determined with a certain degree of precision from experiments such as these. However, as in the case of the measurement of charge-to-mass ratios for individual ions by the methods of Aston and Dempster, there is little incentive to develop the accuracy of the method to the highest possible extent; for most of the energy-values in question can be determined with very great accuracy in another way, which we will now examine.

Absorption of Radiation Through Ionization

When a beam of radiation of frequency ν is transmitted through a layer of matter, from the atoms of which it extracts electrons with an expenditure of energy $h\nu$ at each extraction, we should expect to find it correspondingly reduced in intensity when it emerges from the layer.

This effect is strikingly conspicuous with radiation high enough in frequency to detach the tightly-bound electrons of massive atoms. Let a narrow beam of "heterogeneous" radiation, containing all frequencies throughout the widest possible range, fall from an X-ray tube through slits and diaphragms upon a thin layer of such atoms; let the transmitted rays be dispersed by some appropriate spectroscope, and fall finally upon a photographic plate on which their spectrum—in the ordinary sense of the word, not in the sense of "electronic spectrum"—is outspread.

In Fig. 10 there are three such spectra, of heterogeneous beams which have passed through layers of cadmium, antimony, and barium respectively. The frequency increases from right to left. The darkening at any point is a measure of the intensity with which the X-rays acted at that point.

Below a certain frequency identical for all three elements, the photographic films have evidently been little affected; as soon as this critical frequency is exceeded, the effect suddenly becomes enormous. This critical frequency is the one for which the quantum-energy just

suffices to extract a K-electron from a silver atom; for the photographic film contains silver, and it is the expulsion of electrons from the atoms in it which initiates the photographic process. Proceeding always toward higher frequencies, we see that presently the plates suddenly become whiter, at another critical frequency which however

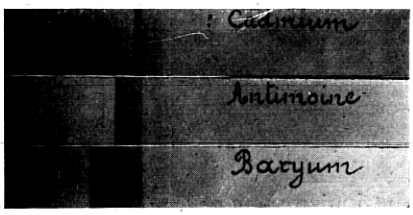

Fig. 10

is not the same for the three elements. The photographic film is not responsible for these "absorption-edges" as they are called; each of them occurs at the particular frequency for which the quantum-energy just suffices to extract a K-electron from an atom of the element which formed the absorbing-layer placed in the path of the beam before it reached the plate. To the right of the absorption-edge we have the lower frequencies, unimpeded by the cadmium (or antimony, or barium) atoms because unable to ionize them; to the left we have the higher frequencies, reduced in intensity by the intercalated matter because some of their energy was drawn off to detach electrons.

From the frequency ν at such an absorption-edge, the extraction-energy W of the class of electrons in question for the kind of atom in question is determined by the equation

$$h\nu = W.$$

This is a much more delicate way of measuring extraction-energies than the observations upon electronic spectra afford. Nevertheless the measurements upon the energies of the ejected electrons are of the greatest importance, for they show what is effected by the energy-transformations which set in when one or another of these critical frequencies is overpassed.

Likelihood of Ionization by Electrons Having More Than the Least Ionizing-Energy

We have seen that electrons projected into a gas of ionizing-energy V_0 are able to ionize it if their kinetic energy exceeds V_0, otherwise not (apart from ionizations effected upon atoms in abnormal states). This

question now suggests itself: Suppose that a great number Q of electrons, all having kinetic energy V, falls upon a thin stratum of gas containing dN atoms per unit area: how many atoms will they ionize, how many ions will be produced? Designating this number by $Qf(V)dN$: what is $f(V)$?

This question is much easier to formulate in words than to answer by experiment. Suppose for instance that one should try to answer it by means of the scheme of apparatus sketched in Fig. 1. In going from G_1 to G_2, coming to a stop between G_2 and G_3, and returning again, the electrons pass successively through all values of kinetic energy from their highest down to zero and back to their highest again; and ions are produced by electrons of all values of kinetic energy, from their highest down to the ionizing-energy. The ions collected by the collector at C represent a sort of integral of $Qf(V)dN$ taken between V_o as minimum and the energy possessed by the electrons at G_1 as maximum. To determine $Qf(V)dN$ it is necessary to measure the total ionization at several values of V and then construct a sort of differential curve. To determine Q it is necessary to know how many electrons come from the filament into the ionizing-region, and in addition how many extra ones are introduced through primary electrons knocking them out of the gauze of G_1.

