n, the atomic volume becomes comparable to the mean volume occupied by each atom. Hence the electron is no longer under the influence of a single nucleus, but comes under the influence of other nuclei; it passes, so to say, into no man's land. Hence the series must be cut down at a certain point. Becker has shown that while $q=n(n+1)$ when the electron is far from the influence of other nuclei, it becomes a function of the mean volume V occupied by an atom when the pressure is sufficiently high. For smaller values of V, q tends to nil.

Fowler and Milne have, however, deduced some very interesting relations from (3). They noticed that while the lines of the principal series of a neutral element, *e.g.* the g-line of calcium, are most intense in the coolest stars and gradually decrease in intensity in the higher classes, it is not so with the lines of the subordinate series, *e.g.* the Balmer lines of hydrogen, or calcium or magnesium. These, it may be remembered, are the lines which are due to absorption by atoms in an excited or metastable state. These lines are rather faint in the coolest stars, but gradually increase in intensity, and reach a maximum somewhere, and then again decline in strength till they disappear. The explanation is obvious; at the lowest temperature atoms are all in the normal state; there are no excited atoms. These are produced in increasing proportion as the temperature rises, according to the law:

$$f_r=q_r e^{-(x_1-x_r)/k\mathrm{T}}/\mathrm{B(T)},$$

where f=fraction in the rth state. But with still higher temperatures a fraction x gets ionised. Hence the concentration of atoms in the excited state reduces to

$$n_r=f_r(1-x)$$

Now intensity of absorption lines proceeding from the rth state will be maximum when n_r is maximum.

Now n_r can be calculated from (3), and putting $\frac{dn_r}{dT}=0$ we obtain a relation involving $\mathrm{P_e}$ and T. As the temperature is roughly known, the relation enables us to find out the pressure in the reversing layer of stars. Fowler and Milne have discussed the stellar data on subordinate series lines from the above stand-point and find that the pressure is of the order of $10^{-3}-10^{-6}$ Atm.

Ionisation of Elements of Higher Groups

In considering the mechanism of ionisation, we have been assuming that there is only one (viz. the outermost) electron, which is affected by the ionising agency. While this may be quite true in the case of H and the alkalis, it is not true for the elements of higher groups. Taking the case of calcium, we know that it has two elcetrons in the outermost ring, which are, so far as can be seen, similarly situated with regard to the atomic residue (Rumpf). When an ionising agency acts on Ca, it may tear off either the one or the other electron. Hence with the same stimulus, the probability of ionisation will be much higher in the case of Ca or Ba than in the case of alkalis, everything else remaining the same. This is illustrated by the comparative behaviour of Ba and Na. They have the same ionisation potential, but in the Sun barium is almost completely ionised, while the ionisation of sodium is not more than 60 or 70 per cent.

The above hypothesis is partly confirmed from a discussion of Lockyer's data on the successive stages of appearance and disappearance of the lines of

Si,	Si^{+},	Si^{++},	Si^{+++},
C,	C^{+},	C^{++},	C^{+++},
Ti,	Ti^{+},	Ti^{++},	Ti^{+++},
Mn,	Mn^{+},	Mn^{++},	
V,	V^{+},	V^{++},	
N,	N^{+},	N^{++},	

in stellar spectra.

As a rule, elements belonging to higher groups are more easily ionised than elements of the preceding group, and the successive steps of ionisation follow each other in rather quick succession.

The fact is probably partly accounted for in the author's "steric factor" or Fowler and Darwin's "Symmetry Factor", but an exact theory is clearly impossible unless we know the steps by which the atom loses its outer electrons. This cannot be attempted until a complete analysis of the spectra of these elements is available. Thanks to the works of Fowler, Catalan, Paschen, Russell, Laporte, Landé, and others, the analysis is proceeding at the present moment with the greatest amount of vigour, and it is to be hoped that before long we shall be in possession of all necessary facts. The case of calcium is extremely interesting. Russell and Saunders, and simultaneously Laporte, have shown that when a stimulus is given to Ca, then in certain cases both the electrons may be simultaneously excited, giving rise to a group of lines (pp′ and dd′ combinations) which are sometimes extraordinarily strong. There seems to be strong reasons for believing that the phenomenon is quite general, and a stimulus, if it is sufficiently strong, may excite not only two, but sometimes three or more outer electrons simultaneously. The idea of ionisation potential, therefore, loses some of its primary significance, but an exact theory is clearly impossible unless we thoroughly understand the mechanism.

Influence of Radiation on Ionisation Equilibrium

The formulae for ionisation which have been given above suffer from yet another defect. We have been making the tacit assumption that the radiation is in equilibrium with matter at the temperature concerned. While this assumption is quite true when we heat a metal in a closed space, or in the interior of stars, it is evident that in many cases the assumption is far from actual truth. We take the following typical examples:

(1) When continuous radiation is allowed to pass through a mass of sodium vapour as in Wood's absorption experiments. Here the vapour may be at a temperature of 500°C. to 600°C., while the radiation if it comes from the arc, is at a temperature of 4000 K.

It may be pointed out that all photo-chemical reactions—such as the ozonisation of oxygen by ultraviolet light, etc.—belong to this class. In this case, however, the mechanism of the reaction is not quite so clear as in the case of sodium absorption.

(2) The chromospheric phenomena.

The chromosphere is at a much lower temperature than the photosphere (say 5000 K to 6000 K). Hence the radiation from the photosphere which is pouring through chromospheric gasses is at a higher temperature, as was pointed out by Milne.

In these cases we cannot speak of thermodynamic equilibrium in the strict sense, but there is a sort of dynamical equilibrium.

(3) The phenomena in the Novae and O-type of stars.

There are reasons to believe that in many stars, particularly in Novae and those with a dense atmosphere, the region from which the continuous radiation comes and the outer envelope where the absorption takes place are at different and varying temperatures.

sometimes the one, sometimes the other temperature becoming higher.

In all these cases, the reacting radiation is to be regarded as a new component. The equilibrium condition can be deduced thermodynamically, and the law of ionisation takes the form

$$\log \frac{x^2}{1-r_2} P = \frac{(U-Nh\nu)}{2\cdot3RT} + \log \frac{\rho_v}{8\frac{\pi\nu^3}{c^3}+\rho_\nu} + \frac{5}{2} \log T - 6\cdot5 \qquad (4)$$

When the radiation is due to the temperature of the system, *i.e.* when there is thermodynamic equilibrium between matter and radiation, the equation reduces to the form (1).

The formula (4) is the general form of a formula given by Einstein 1911 for photochemical reaction.

Conclusion

This brief sketch of the recent works on "Dissociation" probably illustrates how much the recent progress in astrophysics runs on the lines initiated by Lockyer. Celestial physics has tow eyes—observation and laboratory work—and Lockyer was one of the few investigators who saw with both eyes. Naturally, he saw much more than his contemporaries, but he failed to rally them to his views. His lot was like that of Icarus, who in trying to fly to the sun with wings of wax, had to end by falling into the sea; while lesser men, confining their flights like the prudent Daedalus to the sea level, had a happy and comfortable journey. But for the progress of science. Icarus's unsuccessful flights are more fruitful because they bring to our view fresh lands and fresh sights, while Daedalus's flights do not add much to existing knowledge.

The scientific world is only just beginning to appreciate Lockyer's works and views, and we can only wish that in our quest after truth—"May the Spirit of Lockyer be always with us."

1.2.2—SIX LECTURES ON ATOMIC PHYSICS*

LECTURE 1: THE ATOM—THE ELECTRON—THE PROTON

DEEPLY as I appreciate the honour which the Patna University has conferred on me by inviting me to deliver these Readership lectures, I am none the less aware of the difficult nature of the task before me. I understand that the University expects me to describe the current progress in Atomic Physics and Subatomic Thermodynamics. As you are all aware, the attempt to explain the Physical World in terms of 'The Atom' can be traced to the ancient Hindu and Greek sages. The founder of the 'Vaisesika' System of Philosophy in our country received from his rival metaphysicians the nickname of 'Kanad' or the atom-eater because he based his philosophy of the World on small particles. In Greece, a form of the atomic theory was put forward in the fifth century B.C. by Leucippus and Democritus. These atoms were small, indivisible particles, infinite in number, capable of various shapes and sizes.

Empedocles affirmed the existence of four elements to which a fifth was added later. The first four were earth, air, fire and water and the fifth was aether. The same belief existed also amongst the Hindus, but it is not clear with whom it first originated. It is also not clear whether the elements were conceived as 'principles' or as 'atoms.' This explanation of Nature persisted amongst men of science up to the end of the eighteenth century, when the strictly quantitative and experimental study of Nature was initiated by Lavoisier. The rationalistic methods of Lavoisier still dominate scientific thought and are responsible for the extraordinary expansion of our knowledge of the Physical World within the last hundred and fifty years.

I believe that you will agree with me that the theory of the ancient —that this polyglot world is built out of five elements—received its deathblow when Nicholson and Carlisle decomposed one of these ancient elements, viz, water-into two elementary gases by sending a current from the newly discovered Voltaic pile. (Fig. 1)

Cavendish passed a current of electricity through these two gases

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*Readership Lectures delivered before the Patna University in 1927. Published in 1931.

hydrogen and oxygen, as they are called now, and synthesised water thus proving that the so-called element water could be decomposed into two distinct and simpler constituents.

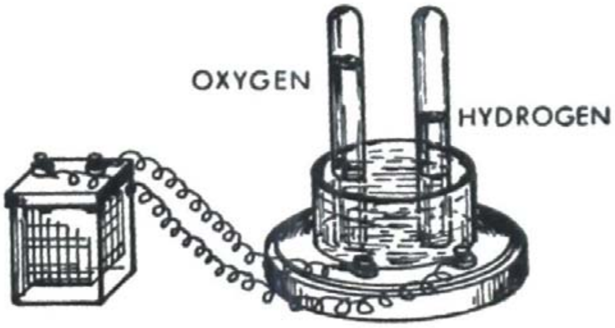

Fig. 1 Apparatus for Electrolysis of water.
(From Mellor's *Introduction to Modern Inorganic Chemistry*).

Following this discovery, chemists and physicists went on discovering one elementary substance after another till, when a census was taken, it was found that they could not be limited by the magical properties of any number. By the time Dalton formulated his 'atomic theory' and the researches of Clausius and Maxwell on the "Kinetic Theory of Matter" were successful in assigning definite values for the number and size of atoms, the total number of elements had reached well over fifty. But the human mind refuses to believe in complexity; so before long philosophers began to ponder whether the so-called chemical elements were elements at all, whether they might not turn out to be compound of some more elementary stuff. The most sensational effort was made by Prout; he thought that hydrogen was the elementary atom, and other atoms were merely its condensation products. But experiments showed that the weights of the atoms were not integral and Prout's theory failed to live through. In the nineteenth century, scientists with a few exceptions, notably the astronomer Sir Norman Lockyer, continued to believe in the non-divisibility of the atom.

But in 1896, the atom was definitely shown to be capable of further subdivision.

The Cathode Particles

For tracing the history of the discovery of the electron, we have to go back to the Geissler tubes. They are, as you see, glass tubes having two metallic electrodes sealed into them and containing some gas at low pressure. If we pass an electric current through one of them from an induction coil, the tube glows with a vivid colour.

The Geissler tube, first made by a glassblower named Geissler in the service of Prof. Plücker of Göttingen, is the ancestor of Vacuum tubes, X-ray tubes, and other apparatus which have contributed largely to our present knowledge of atomic physics. By giving the tube a slightly different form, and pumping out as much gas as possible with a highly efficient pump, we find that the nature of the discharge changes entirely. We shall not stop to describe these intermediate stages, ultimately we come to a stage when is it found that something apparently much finer than gaseous particles are being ejected from the cathode. These are generally known as the cathode particles.

Nature of the Cathode Particles

Sir W. Crookes realized from the start that these cathode particles were something much finer than the atoms, and gave to them the imposing name of protyles or the fourth state of matter. But their real nature was not elucidated till long afterwards. The earlier workers, Plücker, Hittorf and others had noted the following facts about them:

They travel in straight lines, are deflected by magnets, possess momentum and energy. Lenard showed that they can pass through thin foils of aluminium.

The first observations indicate that the cathode rays are charged particles of matter. But Lenard maintained that they are electromagnetic waves, otherwise he thought they could not pass through matter.

The crucial experiment was performed in 1895 by J. Perrin who proved that the particles carried a negative charge.

Lorentz and Larmor developed equations for studying the motion

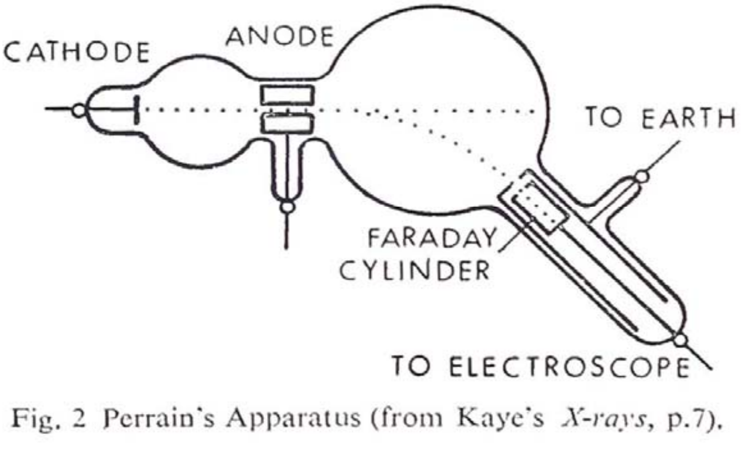

Fig. 2 Perrain's Apparatus (from Kaye's *X-rays*, p.7).

of these particles. Since they are charged particles, they are subjected to force arising from electrostatic fields. On account of their motion with high velocities, they can be regarded as equivalent to small bits of current, and can be deflected by a magnetic field. The total force acting on them is the sum of these two, viz.—

$$F=mf=eX+\frac{e}{c}\left[\vec{v}\times\vec{H}\right]$$

J. J. Thomson calculated the path of these particles under crossed electric and magnetic fields, and found that the values of $\frac{e}{m}$ and v can be experimentally determined.

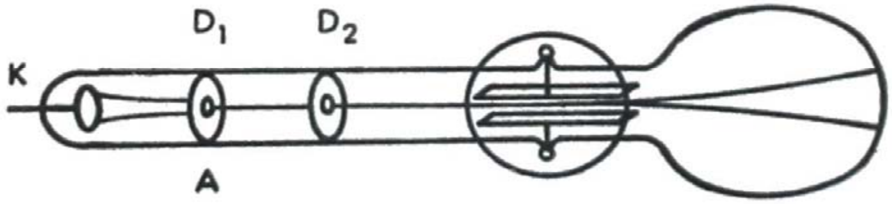

Fig. 3 Classical apparatus of J. J. Thomson for determining $\frac{e}{m}$ and v
(from Handbuch der Physik, vol. 28)

[A narrow pencil of Cathode Rays, rendered parallel by the diaphragms D_1 D_2 is passed between two parallel plates which are connected to the opposite terminals of a high-potential battery. The beam is deflected and falls on a Willemite screen, and is detected by the blue phosphorescent light it produces on the screen. By applying a magnetic field at right angles (perpendicular to the plane of the paper), the spot can be deflected in the opposite direction and brought back to its original position. It can be shown that $\frac{v}{c}=\frac{X}{H}$, $\frac{e}{mc}=\frac{Xc}{\rho H^2}$ where X, H are the electric and magnetic fields. ρ=radius of curvature of path.]

The value of $\frac{e}{m}$ was found to be $1{\cdot}77\times10^7\times c$, where c=velocity of light. The velocity was found to range between 10^8 cm to 10^{10} cm per sec and depended upon the voltage applied to the tube. In fact, we can calculate the velocity on the assumption that as the particle falls through the potential V, it does the work eV, and this is converted into the kinetic energy $\frac{1}{2}mv^2$, just as a particle falling through a height 'h' acquires the energy $\frac{1}{2}mv^2=mgh$. We have here—

$$\tfrac{1}{2}\,mv^2 = eV, \text{ or } v = \sqrt{\frac{2eV}{m}} = 5{\cdot}92\times10^7\,\sqrt{V\text{ cm}} \text{ per sec.}$$

This experiment tells us nothing about the charge 'e'. There were reasons to believe that all cathode particles carried the same charge 'e', and this charge was the same as the charge carried by the charged hydrogen atom in electrolysis. We know that a gm-molecule of HCl, when electrolysed, deposits 96,450 coulombs, or 9645×e units of electrostatic charge.

$$\therefore \frac{e}{m_H} = \frac{eN}{m_H N} = 9645\times c$$

Since $m_H N$ = total mass of one gm-atom of hydrogen = 1 assuming that 'e' is the same in both cases.

$$\frac{m}{m_H} = \frac{9645}{1{\cdot}77\times10^7} = \frac{1}{1836}$$

Thus the mass of the electron comes out to be 1836 times smaller than the mass of the H-atom.

But the assumption that the charges on all the cathode particles are the same, and the same as on the H^+-particle in electrolysis took a long time to be securely established.

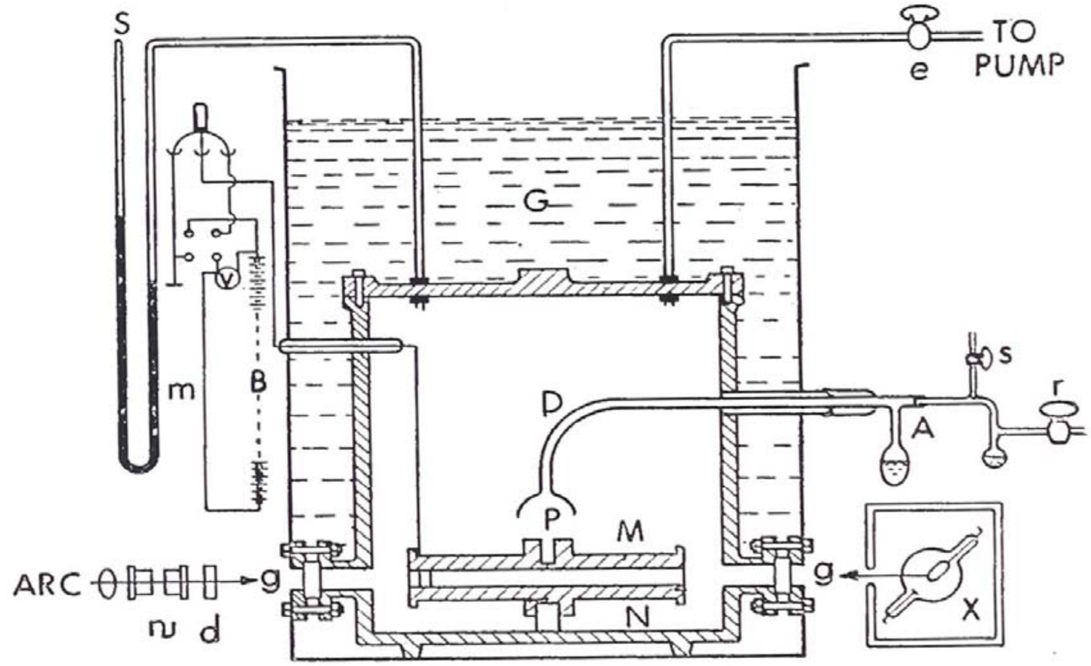

Fig. 4 Millikan's Apparatus for determining the quantum of Negative Electricity (from Handbuch der Physik, Vol. 23)

The first experiments were carried out at the Cavendish Laboratory by Townsend and Thomson. But the atomic nature of the 'negative charge" is very clearly shown in the experiments of Millikan which prove that in all electrical reactions (processes in which electricity is generated by friction or ionisation), the charges always occur in multiples of a certain unit.

(Millikan introduces small particles produced by an atomiser A in the space between the two plates of the condenser M. N. The particle is charged by friction while being produced. The field is such that the particle is held up against gravity. By following the motion of the particle, it is shown that the charges of electricity which it gets from the surrounding medium, as well as the original charge on it, are multiples of e. The particle is illuminated by the arc-light A, which is focused on P, and is viewed by a low-power microscope from the sides. X is an X-ray tube for producing ionisation in the condenser space T.)

Thus, the atom of negative electricity or the electron is found to have a

$$\text{Charge} = 4{\cdot}77 \times 10^{-10} \text{ e.s. units}$$

$$\text{Mass} = \frac{1}{1836} \text{ mass of the H atom.}$$

Subsequent researches proved that the genesis of the electron is not confined to such an artificial source as the vacuum tube, but it occurs in all chemical and physical reactions, amongst which may be enumerated—

(1) Heated metallic filaments.
(2) Metallic plates illuminated by ultra-violet light.
(3) All chemical reactions.
(4) Radioactive disintegration.

After it was established that the electron is a universal constituent of all matter, and carries a negative charge, it became imperative to look for its positive consort. For all atoms are electrically neutral and therefore must contain equal quantities of positive and negative electricity. But the positive electron turned out to be quite different from that early expected by physicists.

Canal Rays

If the cathode in a vacuum tube is perforated, a stream of particles having characteristic colours issues in the opposite direction, and experiments prove that they are positively charged particles. These rays were named Canal Rays by their discoverer Prof. Goldstein.

But though their charge is positive and found to be an integral multiple of the electronic charge, the mass is always found to be very much higher, indeed the same as that of the atoms or molecules of the gas contained in the tube. Indeed they are simply the residues of the atoms or molecules after one electron or more has been torn from these. In no case, a positive particle having a smaller mass than that of the H-atom has been found.*

Radioactivity

You have certainly heard of Radium, the wonder-element, 2 milligrams of which were extracted by M. and Madame Curie after painstaking analysis of 30 tons of minerals. They followed a discovery made by Bequerel that certain Uranium-containing minerals apparently cast off,—quite spontaneously,—charged particles which can affect a photographic plate or discharge an electroscope.

Radium, and other substances analogous to Ra were found to emit rays which, according to stricter analysis, can be distinguished into three types:—

> α-rays-which are positively charged particles with 2 electronic charges, and a mass equal to that of 4 hydrogen atoms,
> β-rays-which are swiftly moving electrons, and
> γ-rays-which are neutral,

α-rays suffer small deflection, β-rays rather large deflections in the opposite directions, the γ-rays proceed straight on, when a magnetic field is applied.

It was proved that Radium is spontaneously casting off these particles, and transforming itself slowly into other chemical types.

All these phenomena were quite unexpected and quite unlike anything the chemists and physicists had known before. So all kinds of wild theories sprang up till Rutherford and Soddy set the world at rest by bringing forth a very far-reaching and ingenious explanation of the phenomena.

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*Positron was not discovered till then—Ed

The main feature of their explanation is that the radioactive atoms are more or less unstable, presumably due to their heaviness. Like certain heavily outgrown political systems, they are spontaneously falling to pieces, owing to some internal commotion. The α and β-rays which mark the activity of the atom are simply the cast-off fragments due to this internal disruption.

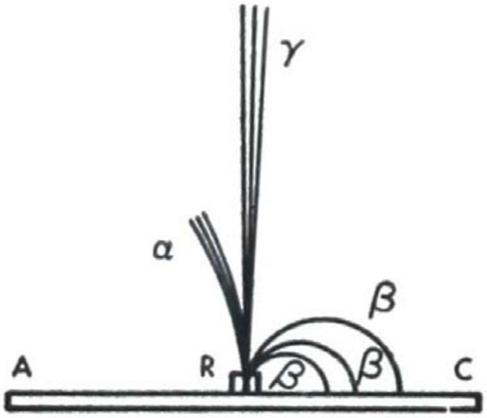

Fig. 5 Deflection of α, β, γ-rays under a magnetic field (from Hevesy and Paneth's *Radioactivity*)

The theory of spontaneous disintegration proved not only to be distinctively original but extremely fruitful. In chemical reactions, molecules are broken up into atoms, due to mutual collision. In the vacuum tube, the atoms are deprived of their electrons by the onrush of electricity. But spontaneous breaking was quite a new idea. However, subsequent investigations showed that there was no second way besides the one proposed by Rutherford and Soddy. Madame Currie and Kammerling Onnes established that radioactivity was not in the least influenced by widely varying physical conditions, e.g., extremely high temperature, or extremely low temperature.

Passage of α and β-Rays through matter

The α and β-rays are concentrated atomic charges of electricity carrying in comparison to their bulk, enormous momentum and energy, and hence it was expected that much information would be obtained from a study of their passage through atoms. The atoms as we have seen, contain equal quantities of positive and negative electricity and exert no electrical force on bodies passing at a distance from it. But it is not so when the charged particle passes through the interior of the atom.