Another scheme consists essentially in making G_2 into a solid wall and using it to collect the electrons, so that after passing from G_1 to G_2 they vanish from the scene. This would be excellent if the region between G_1 and G_2 could be left equipotential; but it is necessary to intrude a negatively-charged electrode in order to collect the positive ions, and apparently whenever this electrode is sufficiently large and sufficiently negative to capture the ions it is also sufficiently large and sufficiently negative to distort the field between G_1 and G_2 quite seriously; so that the electrons are at first slowed down and later speeded up again as they pass from G_1 to G_2, and the ions received by the collector are as before a sort of integral of $Qf(V)dN$.

In spite of these difficulties the various experiments performed with extremely rarefied gases yield fairly concordant results.[18] The function $f(V)$ mounts steadily, from zero at the ionizing-energy V_o, to a broad and flattish peak culminating somewhere between 100 and 400 volts (depending on the gas), and thereafter declines slowly as V increases. Thus, although an electron striking an atom (or molecule) can detach the loosest electron if it has just the requisite energy, its chance of doing so is improved if its energy is greater than the just-sufficient

[18] K. T. Compton and C. C. van Voorhis, *Phys. Rev.* (2) 26, pp. 436–453 (1925) and literature there cited; also W. P. Jesse, ibid. pp. 208–220.

amount. However, it would not be safe to infer that throughout the range of these observations all of the ionizations consist in detachments of valence-electrons from various atoms. Sooner or later transfers of atoms into other states of ionization must commence. This is rendered all the more probable by the fact that the values of $f(V)$, determined at or near the peak for each gas, show a very definite tendency to increase steadily with the number of electrons in the atom or the molecule in question.

If a stream of electrons is projected into a sufficiently dense gas, the electrons are gradually slowed down and even stopped, and the stream is dispersed. Measurements of the number of ions produced per electron per millimetre have been made under such conditions,and measurements also of the "total ionization" produced in a volume of gas so large that the electrons lose their forward speed altogether before reaching the walls; but though the intrinsic interest of such measurements is great, it seems practically impossible to deduce $f(V)$ from them.[19] The difficulties may be compared with those arising in the study of alpha-particle scattering when the metal foil is too thick.[20] When, however, the electrons are moving with the enormous speeds possessed by those ejected from radio-active substances, or when ionization by alpha-particles is studied, the conditions again become simpler and relatively intelligible.

Ionization by Alpha-Particles and Very Fast Electrons

Ionization by particles possessing kinetic energies amounting to millions of equivalent volts, such as alpha-particles and many of the electrons emerging from radioactive substances, might well be expected to follow other laws than ionization by particles possessing little more than enough energy to detach an electron from an atom. Such indeed is the case; yet it would not be justified, either by reasoning or by experiment, to suppose that even such highly energetic particles expel electrons of any and every class tightly-bound alike and loosely-bound alike, with equal ease and abundance from the atoms which they strike.

It is not particularly difficult to measure the total number of ions produced by an alpha-particle in its course through a gas from the moment it enters, with a measurable initial speed, to the moment when it goes into retirement (so to speak) as an ordinary helium atom; nor to

[19] G. A. Anslow, *Phys. Rev.* (2) 25, pp. 484–500 (1925) and literature there cited.

[20] Anyone desiring to learn how complicated the circumstances may become when electrons are shot into a dense gas should read P. Lenard's brochure "Quantitatives über Kathodenstrahlen," published by the Heidelberg Academy in 1918.

divide this number into the kinetic energy which it originally had, thus obtaining the average energy spent per ion (or rather per pair of ions generated, since each ionization produced two ions of opposite sign)—a quantity amounting generally to several tens of equivalent volts (33 volts for air).[21] By performing such experiments with alpha-particles of various initial speeds, it is possible to determine a function analogous to the function $f(V)$ defined for electrons in a previous section. This function increases rapidly as the aplha-particle approaches the end of its sharply-terminated trail, varying approximately as the reciprocal of the cube root of the distance it has yet to go.

Alpha-particles as they pass through a gas thus produce a countable number of ions and suffer a measurable loss in kinetic energy. It is interesting to enquire whether these two processes can be identified with one another and explained by the nuclear atom-model—whether the lost kinetic energy is altogether spent in detaching electrons from the atoms of the gas and supplying them with extra kinetic energy.

Before comparing any theory with the experimental data, one must be aware of two complexities. In the first place, an alpha-particle may transfer energy to an atom without ionizing it; so that the energy it loses in passing through a gas may exceed that which it spends in ionizing. In the second place, some of the ions produced by an alpha-particle—notably, the detached electrons—may themselves be endowed with energy enough to ionize, so that a measurement of the total ionization in the gas may yield an excessive estimate of the number of ions actually and immediately produced by particles striking atoms. Naturally the energy for producing all of these ions, "primary" and "secondary" alike, comes from the alpha-particles, so that such data as the aforesaid values for energy-spent-per-ion-generated have a definite meaning.

Discrimination between ions produced directly and indirectly is desirable, indeed essential, for testing any theory; but thus far there is no way for distinguishing the two, except in the case of very fast electrons for which the trails have been photographed with great magnification by C. T. R. Wilson[22] by his celebrated expansion-method, in which each ion formed in the passage of such an electron through a gas becomes the center of a visible droplet of water. In some of his pictures, in Fig. 11, pairs of droplets and also groups of four, six and more are seen. The paired droplets have condensed upon the two ions, positive and negative, produced by a single primary ionization (and

[21] R. W. Gurney, *Proc. Roy. Soc.* A107, pp. 332–340 (1925) and literature there cited.

[22] *Proc. Roy. Soc.* A104, pp. 192–212 (1923).

then drawn apart by an appropriate electric field); the groups of more than two bear witness of a primary ionization followed by secondary processes of the same type. In Fig. 12 there is an actual long branch to the primary trail; the original fast electron has detached another and endowed it with so great an energy that in ionizing-efficiency it

Fig. 11

rivals its liberator. These figures show that a mere count of all the ions formed by a particle flying through a gas is no estimate of the detachments of electrons from atoms which the particle of itself and at first hand effected.

Various theoretical expressions have been derived for the rate of slowing-down and the rate of ionization of an alpha-particle or fast

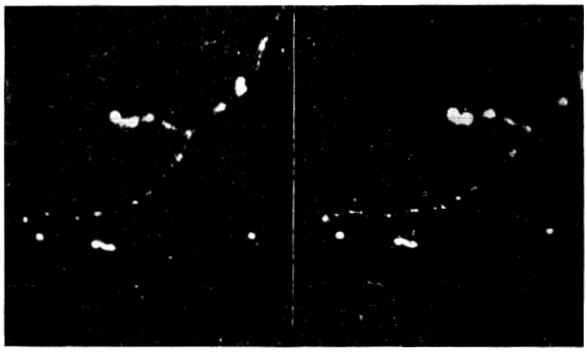

Fig. 12

electron proceeding through a gas. Most of them lead to what are known as "order-of-magnitude agreements," but none to a close quantitative agreement—which is, perhaps, after all better than could be expected. They are founded upon an equation originally proposed by J. J. Thomson. Suppose a stratum of an element of atomic number Z, containing N atoms; using the nuclear atom-model, we conceive this as a region containing N nuclei and NZ electrons. If the electrons (of

mass m) were free and stationary, an alpha-particle of mass M moving with speed U along a line passing at distance p from the initial position of any one of them would communicate to it an amount of energy:

$$W = \frac{8e^2}{mU^2(p^2+a^2)}$$

where

$$a = \frac{2e^2(M+m)}{mUM^2}. \tag{8}$$

Imagine Q alpha-particles passing through this collection of NZ electrons; the number of encounters for which this energy-value lies between two values W and $W+dW$ is equal to $2\pi p(dp/dW)dW$. Multiplying this by W and integrating over all values from $W=0$ (corresponding to $p=\infty$) to $W=8e^2/mU^2a^2$ (corresponding to $p=0$), we arrive at a value for the total amount of energy communicated by the alpha-particles to the electrons, which value is infinite. This absurd conclusion rests on the absurd assumption that the electrons are free, which, of course, is not made. Generally it is assumed that whenever p exceeds a certain value, selected for one reason or another, equation (8) loses its validity and W is zero; for instance, that whenever p is so great that the value computed by (8) for W is smaller than the least energy sufficing to remove the electron altogether from the atom or to put the atom into a Stationary State, then there is no transfer of energy whatever; but, whenever p is so small that W as computed by (8) exceeds the extraction-energy for the electron in question, then the electron is extracted and carries off, as kinetic energy, the difference between W and its extraction-energy.