Many of you will ask what is meant by the term 'Interior of the

Atom'. The idea is indeed quite unfamiliar to those who are accustomed to the lead-bullet type of rigid, non-divisible atom of the nineteenth century chemist. But we have seen that the atom has a structure which is concentrated within a space of 10^{-8} cm, and our problem is to find out this structure. Positive and negative electricity are discontinuously distributed within this volume, and hence within the interior, there are electrical fields of large and varying value. The nature of these fields can be explored only if we send charged particles of either sign, viz. α or β-rays.through the interior of the atom.

It has been assumed from the very start that positive electricity, is concentrated in the centre and negative particles (electrons) revolve about it. This is quite understandable because positive electricity has very large mass, and would be more or less stationary. But can we have any idea of the dimension of the positive sphere ? Lenard, in 1903, sent a linear beam of electrons through atoms, and found that on emergence they became very diffuse, as we would expect. But the most interesting part of the experiment is that he found very little absorption, scarcely one in a million collisions. Now absorption can take place only when an electron hits the positive sphere; hence it follows that the positive sphere presumably occupies a very small part of the atomic space—there are, therefore, large empty spaces between the positive sphere and the electron.

Lenard's conclusions were couched in very difficult language, and did not receive the attention they deserved. Shortly afterwards Nagaoka in Japan proposed a similar hypothesis. He assumed that the positive electricity occupied a small volume in the centre, while swarms of electrons revolved about it in rings.—the system being very much like the planet Saturn with its rings. But it is to Sir Ernest Rutherford that the world is indebted for the crucial experiments on the structure of the atom.

Rutherford sent a beam of α-rays through matter, and studied their scattering. He found that for small angle scattering, the results were in accordance with the then prevalent theory that the atom consisted of a large positive sphere of electricity with electrons going about it. But in course of an experiment performed under his guidance by Geiger and Marsden, he was puzzled to find that about one in 10^{-s} particles were returned on the same side from which they were projected, i.e., they suffered an abnormal deflection of about 180°. This can happen if the α-particle is subjected to the most intense repulsive forces; which can arise only from positive core of the atom and an exact calculation shows that the distance of nearest approach is about 10^{-13} cm The atom has a diameter of 10^{-8} cm so that the positive electricity is reduced to a mere point in the centre.*

The central nucleus has a positive charge of Ne, where N denotes the ordinal number of the element in the periodic table. The nucleus contains the whole mass.

There are N electrons arranged about the atomic nucleus in different layers.

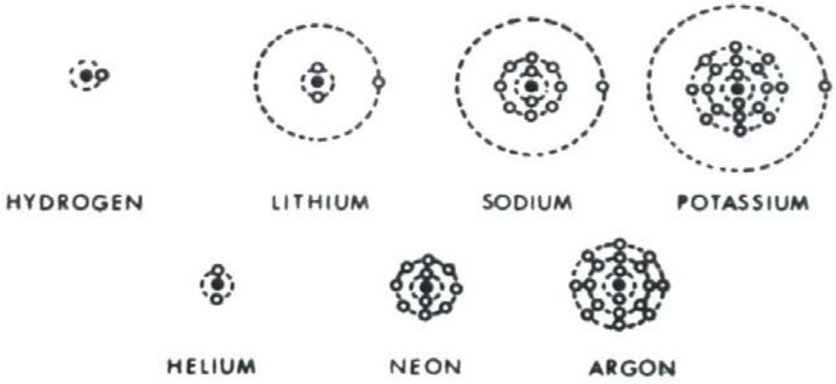

Fig. 6 Models of Atomic Structure: The central fully inked little circles represent nucleii. The empty little circles represent electrons

I reserve a later chapter for relating to you how the arrangement of electrons within the atom, their motion, and the other allied physical phenomena have been studied. But probably this chapter will be incomplete if I do not tell you whether the number of electrons in an atom cannot be counted by some direct method. This was rendered possible by the experiments of Barkla on the scattering of X-rays by matter. X-rays were discovered by Röntgen in the year 1895 and I think that everyone in this house has heard of X-rays as the rays which pass through the flesh and lay bare the bones. The physicist, not to be outdone by his medical confrere, utilises the X-rays to lay bare the interior of atoms, and though I have neither the space nor the time to recount in detail how this is done, I will try to place before you a very cursory sketch about their physical nature.

Though X-rays had been discovered in 1896, and physicists all over

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*This observation, which is so far-reaching in its consequences, might have escaped the attention of a less gifted experimentalist than Sir Ernest Rutherford. But history of science tells us that minute deviations from theory often furnish the clue to the most important discoveries, e.g. the deviation of the value of density of atmospheric nitrogen from that of chemically prepared nitrogen in the third place of decimal led to the discovery of Argon and the other gases of the inert group.

the world began to study their nature since that date, they remained 'x' up to the year 1912, when Prof. Von Laue, by a brilliant conception, proved that they are short waves of light, shorter than ordinary light by about a thousand times. But their identity with 'light' had been already recognised by Stokes, Wiechert and particularly by J.J. Thomson in his theory of scattering. Their wavelength varies from 10^{-8} to 10^{-10} cm, and they are of about the same length as the atoms.

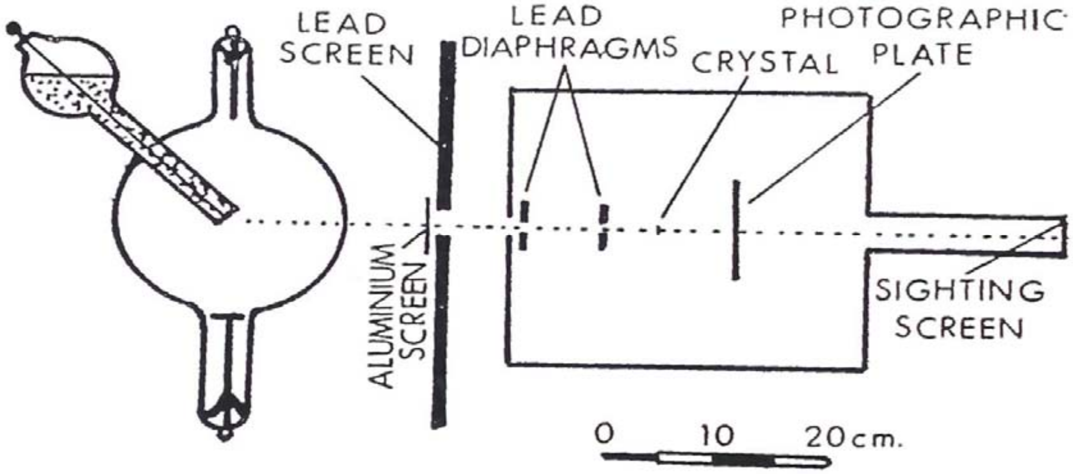

Fig. 7 Laue's Apparatus for determining the wavelength of X-rays by crystals (from Kaye's *X-rays*, page 127)

(A fine beam of X-rays is sent through a crystal and received on a photographic plate. The crystal acts as a space-diffraction grating, and diffraction patterns are produced on the photographic plate. From the angle of diffraction, and the crystal constant, the wavelength can be calculated (*see* Kaye's *X-rays*, Chap. XII).

I believe all of you are familiar with the phenomena of scattering of ordinary light, on which my distinguished predecessor, Prof. C. V. Raman delivered a series of lectures in this very hall about three years ago. If you are in a dark room, closed on all sides, and observe a beam of light coming through a chink in the wall, you find that dust particles are dancing in the beam. The light which was proceeding is reflected sideways by the dust particles which are thereby rendered visible. Even if the particles are of ultra-microscopic dimensions, the light is scattered sideways and a mathematical investigation due to the late Lord Rayleigh shows that the amount of scattered light is, amongst other things, proportional to the number of scattering particles. X-rays also show the same phenomena of scattering: if a metallic foil is placed in its path, much of it is scattered sideways.

Now, J. J. Thomson showed in 1903, that the scattering agents are the electrons of the atoms, and the more the number of electrons in an atom, the greater is its scattering power for X-rays.

This formula was subjected to a very painstaking series of experiments by Barkla who concluded from his results that the number of electrons in an atom is about half the atomic weight of the element.

You will see that we are no longer talking of the unit of positive electricity. In fact, there is no positive analogue to the electron; all the positive charge is assigned *en bloc* to the nucleus. But there are evidences that the nucleus itself has got a structure. In radioactive bodies, the nucleus is breaking up of itself, and throwing out electrons and positive particles. But in no case, a positive particle smaller than an α-particle has been obtained. The α-particle has a mass which is 4 mass of the H-atom, and has two charges. The evidence shows that the nucleus itself consists of distinct units of positive and negative electricity compressed in some inexplicable way within an incredibly small volume.

Within the last few years evidences have been accumulating that the nucleus of the H-atom-the H-particle-is the atom of positive electricity. This was first shown in a beautiful experiment due to Prof. D. M. Bose of Calcutta, and in recent years, Sir Ernest Rutherford has proved that the nucleii of all atoms consist of H-particles.

Rutherford hurled very swiftly moving α-particles on the atomic

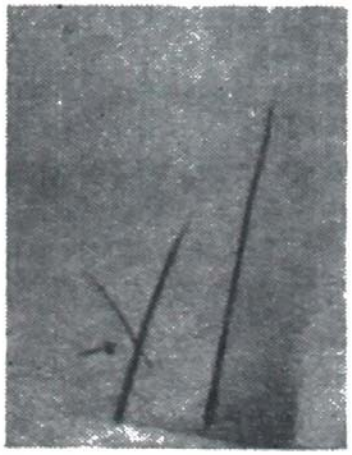

Fig. 8 D. M. Bose's Wilson-Photograph of the Track of H-particles. (α-rays from Polonium were passed through a Wilson-chamber containing hydrogen. The α-rays produced H-particles by collision, and the tracks of these particles are continued beyond those of the α-particles proper. In the reproduction of the photograph, the branching off of the track of the H-particle is indicated by an arrow)

core and shattered them to fragments. In the fragments, H-particles were obtained.

The atom of positive electricity has been christened 'Proton.'

We now arrive at the final* result:—There are, so far as our present knowledge goes, only two primordial elements in the universe—the atom of positive electricity or the Proton, and the atom of negative electricity or the Electron. The proton has almost all the mass. The protons have a tendency of combining together, probably cemented by a lesser number of electrons, and forming the nucleus. The way how this is done is not yet clearly understood. The study of the structure of the nucleus forms a separate branch of study which is at present receiving the name 'Nuclear Physics.' The net nuclear charge in any atom is equivalent to the position which the atom occupies in the periodic table (Atomic number). The electrons are arranged in different layers about the nucleus, and are responsible for the spectra, and all other chemical and physical phenomena. These subjects will be taken up in the subsequent lectures. At present we have to answer a question which is probably uppermost in the minds of many of my listeners:—If the elements are compounds of the proton and electron, we are returning to Prout's hypothesis. But how would you meet the objections which were raised against Prout:—Why atomic weights are not integral numbers ?—The answer has been given by Soddy and Fajans, J. J. Thomson and Aston.

The nineteenth century chemists were under the impression that the relative weights of atoms were invariable. Hence very painstaking and elaborate experiments were undertaken to determine the atomic weights correct to as many places of decimal as possible. These experiments, admirable as they were, and often-times leading to great discoveries, where however useless as far as their immediate objective (viz. determination of an absolute constant of Nature) was concerned. For Fajans and Soddy had already proved from studies on Radioactivity that it is possible to have, from different radioactive sources, lead having such different atomic weights as 206, 208 and even 212. These varieties of lead have the same chemical and physical properties and cannot be separated from each other by any means. The lead which we usually come across is a mixture in varying proportion of these varieties. Even before this discovery, J. J. Thomson found from Positive Ray Analysis of Neon, which has got a fractional

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*'Final' so far as our present knowledge goes.

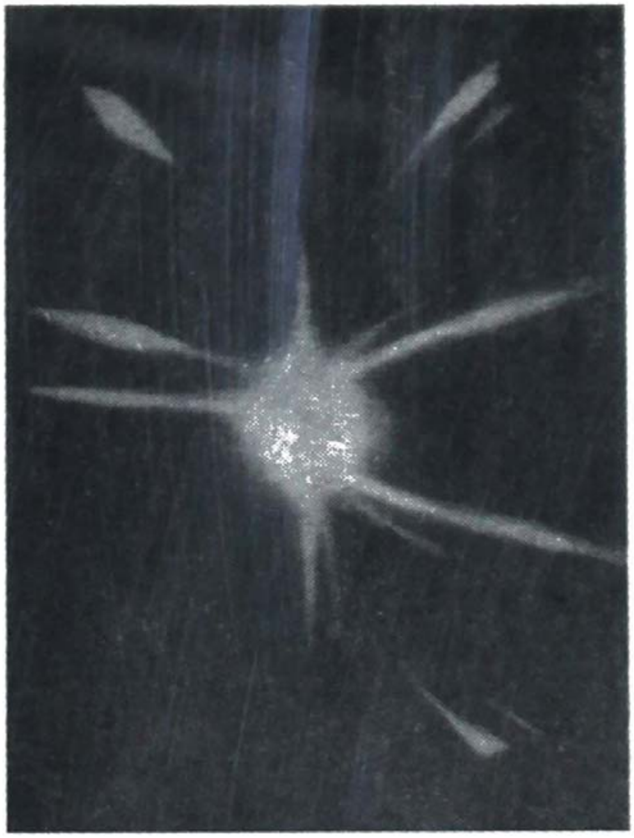


Fig. 9 Positive Ray Spectrum of Neon
(from J. J. Thomson's *Rays of Positive Electricity*)

(The strong line at the top on the right-hand side corresponds to Neon with the atomic weight 20. The thinner line just below it corresponds to the atomic weight 22.)

atomic number of 20·2, that this gas is probably a mixture of two different types having the integral weights 20 and 22.

But the clearing up of the situation, as far as the deviation from the integral number of the weights of all atoms is concerned, is due to Aston. He devised a new type of apparatus for Positive Ray Analysis, and was able to decompose all elements having fractional atomic weights into a number of isotopes having integral weights.

Finer Structure of the Electron and the Proton

I would not like my audience to run away with the idea that there is any such thing as finality in knowledge. The electron and the proton, the discovery of which has caused so much effort, have been so long treated as geometrical points. But is this correct? Is it not possible that they may have finite extension in space, that they may also

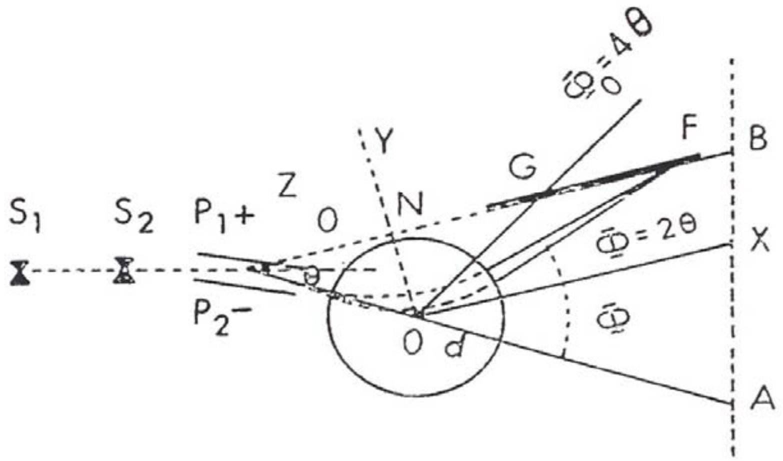


Fig. 10 Diagrammatic sketch of Aston's Mass-Spectrograph

[Positive Rays rendered parallel by the slits S1, S2, pass obliquely between two parallel plates P1, P2 between which the electric field is applied. They then pass through a wide slit O between the pole-pieces (shown as circle with centre O), giving a magnetic field at right angles to the plane of the paper. By properly choosing the fields, the rays having the same mass can be brought to a focus at a point on the plate F. In this way, the resolving power is much increased.]

possess some structure. According to the classical theory, the electron was regarded as a spherical ball of radius 'a'. If this ball be moved with the velocity v it can be shown from classical electrodynamics that it possesses the energy. $\frac{1}{3}\frac{e^2}{ac^2}v^2$, and hence we can suppose its mass to be entirely of electro-magnetic origin and equal to $m_0 = \frac{2}{3}\frac{e^2}{ac^2}$.

The radius of the electron turns out to be 10^{-13} cm. If the mass of the proton has the same origin, its radius must be $\frac{1}{1836}$ times smaller. But this leads to great difficulty in the comprehension of the physics of the nucleus, which is probably much smaller than 10^{-13} cm in radius, and still seems to contain electrons which are much larger. This is contradiction in terms!

The Rotating Electrons

In recent years, two facts of fundamental importance have emerged out regarding the finer structure of the electron. Physicists have long encountered great difficulties in accounting for the phenomena of magnetism. Since the time of Oersted, it has been known that electricity in motion gives rise to magnetism, and Ampere postulated that magnetism of iron and other substances may be due to the presence in the body of small closed currents of molecular dimensions. Barnett, Einstein and De Haas proved the existence of these experimentally, but the value of $\frac{e}{mc}$ comes out to be half of the value obtained from other sources. Apart from this difficulty this experiment proves that either the rotation of the electron round an axis in itself or its revolution in a circular orbit causes magnetism. But if we make the electron spin about an axis fixed in itself, then to account for the observed magnetic moment, the peripheral velocity of the electron has to be made many thousand times larger than the velocity of light. In spite of this stupendous difficulty, the theory of rotating electrons has been revived in recent years by Goudsmidt and Uhlenbeck; and has been found very useful in accounting for the complex spectra of elements.

The Electron as a wave

We have already referred to Lenard's old hypothesis that the cathode rays might be regarded as some sort of electro-magnetic radiation. This view, which was supposed to have been laid in its coffin for all eternity, has curiously been revived in recent years, though in a widely different way from that proposed by Lenard. The two, as a matter of fact, have no point of contact except in the use of the word 'Wave.' The order of events which led to this view will be taken up in the second lecture when we shall come to a review of the theories of light. But suffice it to say that an electron moving with the velocity v, may be replaced by a wave having the length $\lambda = \frac{h}{mv}$, and moving with the velocity $\frac{c^2}{v}$ larger than the velocity of light.

This view of the electron has to be adopted wherever the electron has to traverse dimensions of the same order of length as λ, just as light is to be regarded as a wave only when obstacles of its own order of dimensions are concerned.

The wave-view of the electron readily explains the experiments of Germer and Davisson on the regional reflexion of electrons from metallic crystals, but the experiments of G. P. Thomson who sent a homogeneous beam of electrons through thin foils of metal, and

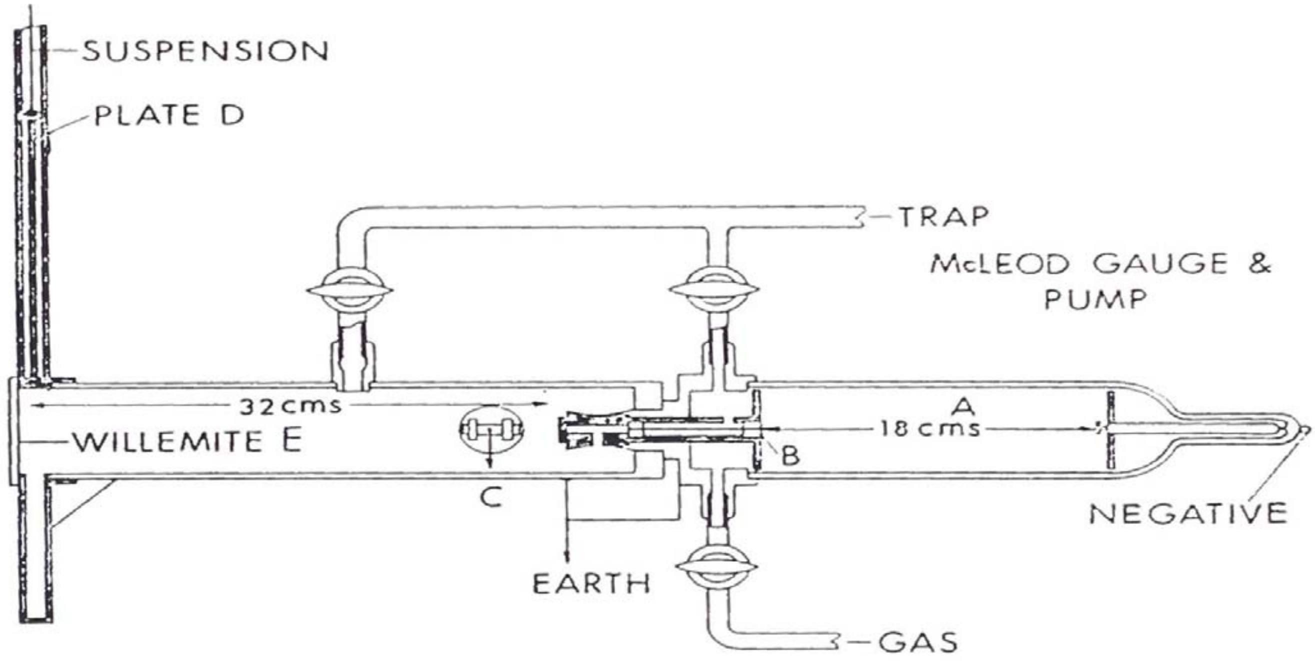


Fig. 11 G. P. Thomson's Apparatus for showing the Diffraction of Electron Waves

(The apparatus is essentially a Cathode Ray tube. A beam of Cathode rays, to which varying velocities can be given, is rendered parallel by passage through the narrow slit B, and is allowed to fall on very thin membranes of gold, aluminium celluloid, etc. placed normally at C: the effect can be viewed on a willemite screen at E, or photographed on plates placed at E. A series of concentric rings is formed round the central spot which is shown in the next figure.)

observed their effect on a photographic plate are more direct, and illustrative.

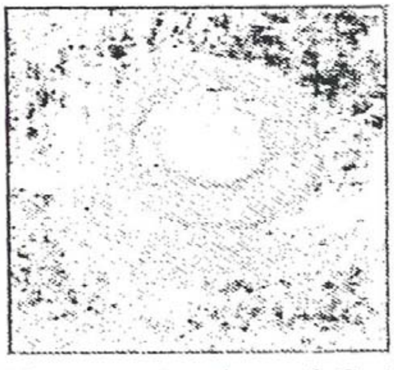


Fig. 12 This is a photographic reproduction of G. P. Thomson's Electron-wave experiment. The beam of electron was passed through a thin gold leaf. The haloes are due to the scattering of the electron-wave by the crystals of gold which are arranged haphazardly in the leaf

LECTURE 2 : RADIATION

I believe that all of you have seen a rainbow, and admired its beautiful display of colours, but you may not be aware of the service rendered by the rainbow to the progress of science. Leaving aside the speculations of the ancients, it is probably the phenomenon of the rainbow which led the philosophers of the mediaeval age to ponder over the nature of Light. Somehow they came to the knowledge that an artificial rainbow can be formed when white sunlight is passed through a triangular piece of glass. This knowledge was followed by the discovery of the laws of refraction (Snell).

Newton showed, about two hundred and fifty years ago, that when the colours of the rainbow (formed by an upright prism) are passed through a second prism, turned upside down the seven colours recombined forming white light.

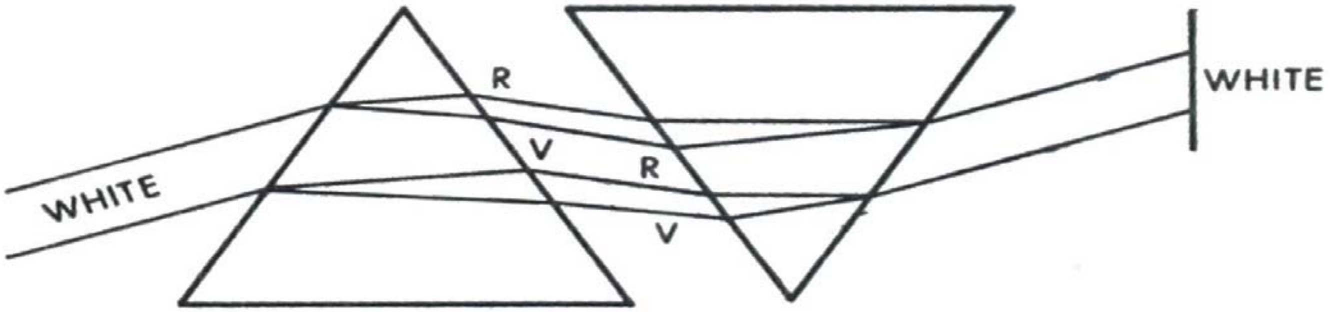


Fig. 13

The prismatic analysis of white light is probably the first experiment from which attempt was made to get at the correct physical nature of light. For two hundred years the best scientific brains of the world are grappling with the problem, but a satisfactory solution is not yet in sight. At times it appears that we are drawing nearer the goal, but like an elusive "Ignis Fatuus" it simply draws us further apart from the starting point.

Let us examine the present situation. If, at the end of the last century, you were to ask a physicist, "What is light?" he would unhesitatingly reply—"Light is an electromagnetic wave-disturbance in a universal medium called aether, and moving in free space with a velocity of 3×10^{10} cm per second." You will probably remark that this is not a very liminous definition of light. But nevertheless, if we wish to get at the bottom of things, we should make an effort for understanding the above definition.

Finite velocity of Light Propagation

To all external appearances, light is propagated instantaneously, but the great Galileo suspected that it required a small though finite time, to cover distances, and planned an experiment for measuring the velocity. The plan of the experiment was identical with that later carried out by Fizeau, but in Galileo's time, the difficulties proved to be insurmountable. It is to the astronomer Römer, belonging to the class of Savants who deal with enormous distances, that the world is indebted for the first clear proof of the finite velocity of propagation of light.

The planet Jupiter has four satellites which were first discovered by Galileo. These moons, as they revolve round Jupiter, periodically plunge into the shadow cast by the planet and are eclipsed. In 1675, Olaf Römer, a Danish astronomer, then in Paris, was measuring the period of revolution of the first moon of Jupiter. He observed the successive moments when the moon either plunged into, or emerged out, of the shadow. The interval found in this way was found to be 42 hr. 28 min. 36 sec. But continuing his observations still further, he found that the time-interval apparently was not the same at all times of observation. He began his observation when Jupiter was in opposition (position ESJ in Fig. 14). Some months later, when Jupiter was in conjunction (position SE_2J in Fig. 14), and the moon was to have appeared out of the shadow for the hundredth time he found that it was late by 16 min. 26 sec. He thought that this apparent retardation was due to the fact that in position ESJ, the light signal indicating the emergence of the moon out of the shadow, had to traverse a larger distance than in position SE_2J. In fact the excess is just the earth's orbital diameter. So the velocity comes out to be

$$= \frac{2988 \times 10^5}{986} = 3{\cdot}03 \times 10^5 \text{ km/sec.}$$

If the hypothesis be correct, Römer argued, then the apparent period of Jupiter's moon, as determined by the time-interval between two successive emergences out of the shadow should vary according to the relative position of the earth with respect to Jupiter. In posi-

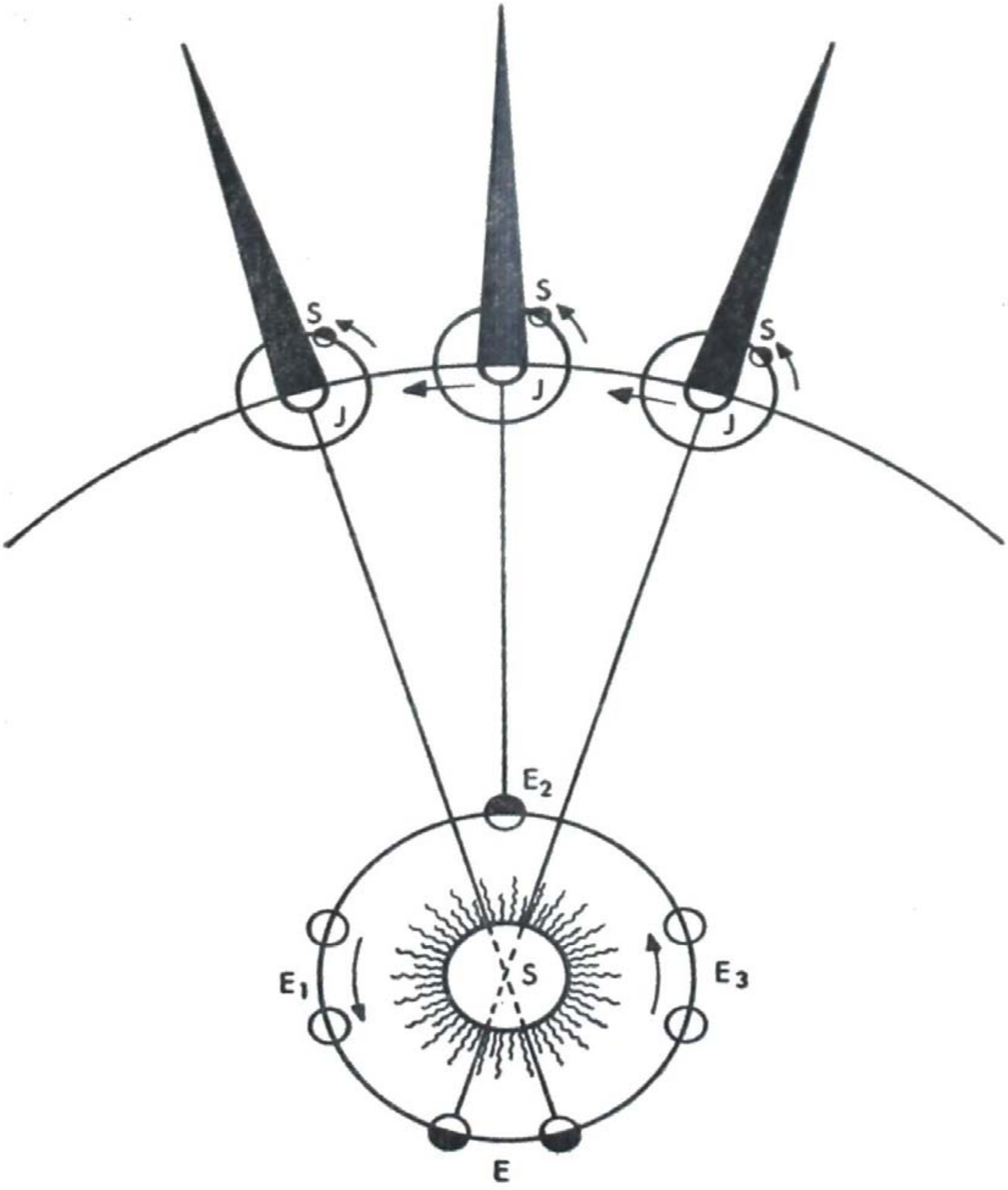


Fig. 14

tion E, the earth is approaching Jupiter, so the light signal has to cover a lesser distance. The amount is just the distance traversed by the earth in its orbit during a period of revolution of Jupiter's moon. The time interval between two successive emergences should therefore be less and Römer found it to be Ca 15 seconds. The earth travels 30 km per sec, so in 42 hr it has travelled ca $4{\cdot}5\times10^6$ km towards Jupiter. Light takes 15 seconds to cover this distance, so the velocity of light comes out to be 3×10^5 km per second.

Römer's discovery was not due to a mere stroke of good fortune as has been supposed in some quarters but was the result of clear intuition followed by arduous work. Yet it appears that his theory was not acceptable to most of his contemporaries. But it became impossible to deny him the credit, or to deny the existence of finite velocity of light-propagation when Bradley, about half a century later (1725), made a brilliant application of Römer's idea in explaining aberration, i.e. apparent displacement of the position of a star throughout the year owing to the relative velocity of the light signal from the star with respect to the moving earth—a phenomenon which Bradley himself had discovered.

The velocity of light, usually denoted by the latter 'c' has now acquired a greater importance than ever, because according to the Theory of Relativity, it is a fundamental constant of Nature.

Light as a wavemotion

You are probably aware of the various steps by which it has been proved that light is a wave-motion. Our usual experience tells us that light travels in a straight line and casts an exact geometrical shadow of any obstacle which is placed in its way. This and other observations gave rise to the corpuscular theory which regarded propagation of light merely as a flight of particles (light particles). But careful experiments show that these ideas are not always correct. Grimaldi, an Italian contemporary of Newton, admitted light through a very fine aperture in a dark room, and the spot of light on the screen was not quite sharp, but was surrounded by a circular ring. Two such rings in close juxta-position produced overlapping rings, and darkness sometimes resulted. The truth of this experiment is denied by many and Grimaldi himself followed the subject no further, being satisfied, that as two beams of light produce darkness, light is not material at all. Hundred years later, Young performed the experiment more carefully, and showed that light, when it encounters a straight edge does turn corner, and two beams of light when combined properly may produce darkness. He discovered the principle of destructive interference.

Ch. Huygens

The above-mentioned phenomena clearly prove that light is some sort of wave-motion, as was first contemplated by Huygens, the Dutch contemporary of Newton. He is justly regarded as the founder

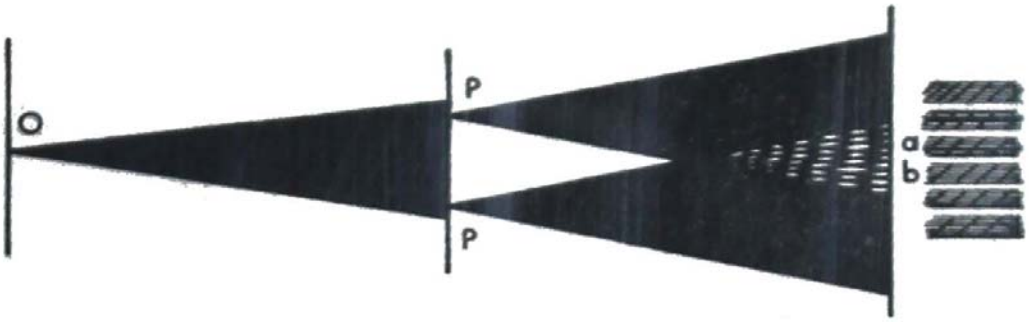


Fig. 15

[O is a minute aperture illuminated by sunlight or better by monochromatic light. PP′ are two fine holes in a screen about a millimetre apart. S is a screen about a metre off. We now get interference patterns on the screen. At A, where PA= P′A there is maximum illumination; at B, where PB−P′B=half a wave there is a minimum illumination. The diagram illustrates the principle of destructive interference. A visual idea of the bands is shown to the right.]

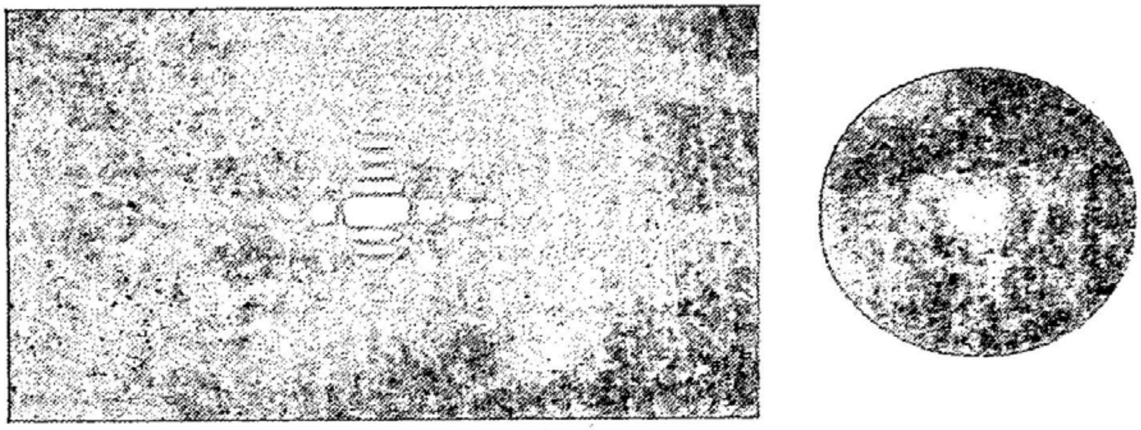
of wave-theory of light, which he set forth in opposition to Newton's corpuscular theory. But the theory remained life-less for about a century as the facts which it could successfully explain (refraction, reflection) could also be explained with equal case by the rival theory, and great difficulty was encountered in accounting for rectilinear propagation, and in finding out a medium with sufficiently materialistic and non-ambiguous properties which could transmit the waves. The first difficulty disappeared with the performance of Young's experiment, and discovery of the diffraction phenomena.

Diffraction

Diffraction is the name given to the phenomenon of bending of light round corners. When a beam of light passes through an aperture, and then falls on a screen, not only is the geometrical projection of the aperture illuminated, but light continues also for some distance into the shadow region. The phenomenon is illustrated in diagrams below.

The diffraction patterns were explained by A. Fresnel on the wave-theory combining Huygens' principle of secondary wavelets with Young's principle of interference.

The second difficulty still remains, though various theories of the luminiferous aether (the term is a legacy from the times of the Greek Philosophers) have been advanced from time to time. In spite of



(a) (b)

In Fig. 16 (*a*) are shown the diffraction patterns produced by a rectangular aperture. Fig. 16 (*b*) shows the diffraction patterns of a circular aperture. Note the bright rings round the central spot which occur in the shadow region

strenuous efforts, aether has, up to this date, remained largely metaphysical, i.e., all efforts to ascribe concrete properties have ended in confusion. Huygens' aether seems to have been a lightly movable liquid, a kind of superfine air, but in such a medium only longitudinal waves can exist. Huygens himself had discovered a phenomenon which could tell him that such a view was inadequate to account for the nature of light.

Polarisation: Two-sidedness of Light

This is the phenomenon of polarisation, or two-sidedness of light. The phenomenon can be very simply illustrated by examining light through two crystals of tourmaline. As one crystal is rotated with respect to the other, at one position, you get the maximum light, at 90° from this position there is no light at all.

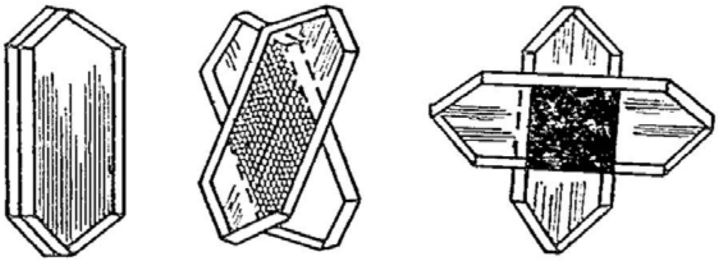


Fig. 17

Wave velocity and Group velocity

Huygens had pointed out that the correctness or otherwise of the two rival theories could be tested by a crucial experiment, viz., by measuring the velocity of light in different media. If light is a flight of corpuscles, the velocity in a dense medium shall be cn, where c is the velocity in vacuum, n=refractive index of the medium. If on the other hand light is a wave propagation, the velocity ought to be $\frac{c}{n}$. About two hundred years later, the crucial experiment was performed by Foucault, and the results turned out to be in favour of the prediction of wave-theory. On account of the importance of the theorem in subsequent developments, a proof is given below:

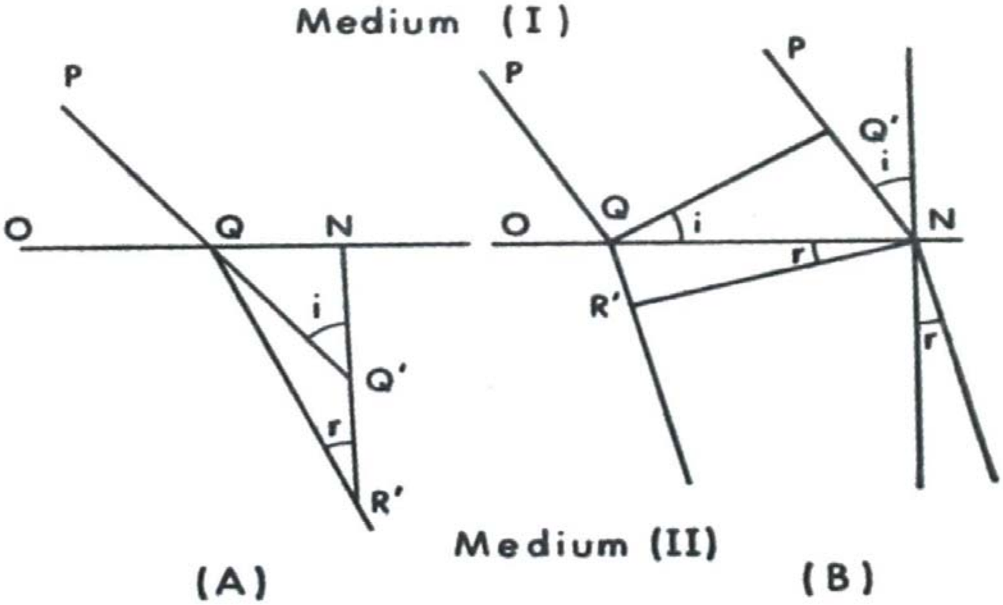


Fig. 18

Diagram 18(A) illustrates the propagation of light on the corpuscular theory. (I) is air, (II) is a denser medium. PQ indicates the ray of light in medium (I). QR in medium (II). If light consists of particles having momentum G, the component, tangential to the dividing surface ON will have the same value. Hence the normal component must be different.

Let G1 and G2 be the momenta in the two media. Then putting their tangential components equal

$$G_1 \sin i = G_2 \sin r$$

$$\therefore \frac{G_2}{G_1} = \frac{V_2}{V_1} = \frac{\text{Sin } i}{\text{Sin } r} = n$$

on $V_2 = nV_1$ or nc if medium (1) is Vacuum

Diagram 18(B) illustrates the propagation of light on the wave-view. PQ is the ray, QQ′ is the wave front in medium (I), QR is the ray in medium (II), NR is the wave front in it. It is clear that by the time the wave front traverses the distance Q′N in (I) it traverses the distance QR in (II). Hence if U_1, U_2 are the wave velocities in the two media

$$\frac{U_2}{U_1} = \frac{QR'}{Q'N} = \frac{\text{Sin } r}{\sin i} = \frac{1}{n}$$

$$\text{or } U_2 = \frac{U_1}{n} = \frac{c}{n} \text{ if (I) is vacuum.}$$

Fresnel's Aether

A. Fresnel is justly regarded as the third great founder of wave-theory of light. We have already referred how by combining Young's principle of interference with Huygens' principle of secondary wavelets, he could explain the phenomena of diffraction. To account for the two-sidedness of light, Fresnel put forward the hypothesis that aether had the properties of an elastic solid, and light consisted of transverse vibrations in it.

Fresnel's elastic solid aether, inspite of its difficulties, remained a living force for over half a century. It is no exaggeration to say that the whole of optics became recast in the Fresnelian mould. Those scientists who were sceptical, or challenged its correctness, had mostly to admit defeat. Whatever Fresnel predicted, or could be deduced from his theory, has been verified (e.g. conical refraction, deduced by Hamilton and verified by Lloyd, existence of a bright spot in the centre of the image of a diffracting disc observed by Delisle as early as 1715).

But the success of Fresnel's aether hypothesis, great as it was, could not mask its essential weakness. We at once ask "If aether is an elastic solid and at the same time fills all space, how do planets and other heavenly bodies move through such a medium without apparently encountering the slightest resistance ? So the old conception of aether, viz., a hyperfine liquid offering no resistance to the motion of bodies had to be retained side by side with the elastic solid properties. Fresnel himself made use of this conception in deducing his famous drag-coefficient.

Wavelength of light—Diffraction grating

When it was clearly recognised that light was a wave-motion, physicists tried to make an estimate of wavelengths of different kinds of light. Young was the first to make a rough estimate from measurements of Newton's rings, and found the wavelengths to be exceedingly small. This fact explained why diffraction of light could not be observed unless special arrangements were made. Precision measurements of wavelength of different colours became possible with the invention of the diffraction grating, a wonderful little apparatus which we owe to Fraunhofer, originally a spectacle-maker of Munich. The original grating of Fraunhofer was a rectangular rigid framework, in which a number of fine wires were stretched at equal intervals.

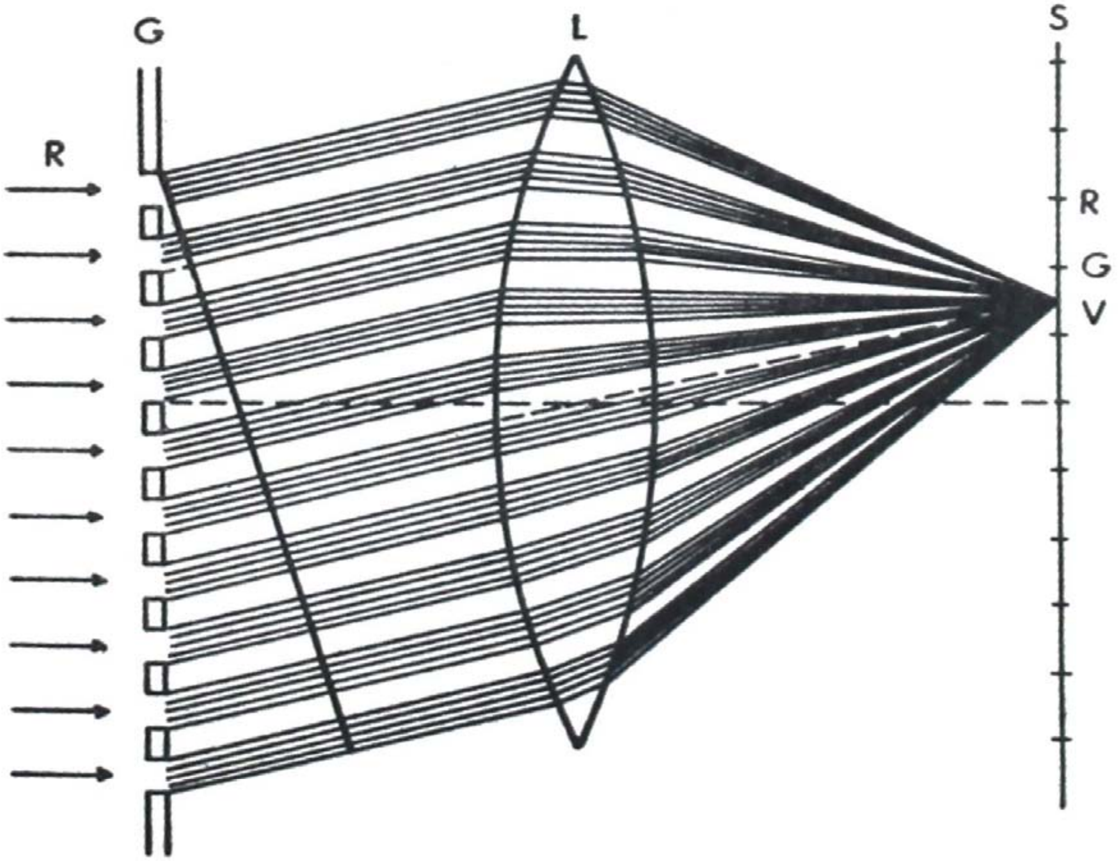


Fig. 19

When a parallel beam of light falls on such a grating normally, the little waves constituting light turn corner, and an application of the interference principle shows that light of a particular wavelength can be brought by means of a converging lens, to a focus on a definite point on the screen. The wavelength is given by the relation

$$n\lambda = 2d \sin\theta$$

other waves of light dying out by mutual interference at this point.

The Prism Spectroscope

As every school boy now knows, the prism spectroscope is the apparatus by which light from any source can be easily analysed. It is a direct descendant of Newton's prism apparatus, but it owes its present form to Fraunhofer.