Definite assumptions must be made about the extraction-energies of the various classes of electrons in the atom, the number of electrons in each class, and the Stationary States of the atom; this being done, formulae are derived for the primary ionization, the scondary ionization, and the rate at which the alpha-particle (or fast electron) loses energy.[23] Apart from these results of elaborate and careful analysis which lead as I have said to order-of-magnitude agreements (in some cases the agreements approach quantitative value) it may be pointed out that the equation (8) leads, when U is so great that a becomes small relatively to p, to the conclusion that as a fast-flying particle proceeds through matter the fourth power of its speed falls off linearly with increase of distance traversed, which is in agreement with much

[23] See R. H. Fowler, *Proc. Camb. Phil. Soc.* 21, pp. 521–540 (1923), and G. H. Henderson, *Phil. Mag.* 44, pp. 680–(1922) for discussion and prior literature as well for their own work.

experimental work. It furthermore indicates that the total ionization effected by a beam of particles in traversing a given thickness of matter should, beyond a certain speed, diminish with increasing speed; which for alpha-particles is true for the entire available speed-range, and for electrons is true beyond the speed of optimum ionizing-efficiency mentioned in a previous section.[24]

Multiple Ionization

The analyses of positive rays issuing from gases sustaining electrical discharges show that under such conditions some atoms are deprived of two, three, or even so many as eight electrons. The recently-developed methods of interpreting spectra make it practically certain that some of the spectrum-lines emitted from gases bombarded by electrons or sustaining discharges, and particularly from the exceptionally violent discharges known as "sparks," are due to atoms lacking one, two, or so many as six of their normal complement of electrons.[25]

Such ions might conceivably be produced either in one operation or in several; that is, the two (or more) missing electrons might have been removed by a single agency at a single moment, or they might have been detached one after the other by separately and successively acting agents. Measurements by the method of H. D. Smyth, such as those upon argon already cited, are capable of showing the minimum amount of energy which bombarding electrons must possess, in order that doubly-ionized atoms may appear in a bombarded gas; but they do not show, at least not directly, whether this minimum amount is what is required to effect double ionization in a single operation, or merely what is required to effect the most difficult among two or several steps leading cumulatively to the result. The same holds true about the experiments in which the least bombarding-voltage sufficient to bring out the spectrum associated with the doubly-ionized atom is measured.[26] Granted that the energy-difference between the once-ionized and the normal argon atom is 15 equivalent volts, and

[24] The attempts to account for "straggling" of alpha-particles—that is, for the fact that different particles of the same initial speed are slowed down at somewhat different rates in progressing through the same gas—by ascribing it to mere statistical fluctuations in the number of electrons close to which they passed seem to have been unsuccessful; the observed straggling is much too great for this explanation. See G. H. Henderson, *Phil. Mag.* 44.

[25] Multiply-ionized atoms are regularly observed in electrolytic solutions of compounds of other-than-monovalent elements; strangely enough they are rarely if ever found among the ions issuing spontaneously from hot metals and salts.

[26] P. D. Foote et al., *Phil. Mag.* 42, pp. 1002–1015 (1921); *Astroph. Jour.* 55, pp. 145–161 (1922); *Origin of Spectra*, 1922.

that A^{++} ions appear in argon bombarded by 45-volt electrons: do 45 equivalent volts constitute the amount of energy necessary to remove two electrons at once from a normal atom, or the amount necessary to remove one electron from an atom which a prior electron-impact has ionized? The question is not different in principle from one arising in measurements of the first ionizing-potential, whether the first appearance of ions signifies simply that atoms are being ionized in two stages; but apparently it is harder to settle by direct evidence.

Analysis of the spectra of the ion and of the atom whenever practicable, discloses definitely the energy-differences between the state of double ionization, the state of single ionization, and the normal state of the neutral atom. Thus with helium the first of these is greater than the second by 54 and then the third by 79 equivalent volts. Similar calculations for magnesium show that the first is greater than the second by 15 equivalent volts; as the spectrum of the ion Mg^{+} in Foote's just-cited experiments appeared at about that energy of the bombarding electrons, the atoms in the vapor must have been ionized by two successive impacts.