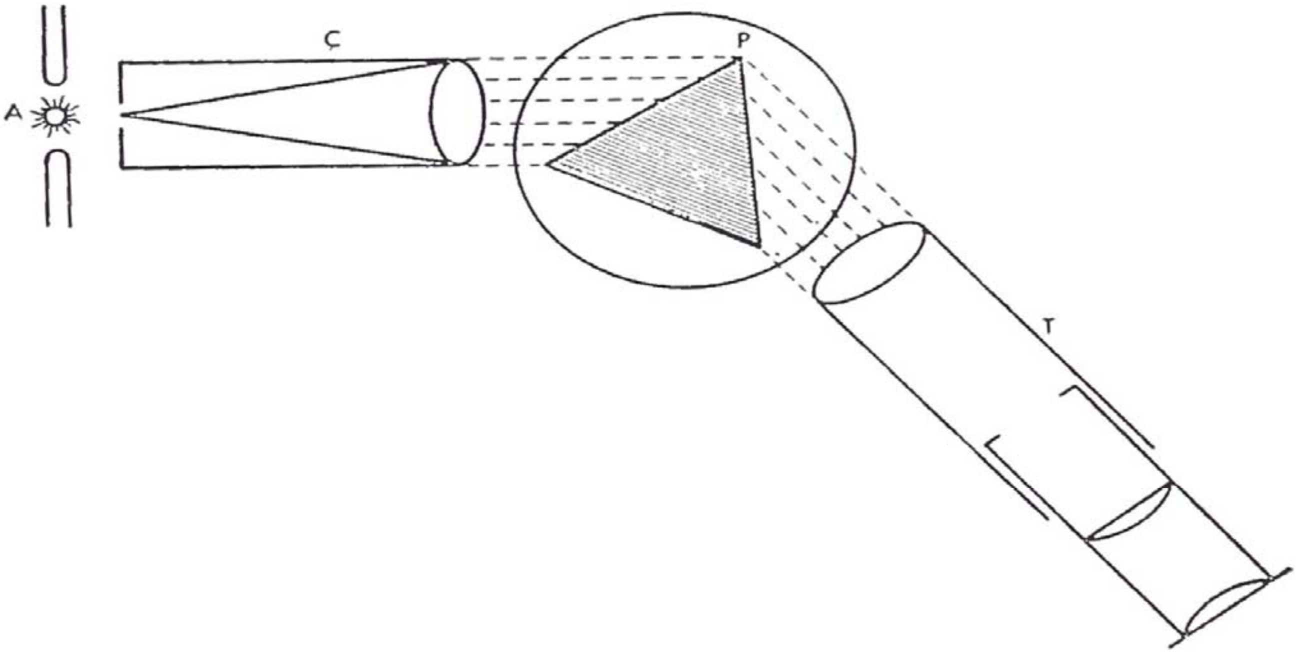


Fig. 20

A=Arc, C=Collimator, P=Prism, T=Telescope

Fraunhofer added the collimator for rendering the light parallel, and the telescope for collecting rays of a particular wavelength at a particular point. With these new improvements he converted the crude prism into an apparatus capable of wonderful precision and of immense potentialities.

Different kinds of Spectra

When different luminous sources were examined by the spectroscope, the light was found to be drawn out into bands to which the name spectrum is given. It was found very early that different sources of light emitted different types of spectrum. A glowing solid gives a continuous spectrum, a flame tinged with NaCl gives an intense yellow line on a dark background, while if we pass an electric discharge through a glass tube containing some gas, the spectrum consists of a number of fine lines extending from violet to red.

The Solar Spectrum

Armed with better apparatus, Fraunhofer examined the spectrum of the sun. To his great surprise he found that the spectrum was not continuous, but crossed by dark lines. Their number is at present known to be 20,000, but Fraunhofer noticed about 500 of them, and denoted the more prominent bands by the letters of the alphabet:—

$$\underbrace{\text{A B C}}_{\text{red}}\quad \underset{\text{yellow}}{\text{D E}}\quad \underset{\text{green}}{\text{F}}\quad \underset{\text{violet}}{\text{G}}\quad \underset{\text{beyond violet}}{\text{H K}}$$

Fraunhofer never understood the nature of these lines, neither did any of his contemporaries, but he realized their great importance, measured them and catalogued their wavelengths. He observed the spectra of stars, and encountered the same dark lines.

We shall see that these black lines are the hieroglyphics in which the Sun-god has written its own story.

Kirchoff—Discovery of Spectrum Analysis

The phenomenon of these black lines remained unexplained for a long time. Some physicists had observed that if the spectrum of the sun is observed side by side with the spectrum from a sodium flame, the yellow line appears just in the same place as the D-band of the Fraunhofer Spectrum. Strange to say, nobody before Kirchoff made any serious effort to connect the two phenomena.

The explanation given by Kirchoff not only completely solved the problem, but was far-reaching and extremely fruitful in its consequences. He supposed that the central body of the sun consists of a glowing mass which emits a continuous spectrum without black lines. But this light has to pass through the atmosphere surrounding the central mass. In this atmosphere, all the elements like Na, Cu.., etc., are present in the gaseous form in addition to ordinary gases like H, O, N, etc.

What will be the effect of the passage of light through this comparatively cooler mantle of vapour ? Balfour Stewart had studied the phenomenon of radiation earlier and had arrived at some very general laws. Every substance when heated emits radiation, i.e., light. Every substance has again got the power of absorbing light. Balfour Stewart had shown that emissive power is proportional to the coefficient of absorption. Kirchoff arrived, apparently without previous knowledge of Balfour Stewart's work at the same law, and applied it with wonderful success to the explanation of origin of the Fraunhofer Spectrum. Sodium can emit the D-lines when it is excited - hence when white light falls on it, it can absorb also the same light, and allows other light to pass through unmolested. The gases in the outer cooler mantle round the sun therefore deprive the continuous spectrum from the central mass, of the lines they themselves can emit and give rise to the black lines. The D-bands therefore prove that there is sodium in the sun's atmosphere.

But Kirchoff's discovery is of much more far-reaching importance than the mere success in explaining the Fraunhofer bands would indicate. It clearly asserted for the first time, that every different type of atom when it is properly excited, emits light of difinite wavelength which is characteristic of the atom. Just as a man is known by his voice, or a musical instrument by the quality of its note, so each atom can be recognised by the particular lines it emits. Thus was born the subject of Spectrum Analysis, which aimed at identifying elements by their characteristic lines, and forty new elements were added with its aid to the list already known. The different atoms are regarded as so many different types of instruments, each capable of producing its own characteristic aetherial music.

Besides spectrum analysis, Kirchoff's great work gave birth to the present science of Astrophysics or Physics of the sun and the heavenly bodies. Light is the only medium which connects us to the heavenly bodies, and any knowledge we wish to have about them can be obtained only by scanning their light. This is precisely the object of Astrophysics.

Extension of the Spectrum

The wavelength of light is found to be extremely small, red light being about $\cdot 7\mu$ long, and violet light about $\cdot 4\mu$ (μ=one-thousand part of a millimetre). Angstrom of Upsala introduced a new unit, now known after his name. It is a ten-millionth part of a millimetre. Red light has got a wavelength of 7000 Ångstrom units.

About 1840, Sir John Herschel showed that the spectrum of the sun is not abruptly limited on the red side, but extends considerably upwards. He put thermometers in the invisible part beyond the red, and found a rise in temperature. He could also establish the presence of Fraunhofer bands in the region beyond the red (see Fig. 21).

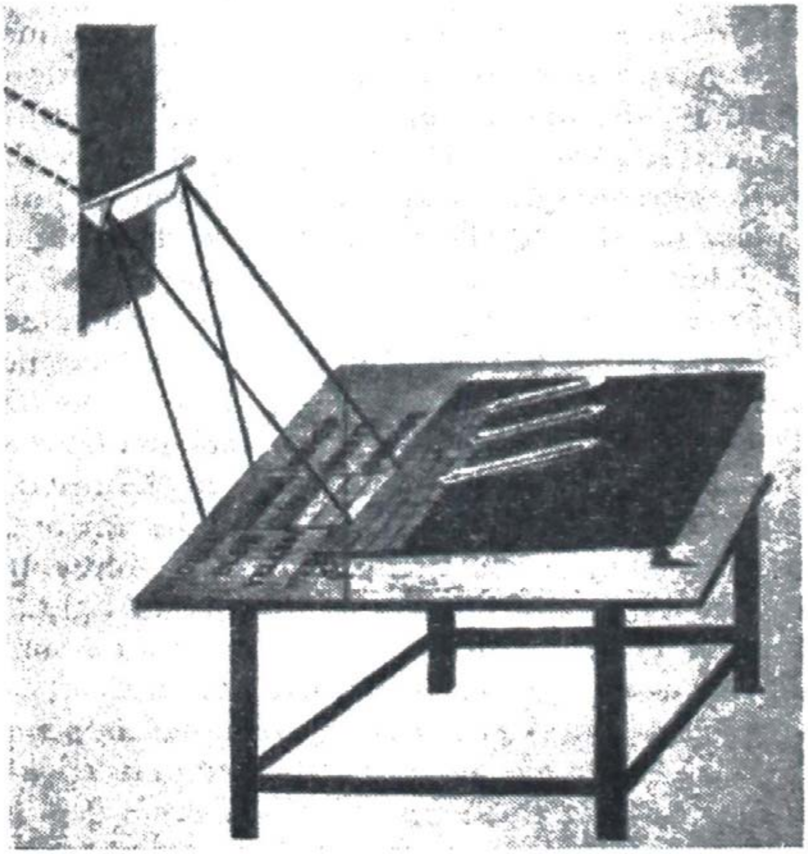


Fig. 21
(From Hale's *Beyond the Milky way*)

Similarly Ritter found that the solar spectrum was not limited on the violet side, but extended considerably downwards. This was proved by the fact that a photographic plate was affected even beyond the visible part. This region is known as the ultraviolet region.

At the present time, the spectrum has been extended on the short side to include X-rays which are simply ultraviolet light about one

Angstrom unit long, and γ-rays which are still shorter. On the long or infra-red side it has been extended to about $\frac{1}{3}$ mm. The whole range includes about 33 octaves, of which less than a $\frac{3}{4}$ octave only makes any impression on our eyes. "We are thus blind in an invisible ocean of light", as Sir J. C. Bose remarked in 1895.

The Electromagnetic Theory of Light

Up to the time of Fresnel, the phenomena of light were regarded only as an isolated group, and no connection had been traced between this and other great groups of natural phenomena such as Electricity and Magnetism. Though such a connection had been suspected by many, the first experimental proof was afforded by the great Faraday (Faraday effect). He put a piece of heavy glass between the poles of an electromagnet and passed a beam of polarized light through the glass parallel to the lines of force. He found that when the magnetic field was switched on, the plane of polarization was rotated through a certain angle. This clearly indicated that propagation of light can be affected by an external magnetic field.

But this experiment does not seem to have been followed by any speculations regarding the connection between light and magnetism. The first useful clue was obtained in the celebrated experiment of Kohlrausch and Weber who found that the ratio between the electromagnetically-measured and the electrosatically-measured units of electricity just amounts to the velocity of light.

In many quarters, this result was interpreted as signifying that electrical action is also propagated with the velocity of light. Gauss, Weber and Riemann indulged in many speculations regarding the modification which has to be introduced in the electrical laws when such is the case. But all these speculations remained barren until Maxwell, with clear intuition concluded that light disturbance is itself electromagnetic in nature. The way in which he did it is expressed by his celebrated field equations. We shall not try to deduce them, or explain them, for according to Hertz, Maxwell's theory consists of simply Maxwell's equations.

The field-equations were derived merely as mathematical theorems, and whatever service has been obtained from them regarding the nature of light is entirely due to Maxwell's imaginative genius. In this, he was, as he himself admits, influenced by Faraday's ideas, who thought that the medium between two charged particles was traversed by lines of forces, whereby the medium finds itself in a state of tension. It is now only a step to identify this medium with Fresnel's luminiferous medium which is also supposed to be thrown in a state of stress when light passes through it. The idea of dielectric polarisation, and the equivalent current when these changes occur, are special features of Maxwell's theory.

Maxwell showed that his equations lead exactly to the same equations for the treatment of optical problems as the elastic solid equations, but efforts to identify the elastic solid aether with the electromagnetic aether have always proved unsatisfactory. But they contain new conception, viz. that a ray of light consists of an alternating electric and magnetic force, mutually at right angles and also at right angles to its own direction, and that light is merely the flow of these quantities in the form of progressive waves.

Hertz

It is to the genius of Hertz that the world is indebted for the demonstration of the fullest possibilities of Maxwell's ideas, particularly of the hypothesis that a light ray is always accompanied by an alternating electric and magnetic force. He demonstrated by mathematical investigation that every oscillatory circuit produces about it electric and magnetic forces which are at right angles to each other and move forward with the velocity of light. The most efficient form is given by the Hertzian open oscillator.

Hertz produced eectromagnetic waves varying from 100 to a few metres in length and showed that these waves had all the properties of light. His experiments were taken up all over the world, and still shorter waves were produced purely by electrical means. Righi, Lebedew, Lampa and J. C. Bose made very short oscillators and could produce waves as short as 4 mm. This is about 3 octaves lower than the longest infra-red ray. Recently this gap also has been bridged by Arcadiew, Nichols and Tears.

Maxwell to Lorentz

Hertz's experiments and the short wave experiments clearly demonstrate that light is produced by a very minute Hertzian oscillator, of atomic dimensions, in other words, when an atom is excited to emit light, it may be likened to a Hertzian oscillator having a minute self-inductance and capacity. To work out this idea more fully, we must have some model of the electrical structure of the atom. This was not forthcoming for a long time, and only crude models were used. But from 1880, the electrical theory of matter seems to have captured the minds of many physicists, and Lorentz in particular introduced the idea of discreet charged particles to supplement the theory of Maxwell.

This was a distinctly progressive step, for Maxwell's theory, as left by that great investigator, was confined to the treatment of light as an electromagnetic disturbance in free space (or free aether as it was then called), and it hardly made any serious effort to explain the light phenomena in the interior of material bodies. The introduction of the electron rendered this possible—this became the go-between between matter and light (or aether as they put it in those days). Thus Lorentz recast the whole theory of dispersion—constructed by Sellmeyer and Helmholtz on the basis of oscillations of elastic solid particles—in the mould of the Maxwellian theory. The vibrations of the electrons took the place of the vibrations of the elastic solid particle. The equivalent electric current due to motion of electrons was added to Maxwell's displacement current, and expressions were obtained for the variation of refractive index with wavelength, which proved to be of great use in subsequent investigations. But the greatest triumph lay in the successful handling of Zeemann effect, which was due simultaneously to Lorentz and Larmor.

The Electron as an Oscillator

In all these investigations, we regard the oscillations of the electron as causing the phenomena of light. The electron becomes the atomic resonator. Following an investigation by Rowland, it was indeed proved by Lorentz that an accelerated electron becomes the source of electromagnetic radiation in the way represented in the following diagram (Fig. 22).

By making use of the idea of the electron-resonator, J. J. Thompson deduced his famous formula for scattering of X-rays which proved to be of the greatest use in the earlier days of investigations on the nature of X-rays. This work therefore presupposed the essential identity of X-rays and light long before Laue's discovery of crystal diffraction placed it beyond all shades of doubt.

The Aether

In all these works frequent reference is made to aether. If we take the view that the aether is simply the carrier of the system of Maxwell's equations, not much confusion is caused. But when

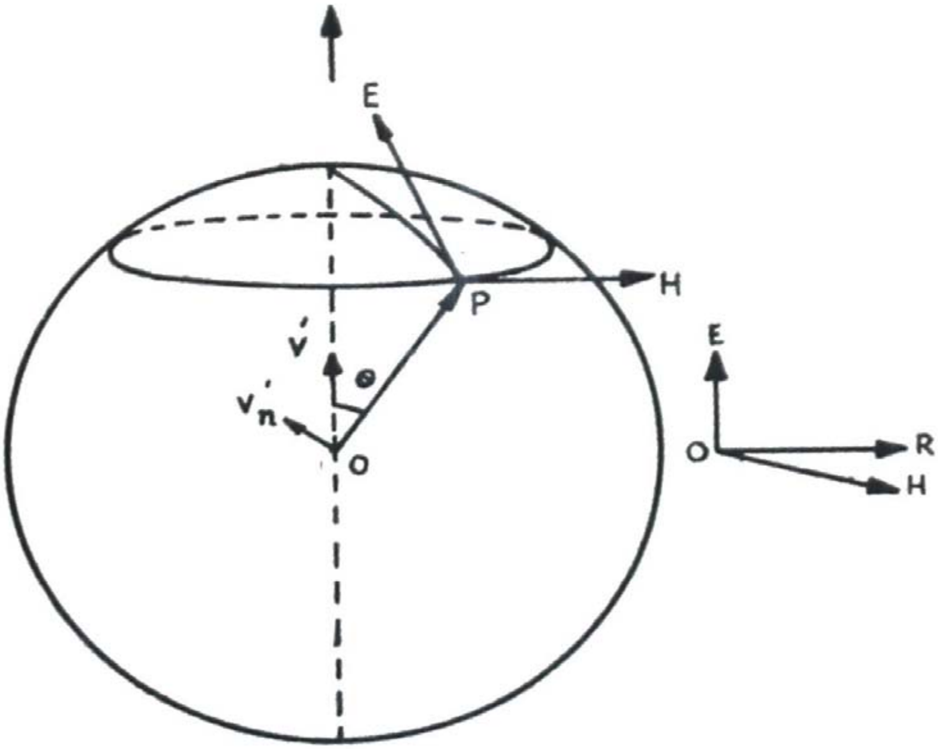


Fig. 22
(O-position of the vibrating election. V-acceleration; PE and EH directions of electric and magnetic force; OR—direction of the ray).

attempts were made to ascribe material properties to aether, confusion always resulted. Not more successful were the attempts to trace modifications in the properties of bodies when they move through aether, or the attempts to detect motion in aether. It is not possible to discuss these interesting topics at this place, though they are of the greatest importance in all theories of light.

The Theory of Relativity

The utter failure of all attempts to detect absolute motion, and Lorentz's demonstration that all optical and electro-dynamical experiments in moving bodies depend only on their relative motion, and not on their motion relative to an aether at rest shattered all hopes of ever giving a material picture to aether. Writing in 1905, H. Poincare expressed the opinion "It appears that this impossibility of demonstrating the absolute motion is a general LAW OF NATURE". In the same year appeared Einstein's profound speculations now known as the Theory of Relativity. In this theory, he makes no mention of aether, but starting with the principle of constancy of light, and the principle of invariance of forms of physical laws, he was able to deduce the transformations of time and space co-ordinates formerly deduced by Voigt and Lorentz as purely mathematical results. Minkowski showed that time and space formed a four-dimensional continuum.

The thoughts introduced by the principle of relativity are now invading all our theories in atomic physics, and causing a radical change in our conception of physical quantities. A deduction of great importance is the equality of energy and mass. Mass is simply energy divided by the square of the velocity of light so that even a quantum of light may be supposed to have a mass of $\frac{h\nu}{c^2}$ In place of the puzzling 'Aether' only pure vacuum occurs.

The generalized theory of relativity, worked out by Einstein in 1916, at present deals with the larger question of the origin of fundamental physical laws of all groups (light, electricity and gravitation) of phenomena, and tries to reduce them to still more fundamental principles. It has succeeded in predicting a connection between light and gravitation (deflection of a ray of light while passing close to a large gravitation field) which has been very satisfactorily verified. It has not yet succeeded in deducing Maxwell's electromagnetism from the same general principles, but the results are being anxiously waited. Whatever may be the final form which the theories of relativity may assume, it is clear that they are of great importance in the clearing up of atomic phenomena and phenomena of light propagation.

Revival of the Corpuscular theory: The Quantum

With the discovery of Hertzian wave, the triumph of the electromagnetic wave-theory seemed to be complete, there rose clouds from other quarters, and in fact from an observation first made by Hertz himself. The Maxwell-Hertz theory deals more with the propagation of light in the medium, it leaves the generation, at least when atomic dimensions are concerned, very much to itself.

About the year 1890, some physicists began to study this problem from another point of view. You are all aware that when we heat a body, it begins after some time, to glow, and emit light. It just becomes visible at a temperature of 525°C, and as the temperature is still further raised, shorter waves of the spectrum begin to be emitted. At 800°C, the colour emitted is still dull red, at 1300°C it becomes yellowish, while at about 2500°C, almost all the colours appear. At the temperature of the arc, the light becomes bluish white. The connection between colour and the temperature is so close that experienced people can tell the temperature by simply looking at the furnace. Still, the nature of colour emission to some extent depends upon the physical nature of the body but Lummer and Wien showed that we can realise a special type of body in which the emissivity has nothing to do with the physical characteristics, but depends only on the temperature of the body. Such a body is known as a perfectly black body and many experiments were performed, chiefly in Germany, to find out how the intensity of light of a particular colour emitted by such a body, varies with the temperature. The results of these experiments form the basis of the theories of temperature radiation to which we now turn our attention.

In the phenomena just described to you, heat is being converted to light. You know that heat is molecular motion, so that in this process, we are disturbing the atoms, they are knocking against each other, and their "electromagnetic" constitution is being disturbed. The question arises if we can find out in what way the emission of light depends upon the temperature? The task is a very arduous one, for it aims at connecting another two great groups of natural phenomena *viz.*, Heat and Light.

After the great success of the electromagnetic theory, the path seemed to be clear enough. Let us take a black body chamber filled up with radiation, and containing some monatomic gas. Let us introduce a via media between radiation and the gaseous molecule. This is achieved by the introduction of Hertzian oscillators of molecular dimensions; these serve a double purpose: they absorb energy from radiation, and transfer this energy by collision to the gaseous molecules. Planck showed from Maxwell's theory and from the theory of Hertzian oscillators, that the following relations subsists between the energy of an oscillator and the density of radiation in the space:

$$E_\nu = \frac{3c^3 U}{8\pi\nu^2} \qquad \ldots \quad (1)$$

Where E_ν = Energy of an oscillator
U_ν = Density of radiation of frequency ν

The oscillator is again in equilibrium with the gaseous molecules. Hence according to the law of equipartition of energy

$$E_\nu = 3kT \quad .. \qquad .. \quad (2)$$

From (1) and (2)

$$U_\nu = \frac{8\pi\nu^2}{c^3} kT.$$

This law, deduced in various ways and at various dates by Rayleigh, Jeans and Lorentz is obviously wrong, as all the energy is thrown into short waves, and was experimentally found to hold good only for long waves. Planck obtained in alternative formula which was subsequently found to be correct within all regions, by making assumptions of very radical nature.

He assumes that the oscillators can have either a quantum of energy ϵ or some multiple of it. It cannot have any intermediate value. Thus if we have an assembly of N resonators, some of them have the energy 0, some ϵ, some 2ϵ. . . and so on. The average energy is easily calculated to be

$$\frac{\epsilon}{e^{\frac{\epsilon}{kT}-1}}, \text{ instead of } kT$$

We have to make $\epsilon = h\nu$, in order that the formula may conform to the experimental results. Planck's assumption therefore marks a radical departure. The energy of an oscillator is supposed to be proportional to its frequency, and it can have, at any instant, an amount of energy which is a multiple of $h\nu$. Since the oscillator derives its energy by absorption from the field of radiation, it follows that radiation itself is atomic in structure, *i.e.*, should occur in cells having the energy-content '$h\nu$'. At least, this was the interpretation which was put forward by Einstein on Planck's hypothesis, and though it was opposed to the usual concepts of light propagation, Einstein brought very strong experimental evidence in support of his view. This is the phenomena of photoelectricity, originally discovered by Hertz, and subsequently elucidated by Righi, Hallwachs and Lenard.

The photoelectric phenomenon is really a very simple affair, and had it been discovered in 1800 instead of in 1900, probably the course of our theories of light would have been quite different. When ultra-violet light falls on a metallic plate, electrons are emitted from the plate which acquires a negative charge. Lenard investigated the velocity of emission of these electrons, and found that it does not depend on the intensity of light, but on its frequency.

Taking for example a piece of zinc it may be illuminated with the strongest red light for hours together. Not a single electron will be released. But if we illuminate it by the ultraviolet light from a quartz lamp, at once a swarm of electrons is released. Lenard found that the maximum energy of these electrons varied linearly with the frequency of light.

Einstein saw that this phenomenon was quite inexplicable from the older views of light propagation, according to which light from a source, as it spreads through space, goes on thinning itself continuously. If we illuminate a metallic plate with very feeble light from a spark, we can calculate the time which will be required by an atom to abstract sufficient energy from the incident radiation, in order that the electron may be released. The light may be made so feeble, that the time calculated comes out to be 45 min while actual observation shows that the phenomenon is instantaneous. We are therefore forced to the conclusion that light is propagated in space as "cells", containing the energy '$h\nu$'. At a great distance from a source, the number of cells decrease according to the inverse square law, but the individual cells retain their energy. If a "light cell" happens to fall on an electron, it transfers the whole energy to the latter, instantaneously a part is spent in releasing the electron from the parent atom, the remaining part is converted into the kinetic energy of the electron. We have thus according to the law of conservation of energy

$$h\nu=\tfrac{1}{2}\,mv^2+\mathrm{A}.$$

This law has been subjected to the most severe experimental test by Millikan, and found to be correct.

There is thus no escape from the view that light-cells do really exist.

But apart from such strong experimental support, the light-cell theory has been successful in a field where the wave-theory has signally failed to give any guidance, *viz.*, in the explanation of atomic spectra. We shall take this theory in detail in the next lecture.

Pressure of Light

There is another set of important phenomena which receive very satisfactory explanation from the 'cell' view of light propagation. These are the "Phenomena of Pressure of Light" in their application to astrophysical problems. These problems are not new, but date from mediæval times. Astronomers had observed that as comets sweep

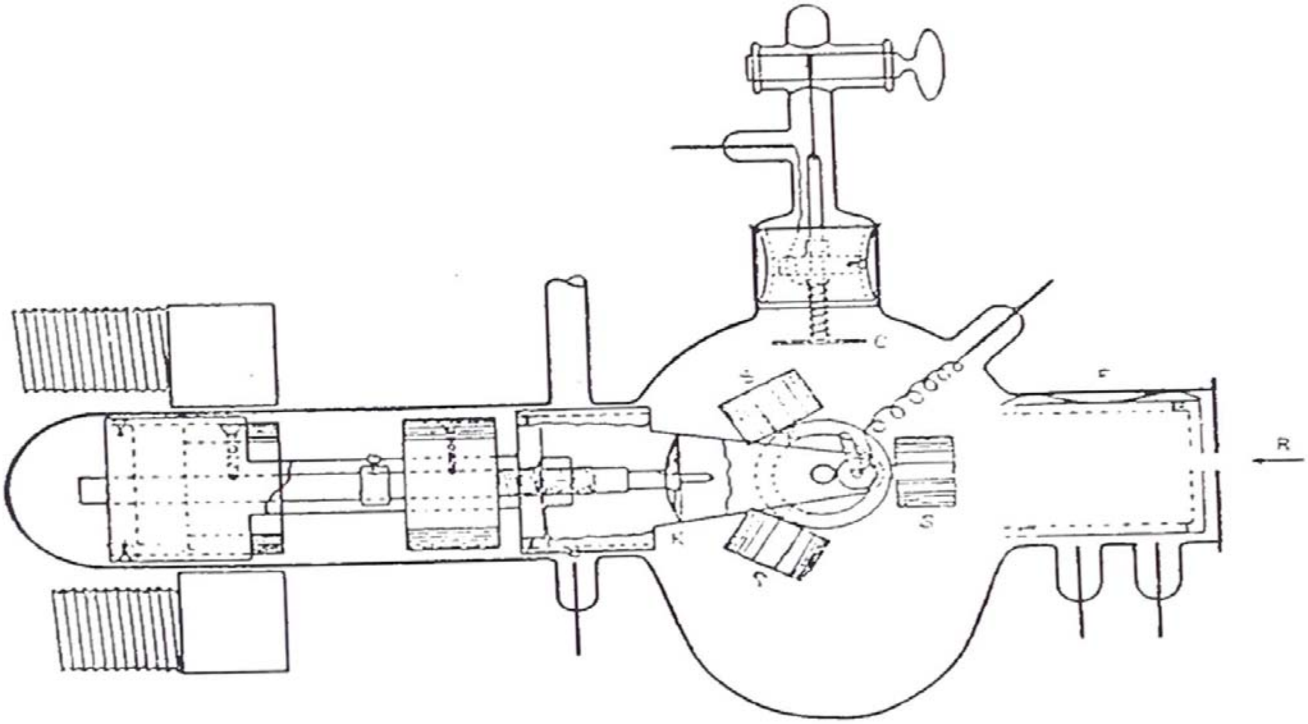


Fig. 23 Millikan's Apparatus for testing Einstein's Law of Photoelectric Emission.

(MILLIKAN'S EXPERIMENT)

[The whole apparatus is worked in vaccum. Connections are made from outside by electromagnetic devices. S is the block of sodium mounted on a rotating spindle. As it rotates, it is cut by the knife-edge K, so that a fresh surface is exposed. R indicates the direction of the beam of light, usually taken from a monochromator. F is a Faraday cylinder. C is a compensating copper disc. As light falls on the surface of S, photoelectrons are emitted, and allowed to charge F. The current is measured by a quadrant electrometer. It is found that the current completely disappears when the retarding potential (voltage imposed between S and F retarding the flow of liberated electrons) reaches a certain value. Light of different wavelengths are allowed to fall on S, and the corresponding maximum retarding potentials are measured. The relation between frequency ν, and the potential V is found to be linear, as we expect from Einstein's law $h(\nu-\nu_0)=e\,V$.]

round the sun, their tails are always projected in opposition to the line joining the sun with the nucleus of the comet.

It was supposed that as sunlight falls on the particles forming the cometary matter, strong pressure is exerted on them, and the particles align themselves opposite the line joining the sun and the nucleus thus forming the tail.

But the pressure of light could not experimentally be detected till 1902, when Lebedew demonstrated its existence on thin metallic mirrors. Maxwell had deduced the existence of the pressure of light

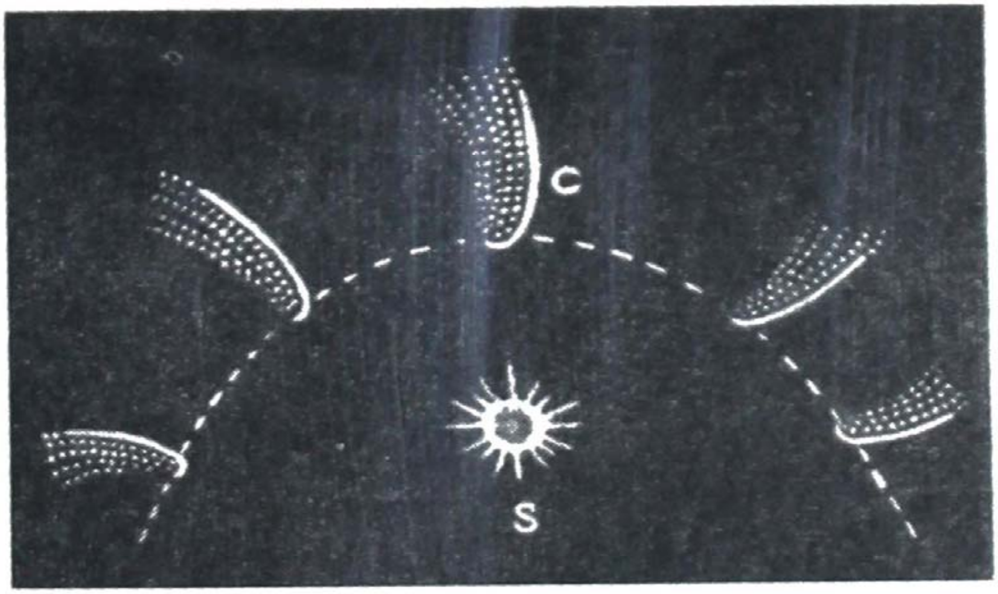


Fig. 24. Diagrammatic Sketch of the turning of the tails of comets opposite the direction of the sun. The phenomenon was known to Kepler, and suggested to him the idea of pressure due to light.

from his electromagnetic theory and found it to be $\frac{I}{c}$ where $I =$ intensity of light. But this theorem applies only to obstacles whose dimensions are larger than the wavelength of incident light. It therefore appears that, according to the electromagnetic theory, light can exert no pressure on atoms, and therefore the theorem of pressure of light can have no application in astrophysics.

But the quantum view removes all this difficulty. Einstein had shown that a pulse of light '$h\nu$' carries with it the momentum $\frac{h\nu}{c}$.

When a pulse of light falls on an atom, and is absorbed by it, it receives a forward kick. The action may be likened to that of a bullet on a target, supposing the bullet to be embedded in the target, and carrying it forward with its own momentum. The resultant pressure on an atom $= \frac{h\nu}{c\mathrm{m}} \times$ the number of times it absorbs the light, and is easily shown to be proportional to the intensity of light. Milne has shown that this occurs about 10^4 times per second on Ca^+ atoms existing in the atmosphere of the sun, and thus completely outbalances the action of gravitation.

Thus the "quantum view" not only removes all doubt regarding the existence of pressure on atoms, but it also says that such pressure can exist only if the atom is capable of absorbing the radiation concerned. The action is therefore selective, *i.e.*, if a continuous beam of light falls on the atom, only that fraction is operative which can be absorbed by the atom. Thus taking a stellar atmosphere where all types of atoms are present, and subjected to the incoming radiation from the photosphere, we find that the different kinds of atoms would be subjected to varying pressures and those who have got their resonance lines in the spectral region concerned would be most affected. This view explains, not only the abnormal distribution of elements in the atmosphere of the sun, but also the fact why the stars have got any atmosphere at all; for the value of gravity is so large on the stars that unless it is compensated by some other force the atmosphere should have practically no extension and stars would be left with the bare photosphere.

Compton Effect

Recently Prof. A. H. Compton of the University of Chicago has performed a beautiful set of experiments in support of the 'Light-atom' theory. We have already talked of Barkla's experiments on scattering. When X-rays fall on electrons, they are scattered sideways. Now if these X-rays are atoms of radiant energy, they must have a momentum, and in fact a far larger momentum than ordinary light atoms, because the frequency is thousand times larger. If they fall upon an electron, a part of this momentum will be communicated to the electron, just as when two men collide, they share the momentum of the shock between them. In this process, the electron will be thrown forward, and thus the scattered light-atom will be deprived of the stock of energy it was carrying. Since according to the atomic view, the frequency is proportional to the energy, the frequency of the scattered radiation will be less, it will have a larger wave-length. Compton proved this conclusion not only qualitatively, but also quantitatively. His experiments leave no doubt of the correctness of the 'light-atom' view and a subsequent experiment by Geiger and Bothe proves that the processes of softening of X-rays, and emission of back-kick electrons are simultaneous, and not average effects as imagined by Bohr, Kramers and Slater.

Fig. 25 illustrates Compton-Scattering. The primary beam of frequency ν_c, momentum $\frac{h\nu_0}{c}$ encounters an electron which may be supposed to be free. On receiving the shock, the electron is thrown

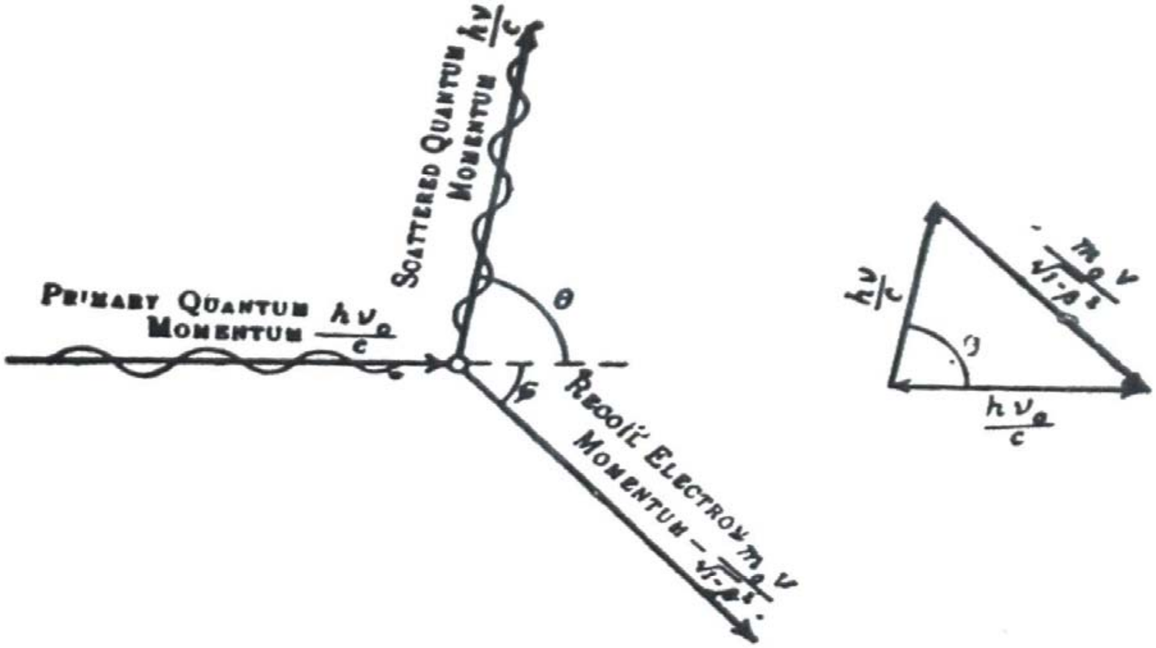


Fig. 25. Compton-Scattering of X-rays.

forward at an angle ϕ, with the momentum $m\nu$. The primary quantum is scattered at an angle θ, and loses a part of its energy which is imparted to the electron. Simple calculation based on the principles of conservation of energy and linear momentum shows that

$$\nu-\nu_0-=\frac{h}{m_0c^2}\nu_0^2(1-\cos\theta)$$

$$v^2=2\left(\frac{h}{m_0c}\right)^2\nu_0^2(1-\cos\theta)$$

The experimental test was carried out with the apparatus shown in Fig. 26.

R is a Röntgen-ray tube, S, S are lead slits defining a narrow pencil of Röntgen-rays, D is the scattering material, Ś , Ś indicates the beam scattered at 90°. The wavelength is measured by the crystal C and the ionisation chamber I. E is the electrometer. It is found that generally if we start with monochromatic radiation, we get in addition to the original beam, a beam modified according to equation given above.

So Compton's experiments prove in a very convincing way that X-rays of frequency ν carry a forward momentum of $\frac{h\nu}{c}$.

Therefore, in the treatment of the Phenomena of Light, we are faced with a puzzling duality. For explaining a class of phenomena

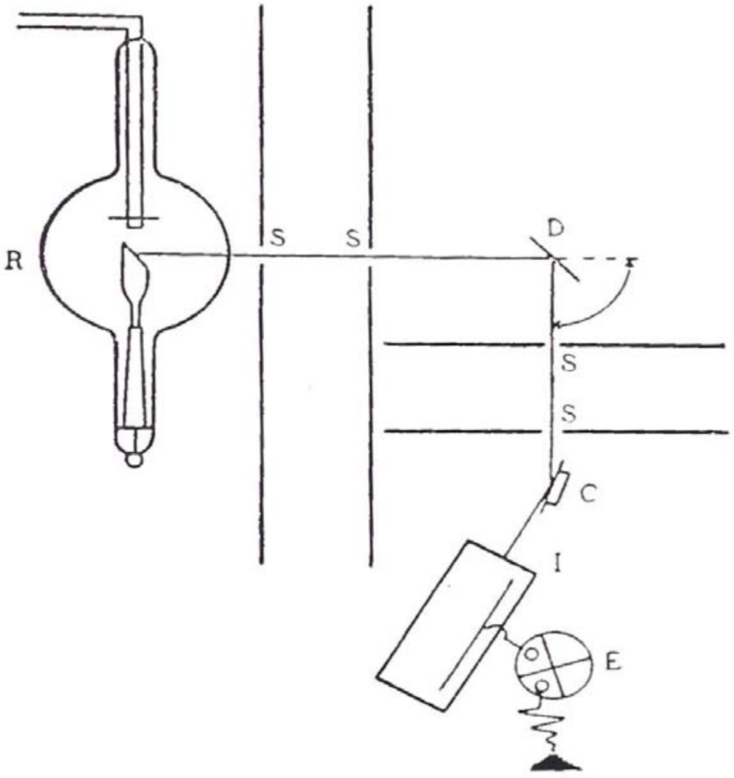


Fig. 26

we have to regard light as a transverse electromagnetic wave. For another class of phenomena, light is to be regarded as a pulse, or quantum of energy which retains its total amount in its journey through space. Apparently the two views are contradictory to each other, but a novel method of reconciling the two views has been proposed by De Broglie.

LECTURE 3 : THEORIES OF SPECTRA OF ELEMENTS & EXPERIMENTAL STUDY OF SPECTRA OF ELEMENTS

DURING the whole of the last century, the belief was almost universal that the atom was a non-divisible particle of mass with certain combining powers. In the first lecture, we have seen how this belief has been completely shattered owing to the discovery of the proton and the electron, and recognition of the fact that all elements are made up of these two which may be regarded as the two primordial elements. But the trouble of the Physicist begins instead of coming to a close at this point. He has now to explain the chemical and physical properties of elements in terms of their electrical structure.

Kirchoff's discovery had shown that the most characteristic property of the atom is its spectrum. As was already remarked we can compare the atom to a musical instrument, each spectral line then becomes a characteristic note of this instrument. But even the most casual acquaintance with spectral data shows that the analogy must not be stressed too far. Even hydrogen, the simplest of elements does not give a single line, but quite a large number. An element like iron gives in the visible range not less than 6000 lines of different wave-lengths. This fact led Rowland to remark that the atom is more complicated than even the grand piano.

The very vastness of spectroscopic data (witness—the seven thick volumes of Kayser and Runge's, and Kayser and Konen's Handbuch der Spectroskopie—even these are not sufficient to report all the results), combined with their complexity repelled even the greatest physicists of the last century against making any serious attempt in understanding them. The late Lord Rayleigh once declared that he did not wish to get engulfed in the bog of spectroscopy.

Work of Systematisation

Balmer's Discovery—The work of systematisation began with Balmer, a teacher in a Gymnasium at Basle, Switzerland, 1885. Hydrogen when excited in the discharge tube, gives a multitude of lines of which four stand out prominently from amongst the rest. These four lines are known as

$H_\alpha = \lambda\ 6562{\cdot}79$, Red
$H_\beta = \lambda\ 4861{\cdot}63$, Green
$H_\gamma = \lambda\ 4340{\cdot}47$, Blue,
$H_\delta = \lambda\ 4101{\cdot}74$, Violet.

Balmer showed that the wave-lengths of these four lines can be represented by the simple mathematical formula:

$$\lambda = 3645{\cdot}98 \frac{m^2}{m^2-4^2} \qquad \ldots \quad (1)$$

m is an integral number >2; $m=3, 4, 5, 6$ for H_α, H_β, H_γ, H_δ respectively. About this time, Hartley showed that it is more convenient to use reciprocals of wave-lengths or wave-numbers, ν, instead of wave-lengths. He observed that the spectrum of Sodium consists of a number of double lines. The difference between the wave-numbers of these doublets is constant for all lines of Sodium. The doublets are shown in Fig. 27, page 234. The wave-number separation is constant

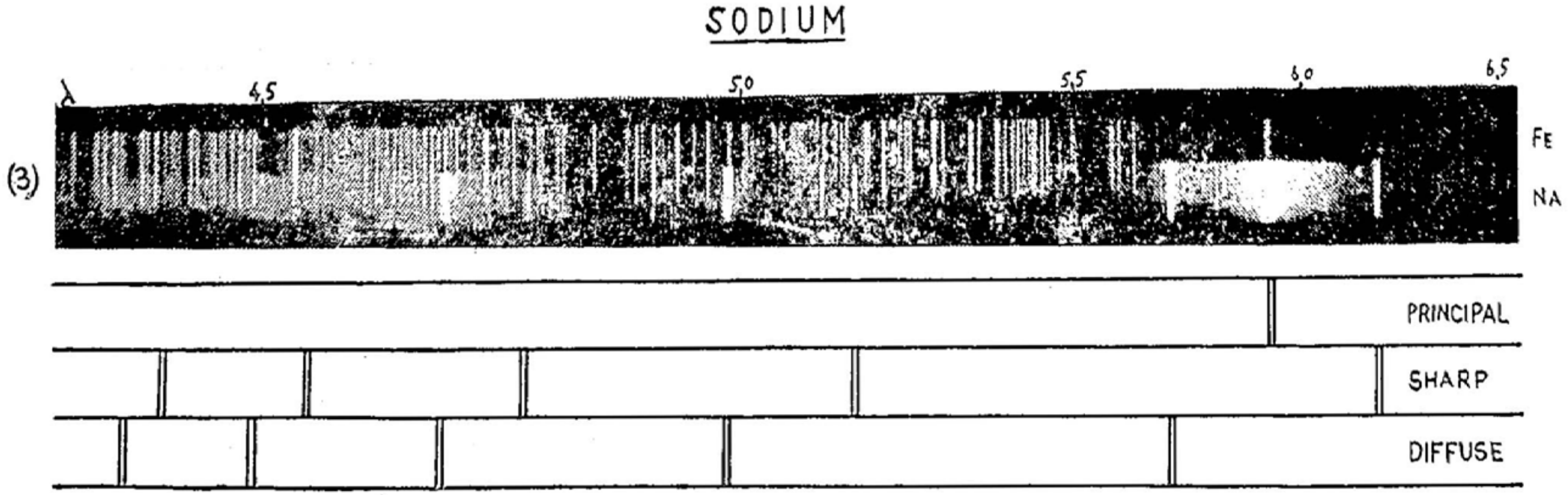


Fig. 27.—Sodium Spectrum, from Fowler's Report. The lines occur in pairs, and can be arranged into groups sharp and diffuse from their appearance. The D-lines do not belong to either group, but form the leading lines of another set of lines, forming the principal series. Spectra of all alkalies show a similar structure. Even hydrogen lines would show the same structure, but the separation being small, the lines appear as simple.

and=17. The lines can be subdivided into two groups: one group consisting of sharp lines, the other of diffuse lines. Each set from a series.

If now Balmer's law is expressed in wave-numbers, it appears that the hydrogen lines can be represented by the formula

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{m^2}\right) \quad \ldots \quad (2)$$

$$N = 109678{\cdot}3$$

If the law be correct, there is no reason why the series should stop at $m=6$. As a matter of fact, the astronomer Huggins discovered about 9 lines in the spectrum of the star Sirius, and 35 lines representable by the above formula have been discovered in the spectrum of the solar chromosphere. With improved technique, about 21 lines have been photographed in a Geissler tube discharge by Prof. R. W. Wood.

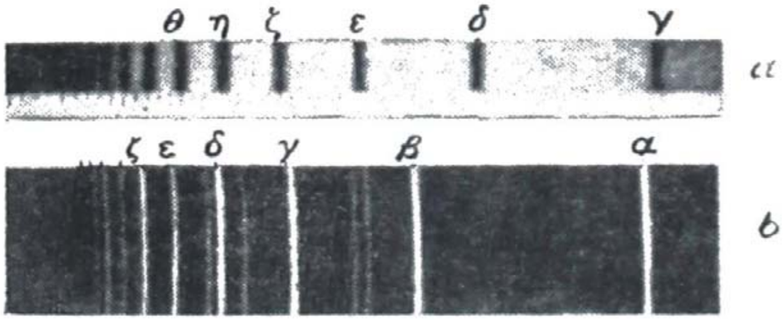


Fig. 28.—(From Fowler Report on Series Spectra.)
The lines of the Balmer series, as obtained in the spectra of Sirius (*a*) Vacuum tube (*b*).

Spectra of other alkalies—It was noted that the constitution of the spectra of other alkalies Li, K, Rb, Cs and partly also of Cu, Ag, Au is exactly like that of sodium. We get the same phenomenon of lines occuring in pairs with constant wave-number separation, the only difference is that the constant wave-number separation varies very roughly as the square of atomic weight.

There is thus, a striking correspondence between chemical properties and spectral characteristics, because all these elements belong to the same group in Mendeleef's Periodic Table, in fact Li, Na, K, Rb, Cs (alkalies) belong to even Group 1, and Cu, Ag, Au to odd Group 1. The analogy is not merely superficial but is far reaching, and was fully utilised by the later spectroscopists.

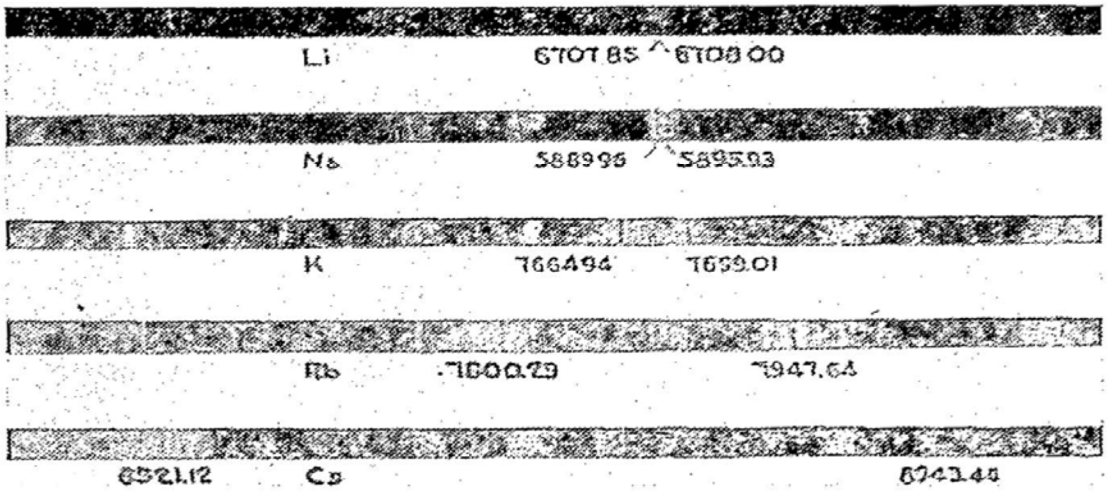


Fig. 29.—(From Foote and Mohler's *Origin of Spectra*, p. 88.)
The black lines represent the principal lines. Note that the separation increases as we pass on to the series Li, Na, K, Rb, Cs.