In the course of R. A. Millikan's observations upon droplets of oil floating in ionized gases, he found that they never captured charges amounting to $2e$ or a greater multiple of e, except in the solitary instance of helium traversed by alpha-particles; in this case about one out of every six positive charges captured was a double electron-charge $2e$. He concluded that not more than one electron was ever detached from an atom in a single operation, except that among encounters of alpha-particles with helium atoms about one-sixth caused both of the electrons of the struck atom to be torn away.[27]

Detachments of two or more tightly-bound electrons from a massive atom, whether effected in one operation or in several, might be revealed by additional absorption-edges in the spectrum of an X-ray beam after passing through matter; certain delicate features in X-ray spectra have in fact been explained in this manner.

Thermal Ionization [28]

In addition to all the information about ionization by particular agents such as electrons of specified speeds and radiation of specified frequencies, there is reason for making certain assertions about ioniza-

[27] The percentage may well have been much greater, since many of the ions left behind after the passage of the alpha-particle were probably produced by secondary, not primary ionization (R. H. Fowler).

[28] General references: E. A. Milne, *Proc. Phys. Soc. London* 36, pp. 94–113, and literature there cited; A. A. Noyes, H. A. Wilson, *Pro. Nat. Acad. Sci.* 8, pp. 303–307 (1922).

tion *per se*, apart from all knowledge or assumption concerning the processes which effect it. There is a thermodynamic method of determining the percentage of dissociated molecules in a molecular gas as a function of the temperature and the pressure of the gas, which can be used if we know the amount of energy required to dissociate a single molecule, the specific heats of the undissociated and the dissociated gas, and the chemical constants of the undissociated and the dissociated gas. An analogy may be established between dissociation and ionization: the ionizing-energy of a monatomic gas corresponds to the heat of dissociation of (say) a diatomic gas; the electrons and the ions resulting from the ionizations may be taken as the particles of two distinct gases mingled with one another and with the gas composed of the neutral atoms; the chemical constant of the ion-gas is taken as equal to the chemical constant of the original gas, and the chemical constant of the electron-gas is identified with that which a gas composed of neutral atoms, each possessing the same mass as an electron, would possess. Utilizing this analogy, a formula may be deduced for the percentage of ionized atoms present in a monatomic gas in thermal equilibrium at any temperature and pressure.

Without developing the formula, it may be taken as a rather obvious inference that the higher the temperature of the gas at a given pressure, or the lower the pressure at a given temperature, the greater the percentage of ionization will be; and of two gases maintained at the same temperature and pressure, the gas having the smaller ionizing-energy will be the more ionized.

Measurements of the degree of ionization in a flame of known temperature, into which a known amount of caesium was introduced, have yielded values in good agreement with the percentage calculated from the thermodynamic formula; and measurements upon the conductivities of the vapors of the alkali metals have shown that they stand in the order of the ionizing energies reversed, although in other respects the agreement with the theory is not good.[29]. The tests and the value of the theory, however, appear chiefly in the realm of astrophysics. The hotter the region of a star in which the lines observed in its spectrum have their source, the more the lines of ionized atoms predominate among these. In many cases it happens that lines of ionized atoms are the only ones characteristic of a given element to be found at all. The assertion once commonly made, that certain elements are absent from the sun or other stars, is invalidated by the fact that under the actual conditions of temperature and pressure prevailing in these bodies,

[29] B. T. Barnes, Phys. Rev. (2) 23, pp. 178–188 (1924); M. N. Saha, Phil. Mag. 46, pp. 534–543 (1923).

those elements if present would be totally ionized and would not reveal their familiar lines at all. Rubidium was thought to be omitted from the composition of the sun, until it occurred to H. N. Russell to look for its lines in the spectra of comparatively cool sunspots. The relative intensities of the lines of ionized and non-ionized atoms of various kinds in the spectra of individual stars are now ascertained and used as a guide in assigning temperatures to these stars, and their guidance is shown reliable by the accord between the conclusions to which it leads and conclusions otherwise attained. The study of ionization in the laboratory thus contributes to the understanding of the stars.