Rydberg Number—The number R was found to have approximately the same value from element to element. It was, therefore, supposed to be a constant and was christened as the Rydberg Number after Rydberg who took up the work of systematisation after Hartley and Balmer.

Work of Rydberg and Ritz

Balmer's discovery of the law of spectral series in hydrogen together with Hartley's law of constant wave-number separation have provided the clue to further analysis of spectra of other elements. With these two guiding clues, Rydberg and after him, Ritz, Paschen and Fowler, tried to systematize the spectra of alkalies and alkaline earths. Rydberg found that the lines with constant wave-number separation in Na (*vide* Fig. 27) can be divided in two groups, one group of lines being sharp, the other diffuse. He found that the wave-numbers of sharp lines could be approximately represented by a formula of the type:

$$\nu = A - \frac{R}{(m+s)^2} \quad \ldots \quad (3)$$

where m is the running integral number 3, 4, 5 . . . . ., s is fraction which has approximately the same value for different lines, A and R are constants.

This formula may be looked upon as a generalisation of Balmer's formula for hydrogen. R has approximately the same value in both cases, hydrogen and sodium.

In sodium, we have the sharp series,

$$\nu = A_1 - \frac{R}{(m+s)^2},\quad \nu = A_2 - \frac{R}{(m+s)^2} \qquad \text{..} \quad (4)$$

and the series of diffuse lines $\nu = \left.\begin{matrix} A_1 \\ A_2 \end{matrix}\right\} - \frac{R}{(m+d)^2}$.

A_1 and A_2 refer to the two members of the doublet, $A_1 - A_2$ is the constant wave-number separation 17.

But a set of lines (including the fundamental D-lines) are not included in this group. Rydberg and Schuster showed that they (D-lines) can be represented by the formula:

$$\nu = \frac{R}{(1+s)^2} - \left.\begin{matrix} A_1 \\ A_2 \end{matrix}\right\}$$

i.e., the D-lines are the negative members of the sharp series (Rydberg Schuster Law).

A_1 and A_2 can be represented as $\frac{R}{(2+p_1)^2}, \frac{R}{(2+p_2)^2}$.

If we write out the expression

$$\nu = R\left[\frac{1}{(1+s)^2} - \frac{1}{(m+p_{1,2})^2}\right]$$

p_1, p_2 are certain fractions and we get all the other lines ($\lambda = 3303$, . . . corresponding to $m = 3, 4...$). These lines are said to form the principal series.

Summarising the above results, we find that every line can be represented as the difference of two numbers, *viz.*, $\nu = \nu_i - \nu_f$.

Every one of the numbers, or terms ν_i, ν_f can be expressed as

$$\nu = \frac{R}{(m+d)} \qquad \text{..} \quad (5)$$

where m can take only integral values, R is a constant, and d is a fraction.

Thus the spectrum of an element like sodium can be expressed in associated families of terms, which is illustrated in the diagram given below:

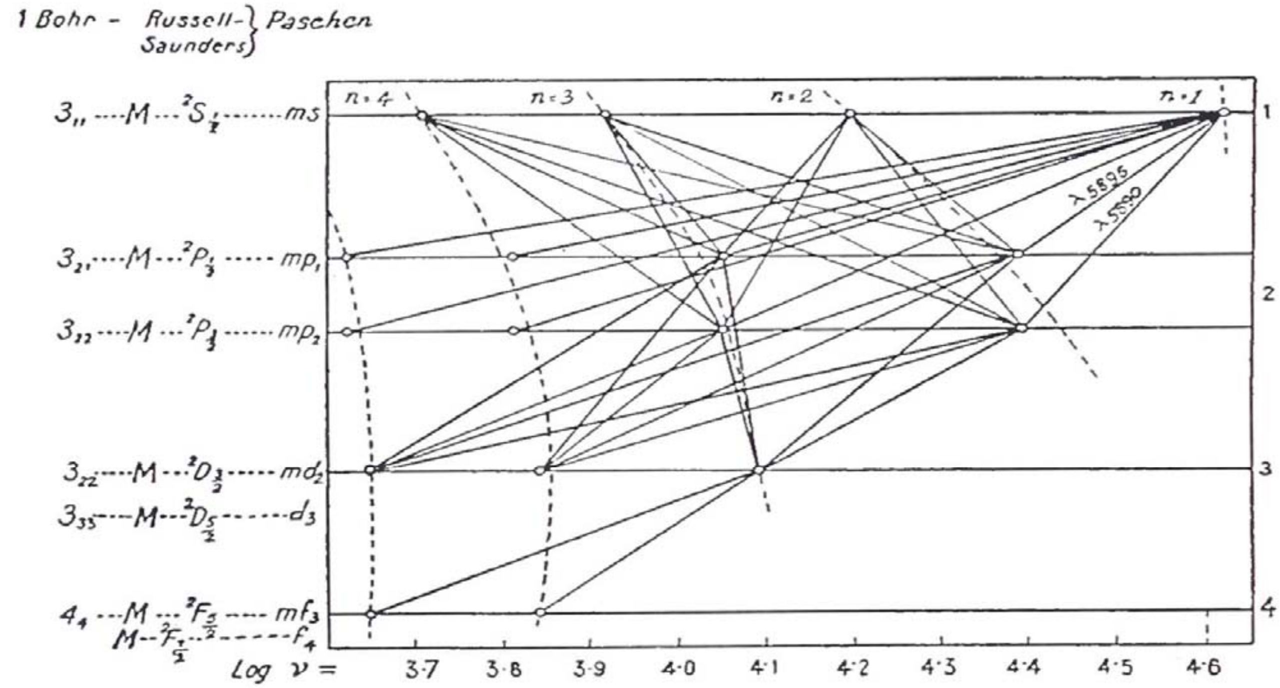


Fig. 30.—(Optical Levels of Sodium.)

(The uppermost horizontal line represents the family of s-terms, the next two represent the pair of p-terms, then we have the d, and f-terms. d and f are also double, but they are shown as single, because the separation is small; for explanation of the other symbols *vide supra*.)

The Principle of Combination

Ritz established from analysis of spectra of elements of Group II that in all cases, the wave-number of every line can be represented as the difference of two terms ν_f and ν_i ; these terms can be grouped into families, and each family can be represented by series formula of a generalized Rydberg type. This discovery is of the greatest importance in atomic physics, and is generally known as the *Principle of Combination*. Attention was now focussed on the terms instead of on the lines, and some idea of discontinuity in line emission is automatically suggested.

It was on the basis of these Keplerian works that Bohr built up his theory of the hydrogen spectrum.

Bohr's Theory of Hydrogen Spectrum

Bohr was impressed with Rutherford's discovery, that the positive electricity occupied a very minute space in the centre of the atom. He compared the atom to a planetary system. The nucleus of positive electricity with its very large mass plays the part of the sun. The electron with its small mass plays the part of the planet. Like the planets, it is attracted according to the inverse square law, and is saved from falling into the nucleus by its constant motion. So the whole theory of planetary motion can be transferred to atomic physics.

But there is one important desideratum: for finding out the motions of planets, merely a knowledge of the masses and the laws of motion do not suffice. We need also the boundary or the initial condition. We must know with what velocity and at what distance the particle has been projected initially. While this is possible in planetary motion, we cannot find out such conditions for the case of the atom.

Supposing that the orbit is circular, we can easily write out the equation of motion and the equation of energy. Supposing the nucleus to be at rest, we have (m=mass, a=radius of the orbit, ω=angular velocity, e=charge on the electron, E=charge on the nucleus)

$$ma\omega^2 = \frac{e\mathrm{E}}{a} \quad \ldots \quad (6)$$

Total energy=potential energy+kinetic energy

$$= -\frac{e\mathrm{E}}{a} + \frac{1}{2}\,\mathrm{ma}\omega^2 = -\frac{e\mathrm{E}}{2a} \quad \ldots \quad (7)$$

(potential energy is taken as negative, because the force is attractive).

Without a further condition, we cannot calculate either 'a' the radius of the orbit, or ω, the angular velocity of revolution in the orbit. Here Bohr made use of a very clever suggestion of Nicholson who had been busy with an alternative theory of spectra. Nicholson had observed that Planck's quantum h has the same dimensions as angular momentum. Bohr assumed that the angular momentum of the electron $ma^2\omega$ is closely connected to h. He put (certainly after some trial)

$$ma^2\omega = n.\frac{h}{2} \quad \ldots \quad (8)$$

With this second condition, we can completely solve the equation of motion. We get:

$$E = -\frac{2\pi^2 e^2 E^2 m}{h^2} \frac{1}{n^2} \qquad .. \quad (9)$$

$$a = \frac{h^2}{4\pi^2 e^2 m} n^2 \qquad .. \quad (10)$$

Thus the quantum condition (8) puts a restriction on the number of possible orbits. Only such orbits are possible which are distinguished by the integral quantum numbers n and have the energy E and the radius a, as given in (8) and (9).

Bohr now introduces a second postulate. If the electron changes from the orbit n' to the orbit n the energy will be changed from $E_{n'}$ to E and the difference will be radiated as a light-pulse. According to Planck, if ν=frequency of the pulse, the energy of the pulse=$h\nu$ and Bohr puts

$$h\nu = E_f - E_i$$

where the subscript 'f' denotes the final orbit, 'i' denotes the initial orbit. Hence we get

$$\nu = \frac{2\pi^2 e^4 m}{h^2}\left[\frac{1}{n^2} - \frac{1}{n'^2}\right] \qquad .. \quad (11)$$

If we put $n=2$, and allow n' to take up all the integral values 3, 4 . . . . we get the Balmer series.

Bohr showed that formula (11) agrees not only in the form but also in the absolute values with Balmer's formula. The Rydberg constant

$$\text{R must equal } \frac{2\pi^2 e^4 m}{h^2}$$

Taking the known values of e, m and h, Bohr found that R should be theoretically 109723 while from spectroscopic data, R=109676 for hydrogen. The agreement is thus excellent, but Bohr's theory predicted more than it proved. If the theory be correct, we should have an orbit corresponding to $n=1$ and a series of lines represented by the formula

$$\nu = N\left[\frac{1}{1^2} - \frac{1}{n'^2}\right] \qquad .. \quad (11A)$$

$$n' = 2,\ 3,\ \ldots .$$

Bohr pointed out that the wave-length of the first line would be about 1216 A.U. This is in the Schumann region. Prof. Lyman of Harvard photographed these lines with his vacuum spectrograph in 1914.

We should also get series corresponding to

$$\nu=\mathrm{N}\left(\frac{1}{3^2}-\frac{1}{n'^2}\right),\ \nu=\mathrm{N}\left(\frac{1}{4^2}-\frac{1}{n'^2}\right)$$

The first series was observed by Paschen before the advent of Bohr's theory the second series has been recently discovered by Brackett. Both of them are in the infra-red.

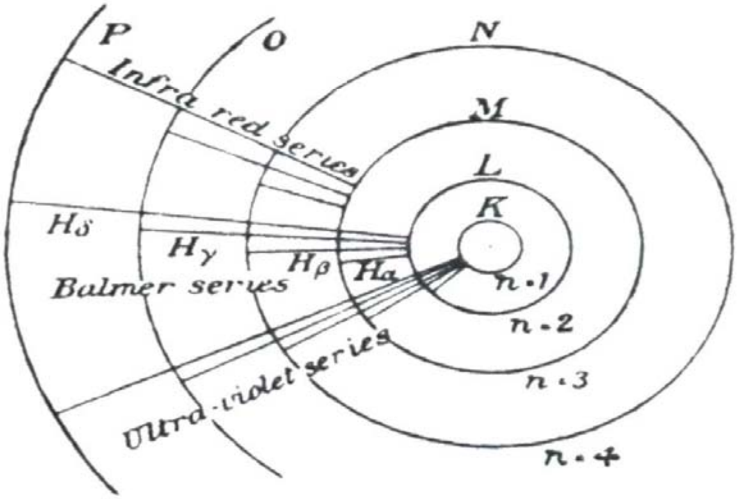


Fig. 31.—(From Crowther, *Electron Theory of Matter*, p. 299.)

Figure 31 gives a geometrical representation of Bohr's theory of hydrogen spectrum. The stationary orbits are represented by 1, 2, 3, 4. . . . when the electron falls from any one of the outer orbits to orbit 1, we get emission of Lyman lines. If they fall to the orbit 2 we get emission of Balmer lines.

In absorption, the opposite process takes place. The electron shifts from the 'inner orbits to some outer orbit' Ordinary hydrogen gas is however transparent to all its characteristic lines, as it occurs in the molecular form. But if an electric current is passed through the hydrogen gas, it is partly atomised, and can then be made to absorb its characteristic spectra. For absorption of Balmer lines, however, the electron must be raised to the second orbit. Ordinarily the first orbit is the most stable and may be called the normal orbit, The outer orbits are sometimes known as excited orbits.

The radius of the 1st orbit $= \frac{h^2}{4\pi^2 e^2 m} = 0\cdot538 \times 10^{-8}$ cm when we calculate it from known values of h, e, and m. It is in agreement, as far as the order of dimension, with the values obtained from the kinetic theory of gases. The radius of the nth orbit.

$$a = a_0 \, n^2 = 5\cdot38 \times 10^{-9} \, n^2 \text{ cm} \qquad \text{.. (12)}$$

For the line H_{35} (observed in the chromosphere)

$$a = 7\cdot5 \times 10^{-6} \text{ cm}.$$

Orbits with such large diameters can be developed only in regions of extreme tenuity. This explains why in ordinary vacuum tubes, only a few series lines can be observed. As the pressure is progressively diminished (as in Wood's experiment) more lines come out. The same phenomenon is shown in stars. In the Fraunhofer spectrum of the Sun, which is a dwarf-star (with a rather dense atmosphere), we get only 5 Balmer lines. In the spectrum of Sirius (dwarf A-star) we get about 10 lines. In the spectrum of α-Cygni (a giant-star with extremely tenuous atmosphere) we get no less than 24 lines.

General Explanation of Spectra

Bohr pointed out that the theory could be developed to give a general explanation of more complicated spectra. In the general case, the atom consists of a central positive charge z with z-electrons revolving round it. We can suppose that the light-vibrations are due to only one or the outermost electron. This moves in the field of a nuclear charge z, and $(z-1)$ electrons. Roughly the field is that due to a net charge of unity in the centre. Hence we should get the same Rydberg number in the spectra of all elements. The fractions which occur in the Rydberg denominators represent the effect of the reisdual field.

The principle of combination is now very easily explained. Every spectral term measures the energy of the stationary states of the atom, which are defined by quantum numbers. The energy is in fact equal to $A - h\nu$, where ν is the value of the term number, A is a constant.

Enhanced Lines

Long before the discovery of the electron, the astronomer Sir Norman Lockyer, guided by his experience of the spectra of different stars, had put forward a hypothesis of proto-elements and sub-atomic particles. He had observed that the nature of the spectrum of an element was not invariable, but varied with the stimulus. To make matters clear, we may take the spectrum of Calcium in the flame, the arc, and the spark. In the flame the excitations is lowest, in the arc it may be said to be average and it is highest in the spark. It may be rendered still higher by putting a number of condensers in parallel with the spark (method of condensed discharge). Lockyer found that certain lines of calcium are peculiarly sensitive to excitation. In the flame the strongest line is the *g*-line of Fraunhofer λ 4227, while two other characteristic lines, *viz.*—the H, λ 3968 and the K, λ 3934 are rather faint. With increase of stimulus, the H and K are relatively much more intensified than the *g*. In the arc, they are almost equal in strength, while in the spark the H and the K are much more intense than the *g*-line. The lines of calcium can be divided into two groups—one set of lines showing a behaviour similar to that of the *g*-line, they are known as arc lines. The second set getting intensified along with the H, K-lines, they are known as Enhanced lines or Spark lines. The phenomenon is quite general and is shown by all elements without exception.

Systematisation of Enhanced Spectra

Lockyer observed that the enhanced lines of elements become progressively more intensified in the hotter stars, which are supposed to be earlier in evolution, and he thought that they were due to some primordial form of the element (protoelements). Thus the *g* was ascribed to ordinary calcium while the H, K were ascribed to proto-calcium. The hypothesis was rather vague. The real clue to change in the character of the spectrum was obtained in the work of systematisation of the enhanced spectrum of Magnesium which was carried out by A. Fowler. He showed that these enhanced lines of Magnesium could be arranged in series, exactly as in sodium, but the Rydberg number is now 4R instead R. This is a general feature of enhanced spectra of all elements, *e.g.*, of Ca, Sr, Ba.

Bohr's Explanation of Enhanced Spectra

Bohr could now easily explain the enhanced spectra of elements. We have seen that the Rydberg number

$$R = \frac{2\pi^2 E^2 m}{h^2}$$

We put $E=e$ for hydrogen, and in a general way for all neutral elements. But if $E=ze$, or the net central charge is z-times the electronic charge

$$R_z=z^2R=4R \qquad \text{if } z=2.$$

This cannot happen with hydrogen, but it is quite possible with Mg or Ca. If the excitation be so great, then Mg loses one electron, then the outermost electron of the ionised atom will vibrate as if the net central charge is 2. The Rydberg number will now be 4R; in other words, the enhanced spectra of Mg, Ca and other alkaline earths are due to the ionised forms of these elements or to be more brief due to Mg^+, Ca^+ . . .

It now becomes clear why the enhanced lines should come out prominently only under great excitation.

Enhanced Spectra of Higher Orders

If the excitation be sufficiently great, the atom may lose more than one electron, and we may have enhanced spectra of still higher orders, with the Rydberg constants 3^2R, 4^2R, 5^2R . . . Lockyer actually obtained enhanced spectra of different orders in Silicon, and other elements and designated them as being due to Si I, Si II, Si III, Si IV.

Fowler had no difficulty in showing that they are due to Si, Si^+, Si^{++}, Si^{+++}.

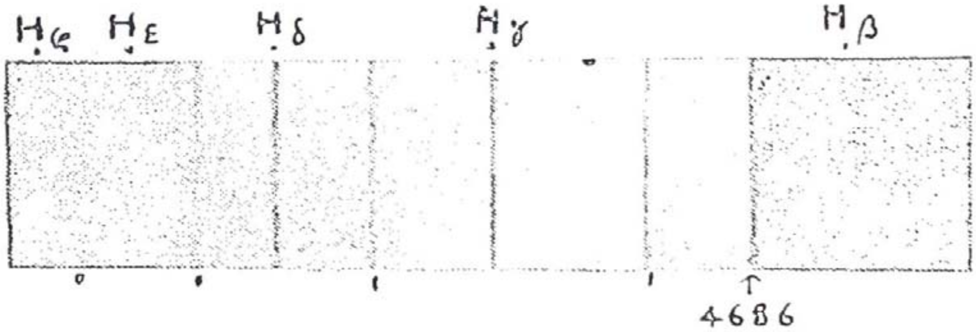


Fig. 32.—(From Annals of the Harvard College Observatory.)

(Pickering's original photograph of lines of cosmic hydrogen, now proved to be due to He^+.)

Lines of Cosmic Hydrogen

Prof. Pickering of Harvard had discovered in 1898, a series of lines in the spectrum of ζ Puppis which were distributed midway between the lines of hydrogen. He found that these lines could be represented by the formula

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{(n+\frac{1}{2})^2}\right)$$

Somewhat later on, Hale showed that the negative line of the family

$$\nu = R\left(\frac{1}{(1+\frac{1}{2})^2} - \frac{1}{2^2}\right),$$

with the theoretical wavelength λ 4688, also occurs very prominently in the spectra of Nebulæ, and very hot stars, though the actual wavelength is slightly less, *viz*., λ 4686.

Owing to the similarity of these lines to the Balmer lines they were ascribed to a form of hydrogen (cosmic hydrogen) existing in the hotter stars. They were obtained by A. Fowler in the laboratory in 1912 by passing a condensed discharge through a mixture of hydrogen and helium.

Lines of Cosmic Hydrogen are due to Ionised Helium

Bohr showed that the lines of cosmic hydrogen form really the enhanced spectrum of helium. Helium is the element next to hydrogen, it has got a nucleus having the charge $2e$, mass $4M$, with two electrons revolving in orbits. The spectrum of helium proper consists of a large number of lines which were systematized in six series by Runge and Paschen. We are not concerned with their explanation at this stage, nor is it strictly possible because we are here dealing with the problem of three bodies. But if helium loses an electron, the problem of spectral radiation becomes mathematically soluble. The lines of He^+ would be given by the formula

$$\nu = 4R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

$$\text{or } R\left(\frac{1}{\left(\frac{n}{2}\right)^2} - \frac{1}{\left(\frac{n'}{2}\right)^2}\right) \quad \ldots \quad (13)$$

It is easily observed that the most prominent line ascribed to cosmic hydrogen can be explained as lines of He^+ due to the transition $3 \leftarrow 4$. The Pickering lines are due to the transitions $4 \leftarrow n'$. The other series which have been predicted from formula (13) have also been gradually obtained in the spectrum of condensed discharge through pure helium.

Fowler pointed out in a letter to Nature dated September, 1913, that the Rydberg constant is not an invariable constant, as has been thought by Bohr, but it slightly varies from element to element. For hydrogen Balmer lines,

$$R = 10\,9\,6\,7\,8,$$

while for the Pickering lines,

$$R = 10\,9\,7\,2\,3.$$

This objection, instead of proving to be any serious obstacle to Bohr's theory, led to one of its conspicuous triumphs. Bohr pointed out that in the elementary theory, the nucleus has been supposed to be at rest. According to dynamical principles, this is not strictly true. It is the centre of gravity of the system which is at rest. We were not led to much error, because the proton being about 2000 times heavier than the electron, the centre of gravity of the system proton-electron very nearly coincides with the c.g. of the proton. But if we apply the theory in a more rigorous way, it can be shown that the object can be met by substituting $\frac{m\,M}{m+M}$ or $m\left(1-\frac{m}{M}\right)$, in place of m in the formula for the Rydberg constant. M is the mass of the nucleus. Thus for

$$\left.\begin{aligned} \text{Hydrogen, } R_H &= \frac{2\pi^2 e^4 m}{h^3}\left(1-\frac{m}{M}\right) = R\left(1-\frac{m}{M}\right) \\ \text{for Helium } R_{He} &= \frac{2\pi^2 e^4 m}{h^3}\left(1-\frac{m}{4M}\right) = R\left(1-\frac{m}{4M}\right) \end{aligned}\right\} \quad (14)$$

Hence the difference in the values of the Rydberg number for H and He enables us to calculate $\frac{m}{4M}$ we have

$$\frac{M}{m} = \frac{3}{4}\,\frac{R}{R_{He} - R_H} = 1836 \qquad .. \quad (15)$$

This is the most accurate value of $\frac{M}{m}$ hitherto obtained.

Bohr's Elementary Theory is not Sufficient

In spite of the conspicuous and imposing success of Bohr's theory in explaining old facts and predicting new ones, it could be seen that the theory could not be regarded as sufficient. The theory makes the hydrogen lines single, while actual analysis shows them to be very close doublets like the lines of sodium. Hence extension or modification of Bohr's ideas seems inevitable.

Elliptic Orbits—Sommerfeld's Generalisation of Bohr's Theory

We know that the orbits of planets round the sun are in general ellipses—and very seldom circles. We should expect a similar case for electron orbits. Already in his first paper Bohr hinted at the possibility of elliptic orbits, but he did not work out the idea. This step was taken by Sommerfeld in 1916.

The motion of a point in a plane can be represented by two variables r and θ. The kinetic energy is $\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2)$. The momenta are $P_r = m\dot{r}$ and $P_\theta = mr^2\dot{\theta}$. In Bohr's theory r is constant, hence $P_r = 0$ and the value of P_θ is taken to be $k\frac{h}{2\pi}$. Instead of this procedure, Sommerfeld introduces the more general condition

$$\int P_\theta d\theta = kh \qquad \int P_r dr = n'h \qquad \qquad .. \quad (16)$$

and the integration is taken around the orbit.

With this modification, Sommerfeld obtains the following values for the constants of the orbits

$$E_n = -\frac{2\pi^2 e^4 m}{h^3}\cdot\frac{1}{(n'+k)^2} \qquad .. \quad (17)$$

$$a_{n'k} = a_0\,(n'+k)^2$$

$$\epsilon^2 = 1 - \frac{k^2}{n^2} \qquad .. \quad (18)$$

The Eccentricity

If we put $n'+k=n$, the total energy of the states comes out to be the same, but the mechanical interpretation of the states becomes different, and more elastic. A state (n) with the energy $-\frac{\mathrm{R}h}{n^2}$ may be due to the motion of the electron in a number n of different orbits in which n is the same, but k varies from n . . . . . . to 1.

For $k=1$, 2, 3, 4, these orbits are shown below:

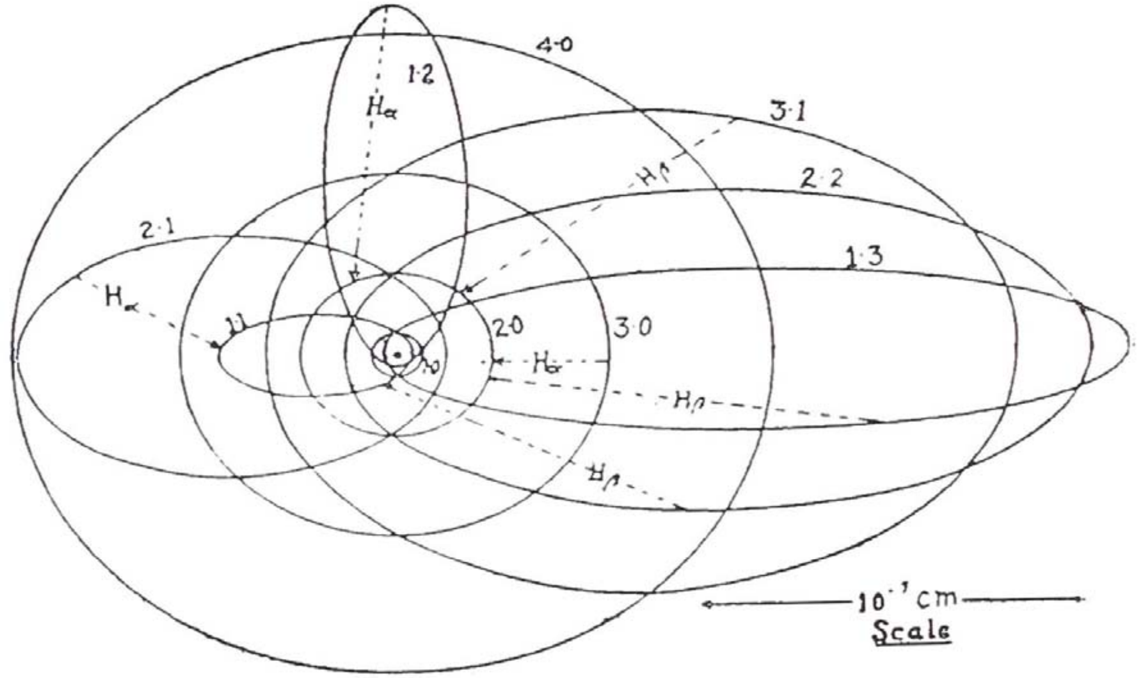
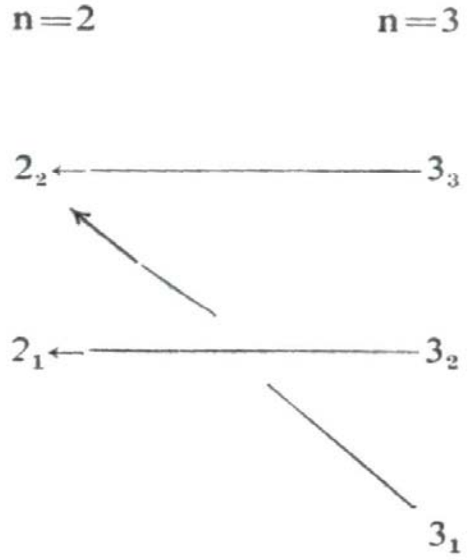


Fig. 33.—(From Foote and Mohler's *Origin of Spectra*.)

There is only one orbit corresponding to $n=1$: this is a circle with radius $a_0 = \cdot 538 \times 10^{-8}$ cm. There are two orbits corresponding to $n=2$, they are denoted by the circle 2·0 (2_2), and the ellipse 1·1 (2_1). The orbits corresponding to $n=3$ are the circle 3·0 (3_3), the ellipse 2·1 (3_2), and the elongated ellipse 1·2 (3_1).

This point is of great interest, and yielded very fine results. In the first form of Bohr's theory a line like H_α is due to the fall of the electron from orbit 3 to the orbit 2, denoted by the symbol $2 \leftarrow 3$, but according to Sommerfeld, the line is really a complex, due to a superposition of lines arising from the following transitions:



Thus to indicate the nature of the orbit, we introduce a new symbol n_k, n denotes the total quantum number, k is the azimuthal quantum number. Thus actually the line H_α should be a complex of six lines (3×2), but Sommerfeld showed that all transitions are not allowed, but they are limited by a principle of selection. The allowed transitions are those for which $\triangle k=\pm1$, $\triangle k=0$, ±2 being disallowed.

Principle of Selection

Let us now see if there is any experimental basis to support Sommerfeld's theory. Sommerfeld pointed out that owing to the simplicity of the case, the three lines constituting H_α are superposed, in the general and more complex cases they should be separated. The separation exists even in the case of hydrogen, though it is very small as is proved by the fact that when high dispersion is used, the lines appear double. Sommerfeld gave an exact theory of the fine structure of hydrogen lines.

Sommerfeld's theory of fine structure is based on the theorem deduced from the *principle of relativity* that when a particle moves with a very high velocity v, the kinetic energy can no longer be represented by the usual expression $\frac{1}{2}mv^2$, but by the formula

$$m_0\left(\frac{1}{\sqrt{1-\frac{v^2}{c^2}}}-1\right)c^2=\tfrac{1}{2}m\,v^2+\tfrac{3}{8}m\,\frac{v^4}{c^2}+\ldots\quad\ldots\quad(19)$$

Taking this expression for energy, the total energy of the system comes out a bit complicated. We get

$$\frac{W}{m_0c^2} = \left\{ 1 + \frac{\alpha z^2}{n + \sqrt{k^2 - \alpha^2 z^2}} \right\}^{-\frac{1}{2}} - 1 \qquad .. \quad (20)$$

where α is the new constant $= \frac{2\pi e^2}{ch}$, it has now received the designation 'Sommerfeld's Fine-structure Constant'. It can be easily shown that for the fundamental orbit $n_k = 1$, we have

$W = \frac{1}{2} m\alpha^2 c^2 \ldots$. approximately

For the general orbit n_K, we have

$$-W = Rz^2 \left\{ \frac{1}{n^2} + \frac{\alpha^2 z^2}{n^4} \left(\frac{1}{4} + \frac{k}{n} \right) + \ldots \right\} \qquad .. \quad (20A)$$

It differs from Bohr's value of energy $\frac{Rz^2}{n}$ in-having the small additional term:— $\frac{Rz^4\alpha^2}{n^4}\left(\frac{1}{4} + \frac{k}{n} \right)$ .. (20B)

With the aid of formula (20A), and the selection principle for k, Sommerfeld worked out a theory of fine structure of hydrogen and He^+. The results were put to experimental test by Paschen, and were found to be in complete accord with Sommerfeld's predictions. But it was later pointed out that the interpretation of results should not be done in the way originally proposed by Sommerfeld. We shall return to this point later on.

According to Sommerfeld's theory, every hydrogen line is really made up of a number of close components. The number of components increases with the serial number of the line, but for the selection principle it would be 6 for H_α, 8 for H_β 10 for H_γ. This deduction can be tested only with the aid of apparatus possessing extraordinarily high resolving power. But it can also be tested if the separations can be increased by some external agency. Such an agency is provided by a superimposed external electrical field (Stark effect). The effect of a superimposed electrical field was first experimentally tested by J. Stark who found that every simple line is split up into a number of components and it was actually found that the total number of components increases progressively with the serial position of the line. The full theory was worked out by Epstein on the basis of Sommerfeld's work, and found to be in striking agreement with facts. Without going much into detail, one may say that the superposed field produces perturbation of the orbits n_k by varying amounts. Though all the n-orbits having the total quantum number n (k varying from n to 1) have approximately the same energy in the undisturbed state, they are perturbed by different amounts, and hence the term is split up into k different terms.

With the aid of the new quantum number k, Sommerfeld was able to give a fuller explanation of the energy levels of the sodium atom. If we refer back to Fig. 30 we see that the levels consist of families of terms, *viz*.

ns-family	beginning with	$n=1$	..	$k=1$
np-family	,, ,,	$n=2$	..	$k=2$
nd-family	,, ,,	$n=3$	..	$k=3$
nf-family	,, ,,	$n=4$	..	$k=4$

The *p*-terms are double, and so are also *d*'s and *f*'s, though the separation is too small.

We get lines due to combinations *ps*, *pd* but seldom lines due to combinations *ss*, or *sd*. Sommerfeld therefore proposed that $k=1$ for *s*-terms, 2 for *p*-terms, 3 for *d*'s, 4 for *f*'s. Thus a term *ns* should be denoted in the Bohr-Sommerfeld notation as n_1, *np* as n_2. . . .etc.

The fact that there are no lines corresponding to *pp* or *sd* is explained by the selection principle

$\triangle k=\pm 1$ .. .. allowed

$\triangle k=0, \pm 2$ .. .. forbidden.

The Inner-Quantum Number

Even two quantum numbers n and k are not sufficient for specifying all the characteristics of the terms. For example, we have two close p terms in sodium and other alkali elements having the same values of n and k. To distinguish them from each other, Sommerfeld formally introduced another subscript j. Thus we denote a term by the symbol n_{kj}, n=total quantum number, k=azimuthal quantum number. To the subscript j was given the name of "inner quantum number".

Thus $2p_1$, of sodium can be written as 2_{21}, $2p_2$ as 2_{22}

The inner quantum numbers, thus introduced in a very formal way, proved to be of the greatest help in the analysis of spectra of elements of higher groups and in the explanation of Zeemann Effect. We shall come to a more detailed treatment of j later on.

Structure of Spectra and the Periodic Classification

We have already noted the close correspondence between the nature of spectra and chemical properties of elements in the case of alkalies. This correspondence is found to be quite general. Coming to the second group, we have Be, Mg. Ca, Sr. Ba in the even group, and Zn, Cd, Hg in the odd group. Their spectra are more complicated than those of the alkalies, but they are strikingly similar amongst themselves. Similarly, elements of the third group B. Al. Ca, In, Th which are chemically trivalent, show quite similar spectra.

The close connection between the nature of spectra and chemical properties of elements was very thoroughly studied by Bohr and Coster, who definitely established that the nature of the spectrum entirely depends upon the number of valency electrons. The term valency electron itself is a bit vague, and it is not possible to define it with more precision unless we study the electronic structure of elements. An element of atomic number z consists of a positive nucleus of z-charges and is surrounded by z-electrons. These z electrons must be arranged in successive layers about each other. Rydberg had shown that the atomic numbers of the inert gases He, Ne, A, Kr, Xe, Nt* follow the remarkable law

$$\begin{array}{cccccc} 2(1^2 & +2^2 & +2^2 & +3^2 & +3^2 & +4^2) \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{He} & \text{Ne} & \text{A} & \text{Kr} & \text{Xe} & \text{Nt} \end{array}$$

It was concluded from this relation that shells consisting of 2, 8, 18, 32 electrons formed a saturated or closed system, having no valency. An addition of one more electron gives us a monovalent element, an addition of two electrons give us a divalent element. Actually, the situation is much more complex, and Bohr discussed the whole problem in a masterly way in his "Auf-bauprinzip" (Principle of construction of the atom by the bringing up of one electron after another).

Moseley's work on the Characteristic X-rays of Elements

The reality of these successive shells of electron was very strikingly established by the fundamental researches of Moseley which were carried out shortly after the publication of Bohr's first works. In the first lecture we have spoken of the identity of X-rays and ordinary

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*Nt-Niton-later remained Radon-Rn

light. X-rays, as von Laue proved conclusively, are essentially the same as ordinary light, only their wavelength is about a thousand times smaller. Before the nature of X-rays was fully elucidated, Barkla and Sadler had proved in 1908 that elements can be made to give characteristic X-radiation, just as they can be made to give characteristic optical spectrum. But unlike optical spectra where the characteristic lines apparently follow no regular law the characteristic X-radiations possess very definite regularity. All elements apparently give two kinds of radiation, which he denoted by K (hard, i.e., of great penetrating power), and L (soft, i.e., of less penetrating power). The absorption coefficients of the characteristic K-radiations of elements were found to follow exactly the succession of the elements in the periodic table. After von Laue's discovery, and Braggs' invention of the X-ray spectrometer, Moseley measured the wavelengths of the K-radiation, and L-radiation of a large number of elements,

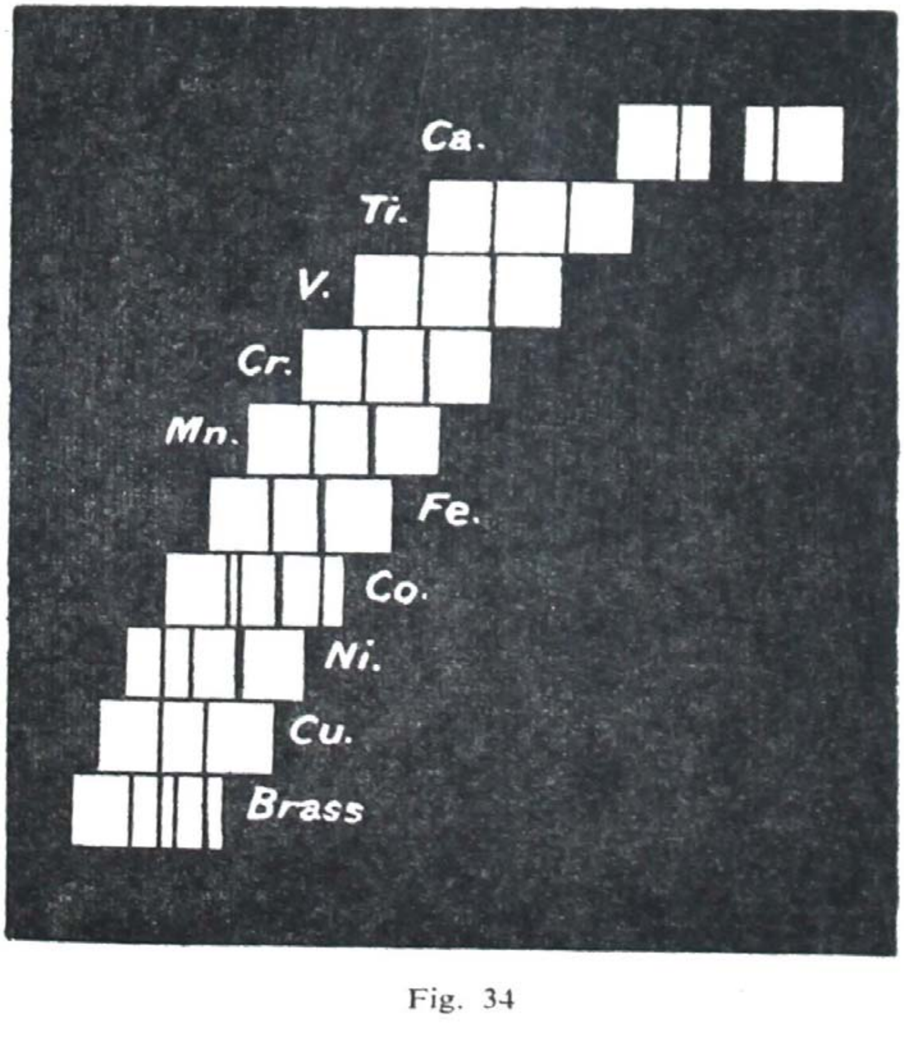

Fig. 34

and found that they decrease progressively with increasing wavelength in a very regular way as shown in the reproduction from Moseley's original work. (Fig 34)

Thus the K-spectrum was found to consist, in the case of comparatively lighter elements, of 2-lines, and the frequencies of the lines were found roughly to correspond to the formula:

$$\nu = \mathrm{R}(z-b)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \qquad .. \quad (21)$$

b = screening factor = nearly unity

The wavelengths of the L-lines were found roughly to correspond to the formula

$$\nu = \mathrm{R}(z-b)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \qquad .. \quad (22)$$

b = nearly 3·5.

Though these formulæ are very rough, they give some indication of the origin of the lines, when we try to interpret them in the light of Bohr's theory.

The K-lines are due to the vibrations of an electron moving under a net charge of $(z-b)$: since the element has a nuclear charge of z, this electron must be very close to the nucleus. There is no difficulty in identifying this as one of the electrons in the innermost shell. The approximate field is that due to the central charge z, the forces due to the outer electrons cancelling each other because they are equally distributed about the inner shell. But the effect of the other electrons in the innermost shell cannot be neglected, they are represented by the screening factor b; similarly the L-lines may be supposed to owe their origin to the electrons in the next layer. In this case, the screening factor will be obviously larger.

Moseley's experiments, therefore establish the reality of successive shells of electrons to which the designation K, L, M, N, . . . are given.

Actually the empirical relationships, and explanation of the K- and L-spectra are not so simple. Moseley's work was carried on by Siegbahn and his students, by Coster, Duane and others who gave accurate measurements of the lines of K, L, M, and N series of elements. It was on the basis of this data that Bohr built up his "Auf-bauprinzip".

Sommerfeld and Kossel's Displacement Law

Before Bohr had given a general discussion of spectra from his Auf-bauprinzip, Sommerfeld and Kossel had discovered a very general law as a prelude to Sommerfeld's more systematic attack on the spectra of higher valency elements. They had observed that though the arc spectrum of two-valence elements are entirely different from spectra of alkalies, the enhanced spectra of the former bear a striking resemblance to the arc spectra of the latter. Thus Mg^+ shows a doublet spectrum, with single *s*, double *p*, *d*, *f*—terms just like Na. The spectrum of Ca^+ is just like that of K (potassium) and the rule is quite universal. Hence they formulated the general principle:

The enhanced spectrum of any order of any element is similar to the spectrum of the element preceding it in the periodic classification by the number of the order.

Thus Mg^+, Al^{++}, Si^{+++} . . ., show a doublet spectra similar to that of Na.

Al^+, Si^{++}, P^{+++} . . . show spectra similar to that of Mg.

Sommerfeld and Kossel's law is therefore illustrative of the principle that the nature of the spectrum depends on the number of electrons outside of the closed shells.

LECTURE IV

Principles of Atom-Structure

The present lecture will be a continuation of the previous one, but I shall discard the historical method of treatment which I have so long tried to follow. The reason is that though at the present time, we possess a complete theory of atom-structure, the discoveries leading to it occurred in a rather irregular way, and a historical method of treatment will be long and round-about. In adopting this method, I shall have necessarily to plead guilty to many acts of omission and logical incompleteness.

Spectra of Two-Valence Elements

In the third lecture, mention was made of the surprising similarity in the Spectra of Elements having similar chemical properties, and illustration was given in the case of alkalies. Let was now take the spectra of the second group, *viz.*, Be, Mg, Ca, Sr, Ba, and of Zn, Cd, Hg, which are all divalent and occur in the second vertical column of Mendeleef's Periodic Table. We shall henceforth call them two-valence elements. The spectra of all these elements are surprisingly alike. The most prominent feature is the occurrence of groups of *three lines* with constant frequency difference. This triplet difference is as typical of two-valence elements as doublets are of alkalies.

The picture (Fig 35) shows the triplet characteristics of the two-valence elements, Cd, Zn, Mg. Note that the triplet separations are approximately as 1 : 2, and go on increasing with increasing atomic weight as in alkalies. Another point to be noted is that the triplets can be separated into a sharp group, and a diffuse group as in alkalies. The sharp group corresponds to the transition p—s, as in alkalies. but p is now triple; we denote them provisionally by p_1 p_2 p_3 in the descending order of value. The diffuse group consists of three chief lines, but use of higher resolving power shows that these lines are not simple. The fine structure of a (pd) group is shown in Figure 36.

As the Fig. 36 shows, the longest line has two fainter satellites, the middle line has one, the shortest line is single, so that the diffuse group really consists of 6-lines.

An examination of the frequencies shows that the lines of a diffuse triplet can be schematically written as follows:

ARC SPECTRA OF Cd, Zn, Mg,

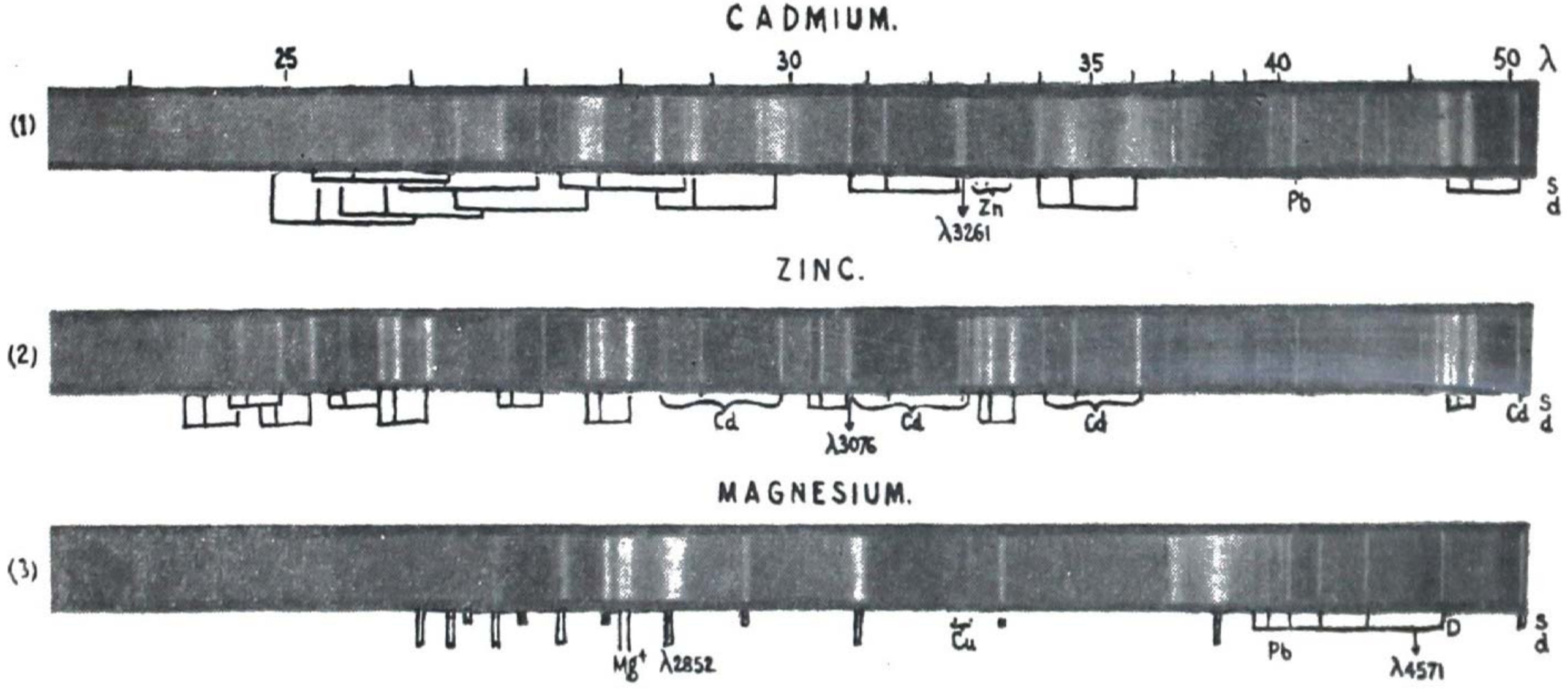

Fig. 35.—(From Fowler's Reports, *Appendix*)

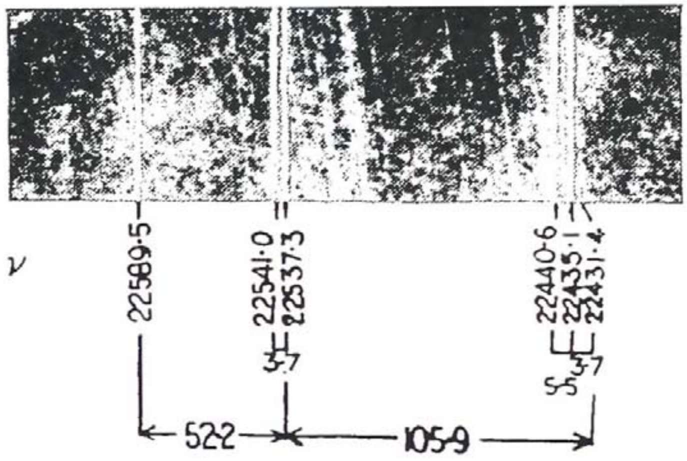

Fig. 36.—(From Fowler's Report showing the constitution of pd-lines of Calcium.)

	0		1		2
	p_1	52	p_2	106	p_3
$1d_1$	22590·4		22538·3		22432·4
3·7					
$2\ d_2$			22542·0		22436·1
5·6					
$3\ d_3$					22441·7

Apparently the three *p*-terms and three *d*-terms are involved in the production of these lines. We can distinguish the d's by d_1 d_2 d_3 provisionally. These integral subscripts are related to the inner quantum numbers introduced in lecture III.

It is evident that there should be some selection principle for inner quantum numbers, for if all the p's combined with all the d's we should have altogether nine lines, whereas we have actually six. As a result of extensive studies, Sommerfeld formulated, the following Selection Principle for j:

$$\left. j \begin{array}{l} \nearrow j-1 \\ \longrightarrow j \\ \searrow j+1 \end{array} \right\} \quad \ldots \text{ allowed except from } 0 \rightarrow 0 \text{ which is not allowed.} \quad \ldots (1)$$

$$j = \pm 2, \pm 3 \quad \ldots \text{ not allowed}$$

The choice of the 'j-' values was finally settled upon after a good deal of trial. For the triplet p's we have j=0, 1, 2; for the d's we have j=1, 2, 3. Application of the selection principle in Fig. 36 shows why we should have six lines, and not nine. Most lines of the spectrum of a two-valence element are thus resolvable into families of triplet terms which, with their quantum numbers can be represented as follows:

$$\left.\begin{array}{llllll} & s_1 & & & \ldots & n=2,\ 3,\ 4\ \ldots \\ p_0 & p_1 & p_2 & & \ldots & n=\ \ \ \ 3,\ 4\ \ldots \\ & d_1 & d_2 & d_3 & \ldots & n=\ \ \ \ 3,\ 4\ \ldots \\ & & f_2 & f_3\ \ f_4 & \ldots & n=\ \ \ \ \ \ \ \ 4\ \ldots \end{array}\right\}\text{ for Mg.}$$

It should be noted that the s-term is single, the others are triple. Also that the largest s-term has the total quantum number n beginning with 2. These terms give rise to the triplet spectra of two-valence elements.

The Singlet Spectrum

But a large number of lines including some of the strongest remains unaccounted for. They are mostly single lines, and analysis has shown that they can be represented by the following system of terms:

$$\left.\begin{array}{llllll} s_0 & & & & \ldots & n=1,\ 2,\ 3,\ 4\ \ldots \\ & p_1 & & & \ldots & n=\ \ \ \ 2,\ 3,\ 4\ \ldots \\ & & d_2 & & \ldots & n=\ \ \ \ \ \ \ \ 3,\ 4\ \ldots \\ & & & f_3 & \ldots & n=\ \ \ \ \ \ \ \ \ \ \ \ 4\ \ldots \end{array}\right\}\text{ for Mg.}$$

These lines form the singlet spectrum.

The singlet 's-term' is the largest in the whole set, and is the only term with the total quantum number n=1.

The whole families of terms are shown in Fig 37.

The Multiplicity Quantum Number

From the description of the spectra of two-valence elements, it is clear that even three quantum numbers n, k, j are not sufficient for describing all the characteristics of a level, but we should have something in addition, to describe the nature of multiplicity. This is done by the introduction of a fourth quantum number 'r', r being provisionally 1, 2, 3 . . . for singlets, doublets, triplets, etc. There is also a

[The terms consist of singlet terms and triplet terms. The singlet system consists of a sequence of s-terms beginning with n=1, the

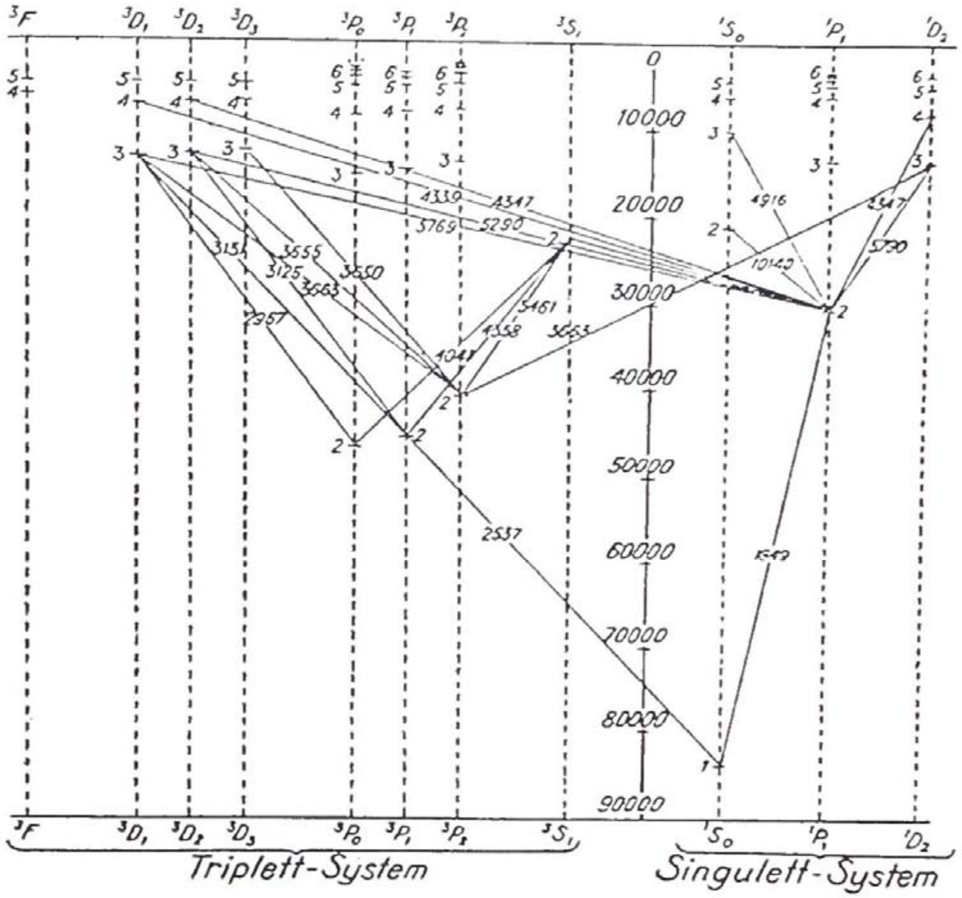

Fig. 37.—Bohr-Grotrian Diagram for Mercury.
(From Handbuch der Physik, Band 23, Quanten.)

sequence of p-terms beginning with n=2, and so on. The triplet system consists of a sequence of s-terms beginning with n=2, the sequence of p-terms beginning with n=2 and so on. The S_0-term is the largest and denotes the ground level. The transitions between different terms are shown by lines drawn in the diagram. Inter-combinations between the singlets and the triplets may also be noted.]

selection principle for this quantum number. We should have $\triangle r = \pm 2$ or 0, as only singlets and triplets combine with each other giving the 'Inter-combination lines', but they never combine with doublets. The full denomination of a term is now given by $n^r{}_{kj}$, where

n	= total	quantum number
k	= azimuthal	,,
j	= inner	,,
r	= multiplicity	,,

The selection principle for r allows $\triangle r$ to be ± 2 or 0, whereas in other cases the difference allowed is ± 1, 0. If instead of using r, we use $s = \frac{r-1}{2}$, then the selection principle becomes $\triangle s = \pm 1, 0$. We see later that actually s is used in place of r.

Spectra of Three-Valence Elements

The three-valence elements B, Al, Ga, In, Th . . . again show a doublet structure, similar to alkalies in certain respects, but differing from in certain important details. In alkalies, the chief term is an s-term but in the three-valence elements, two p-terms form the normal levels.

Spectra of more Complex Elements

The behaviour of elements of the first three groups indicates that the odd valency elements should show even multiplicity and even valency elements should show odd multiplicity. This view was originally pronounced by Rydberg and confirmed by Sommerfeld. But the full systematisation of the spectra of higher group elements presented great difficulties owing to the enormous numbers of lines they are composed of. The clue was afforded by celebrated work of Catalan on the analysis of the spectrum of Manganese which was carried out under the guidance of Prof. A. Fowler in his laboratory at London. This work forms a landmark in the history of Spectroscopy. Catalan observed that in the spectrum of manganese, groups of associated lines occur which show the same features as the pd-groups of two-valence elements (*vide* Fig. 36). Only their number is sometimes much

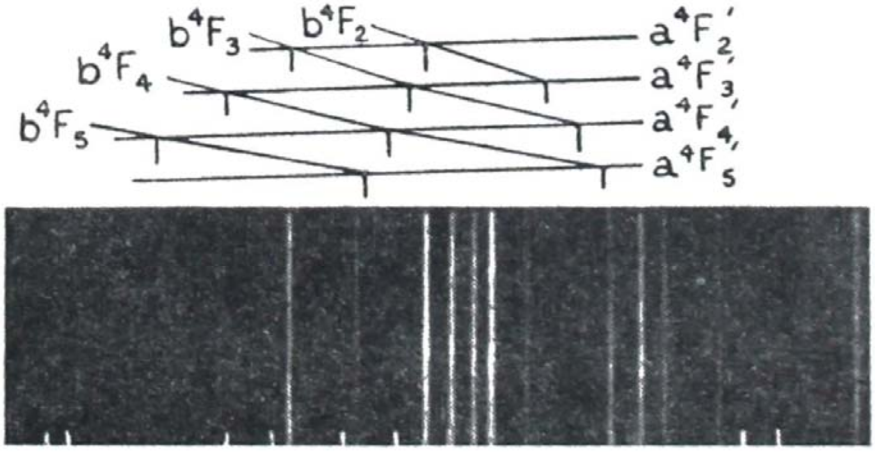

Fig. 38.—(Bull. Bur. Stand., Paper No. 558.)

larger. A photograph of a similar group is reproduced in Fig. 38 from a paper by Russell and Meggers on the arc and spark spectrum of Scandium.

This picture consisting of 10 associated lines shows a typical multiplet group, the lines are seen to arise from two groups, both consisting of four terms. They can be represented as follows:

	$^4F'_2$ 3	8 $^4F'_3$ 5	3 $^4F'_4$ 6	7 $^4F'_5$
$^4F_2$ 43	(40) 19652·68	(15) 19614·97		
$^4F_3$ 59	(15) 1969·582	(50) 19658·13	(25) 19605·40	
$^4F_4$ 75		(30) 19717·57	(60) 19665·17	(10) 19598·09
$^4F_5$			(20) 19740·54	(75) 19673·53

The term 'multiplet' is given to a group of lines which can be arranged as shown in the above diagram. Sometimes the number of associated terms may be 3, 4, 5, 6 . . . or more: terms associated in such a manner obviously form a family. The spectrum of Manganese was found by Catalan to be resolvable into families of terms, consisting of sextets (families consisting of a maximum of six terms) and quartets.

Attack on Complex Spectra

At this point, Prof. Sommerfeld became acquainted with the work of Catalan, and with his usual insight, recognised in this the key to the riddle of complex spectra. He introduced the idea of inner quantum numbers to distinguish the successive members of a group of terms, and armed with this clue, launched a frontal attack on the spectra of complicated elements. The first conspicuous success was achieved by Laporte who, starting from the preliminary work of Walters, succeeded in effecting a full analysis of the spectrum of Fe. Ni and Co fell to Bechert and Sommer. Cr to Gieseler (based on the preliminary work of Catalan); Vanadium to Grotrian, Gieseler, and Laporte. The anomalous terms of Calcium were explained by

Saunders and Russell in a masterly paper, in which the principles of term-synthesis were suggested by the authors simultaneously with Pauli and Heisenberg. We shall come to this important point later on. For the full list of work on analysis of complex spectra, more comprehensive treatises ought to be consulted.[1]

The values of the inner quantum numbers of term-groups of different multiplicities were obtained as a result of combined work on complex spectra and Zeemann effect and are given later.

Mechanical Interpretation of the Various Quantum Numbers

We shall now take the mechanical interpretation of the various quantum numbers. The interpretation of 'n', the total quantum number, and of 'k', the azimuthal quantum number has been already given. What physical magnitudes are represented by '*j*' and '*r*' ?

At first it was attempted to prove that '*j*' is somehow connected with the orientation of the orbit. In considering the motion of the electron round the proton, we have supposed that the orbits lie all in one plane. This is obviously not correct, we should also take into account the effect of the possible change of the orbits from one plane to another.

This object is achieved by considering the motion in three dimensions, and using the three variables, r, ϕ, θ. The energy is now $\frac{1}{2}m(\dot{r}^2+r^2\dot{\theta}^2+r^2\sin^2\theta\dot{\phi}^2)$, and the momenta are $p_r=m\dot{r}$, $p_\theta=mr^2\dot{\theta}$, $p_\phi=mr^2\sin^2\theta\dot{\phi}$'. We now put $\int p_r dr=n'h$, $\int p_\theta\, d\theta=k'h$,

$$\int p_\phi\, d\phi=k''h.$$

The net result is not different. The energy comes out to be—$\frac{Rh}{(n'+k'+k'')^2}$. Hence $k=k'+k''$. The motion therefore becomes degenerate. It is not possible to distinguish between two orbits differently oriented with respect to an external axis.

Zeemann Effect

But this degeneracy can be removed by the application of an external magnetic field. As is well-known Zeemann made the most profound discovery in 1896 that when a spectrum is excited in a magnetic field, every line which is otherwise single, is split up into three

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[1] *Handbuch der Experimental Physik*, Vol. XXII

components. Lorentz and Larmor gave rather slightly different explanation of this phenomenon. They treated the atom as a dipole oscillator and calculated the result of interaction of the magnetic field on the moving electron. They found that the frequency of the oscilator is changed from ν to $\nu \pm \frac{eH}{4\pi cm}$ in a magnetic field H. A pictorial representation of the separation is given below:

Types of Zeemann Resolution.

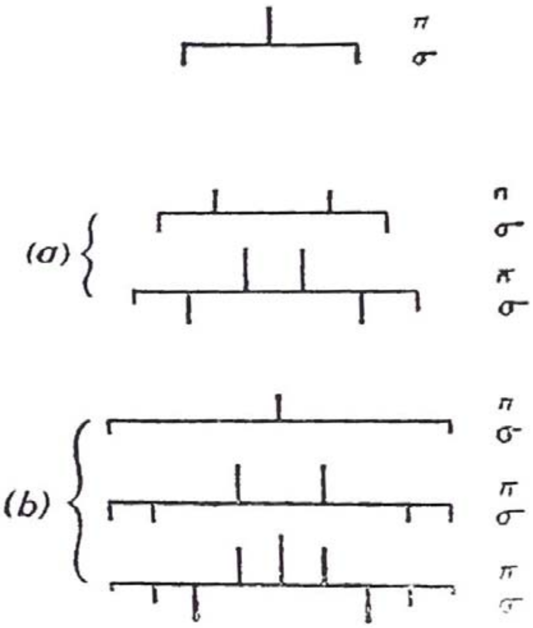


Fig. 39.—(From Andrade's Structure of Atom.)

Top—Normal triplet, π polarised parallel to the field. σ polarised perpendicular to the field.

(a) Zeemann type of D_1 and D_2-lines. D_1 is decomposed into four, D_2 into six components.

(b) Zeemann type of sp-triplets of two-valence elements.

But further study of Zeemann effect of lines of other elements showed that normal splitting was rather the exception than the rule. Most lines show complicated patterns of widely different types. For example, the well-known D_1-line of sodium was found to be decomposed into 4 components. D_2 was found decomposed into 6 components. They are shown in the diagram above.

A more intensive study of Zeemann effect showed that these anomalous results are governed by very significant rules. Preston proved that all lines belonging to the same spectral classification show the same type of Zeemann effect, *e.g.*, the sp-lines of Na and other alkalies are split up like the D-lines of sodium. The second rule was discovered by Runge. He showed that the separations can be represented by $\pm \frac{r_1 a}{r_2}$ where 'r_1' and 'r_2' are small integers, a is the Larmor constant $\frac{eH}{4\pi cm}$.

In D_1, we get four components; the separations are represented by the formula $\triangle\nu = \pm \frac{a}{3}(\underline{2}, 4)$. The inner components $\pm \frac{2a}{3}$ are polarised parallel to the field. This is denoted by underlining 2.

In D_2, we get six components, the separations being given by the formula $\triangle\nu = \pm \frac{a}{3}(\underline{1}, 3, 5)$.

Sommerfeld showed that since every line-frequency was the difference of energy values of two stationary states, these energy values will be modified when the atom is placed in the magnetic field. We have to write $\triangle\nu = \triangle\nu_f - \triangle\nu_i$, '$i$' and '$f$' standing for initial and final states. We have to find out $\triangle\nu$'s for the stable states of the atom. Sommerfeld put $\frac{\triangle\nu.}{a} = \frac{p.}{q}$, where p and q have definite integral values for each class of orbits. This is obviously referring Runge's Rule from lines to the component terms.

It was not difficult to account for normal Zeemann effect on the Bohr-Sommerfeld theory. Several investigators showed that when an H-atom is placed in a magnetic field, then owing to the interaction between the moving charge and the field, the energy of the electron moving in the n_k- orbit is changed to

$$W = -\frac{Rh}{n^2} \pm \left(\frac{eH}{4\pi cm}\right) k \cos\theta, \qquad \text{.. (2)}$$

where θ is the angle of tilt of the axis of the orbit to the magnetic field.

The separations are given by $\pm a\,(k \cos\theta - k' \cos\theta')$, and since $k\cos\theta$, $k'\cos\theta'$ are integral, we get only normal Zeemann effect. Hence the orbital theory is no more successful in accounting for generalized Zeemann-phenomena than the classical theory of Lorentz and Larmor.

Sommerfeld took up the study of anomalous Zeemann effect from a more general point of view in which the atom is supposed to be an elementary magnet with a definite axis, and a definite moment μ. The additional energy of such an atom-magnet placed in a magnetic field $= \mu H \cos\theta$, and the change in the frequency of a line, when generated in a magnetic field will be given by

$$h \triangle \nu = H\ (\mu_i \cos\theta_i - \mu_f \cos\theta_f) \qquad .. \quad (3)$$

where the subscripts (i) (f) refer to the initial and final states.

We must now discuss from what causes the magnetism of atoms may arise. Sommerfeld revived the old theory of Ampere that they are due to currents of molecular dimension. The hypothesis of Ampere had received confirmation from a set of brilliantly conceived experiments due to Einstein and De Haas, and to Barnett, who showed that it is possible to identify the molecular currents with the motion of the electron. The magnetic moment of the electron revolving in an orbit with the k-quantum number is given by

$$\mu = \text{equivalent current} \times \text{area}$$

$$= \left(\frac{e}{cT}\right) S,\ S = \text{area},\ T = \text{time of revolution}$$

$$= \frac{er^2\omega}{2c} . k$$

$$\text{But } mr^2\omega = \frac{h}{2\pi},\ \text{hence } \mu = \frac{eh}{4\pi cm}\ k \qquad .. \quad (4)$$

The quantity $\mu = \frac{eh}{4\pi cm}$ is known as the Bohr-magneton, and may be regarded as the unit of magnetic moment. We also note that magnetic moment: mechanical moment as $\frac{e}{2mc}$

If we put this value of 'μ' in (3) we get only normal Zeemann effect. Let us therefore give up the idea that the magnetism of the atom can be wholly due to orbital motion of electrons, and assume the more general expression

$$\mu = g . \left(\frac{eh}{4\pi cm}\right) . j$$

The introduction of 'j' in place of 'k' which we called the inner quantum number is the most significant step taken by Sommerfeld. He was led to this step from the preliminary systematisation of Zeemann data. It is found, as exemplified in the case of D-lines, that the number of components increases with the j-value and treatment of a large amount of data showed that there must be intimate connection between 'j' and the number of components.

The factor 'g' depended upon multiplicity as well as k and j, and was obtained after some trial in each case.

The change in energy of an atom magnet measured in frequency is therefore

$$\frac{H}{h}\cdot\left(\frac{eh}{4\pi cm}\right).\ g.\ j\cos\theta,\ \text{or}\ a.\ g.\ m,$$

where $m=j\cos\theta$; the different values of m, the magnetic quantum numbers are now

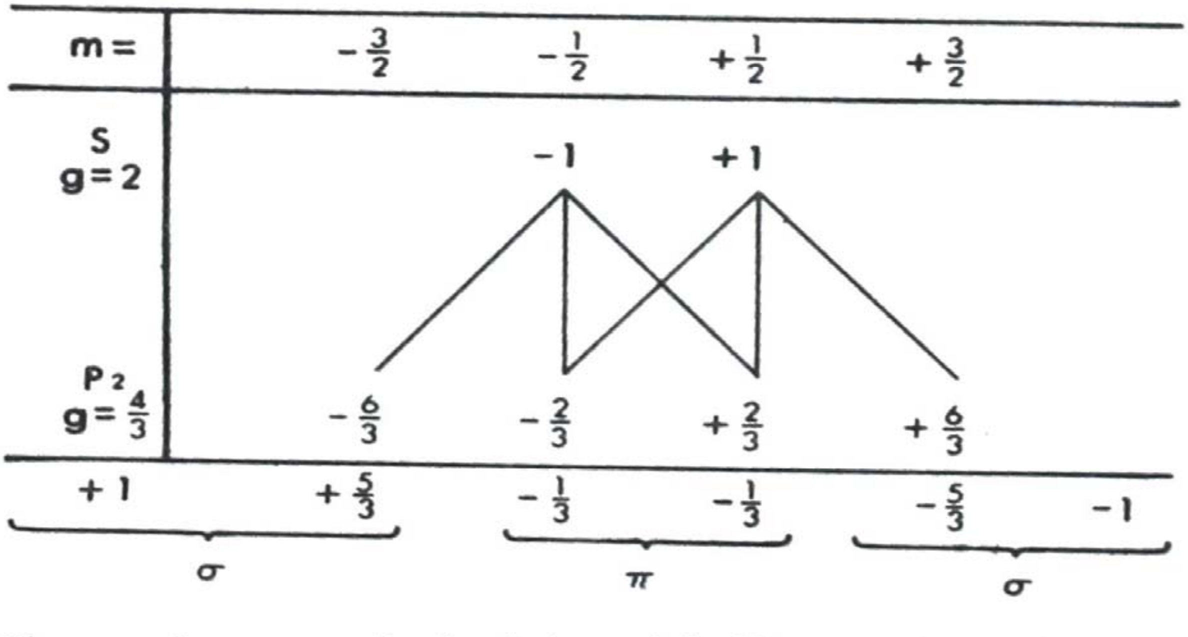
$$j,\ j-1\quad \ldots\quad,\ -j,\ \text{altogether}\ 2j+1\ \text{in number.}$$

They are the projections of j on an external fixed axis.

Thus an orbit with the inner quantum number j can give rise to $2j+1$, magnetic quantum numbers corresponding to the different quantized tilts of the orbit.

$$\text{Hence}\ \frac{\triangle\nu}{a}=g_i m_i-g_f m_f.$$

The actual components are obtained by writing out $g_i\ m_i$ and $g_f\ m_f$ in two horizontal rows and subtracting:—we give the illustration for the D-doublets.



The g-values are obtained by trial. The number of m-values are found to be even for doublets and even multiplets hence 'j' must be half-numbered in doublets as well as in all even multiplets. The previous 'j' values were obtained empirically but study of Zeemann effect enables us to find out j exactly.

There must be a selection principle for m,* and this is the same as that for j. Allowed transitions are:—

$$m \longrightarrow m \qquad .. \qquad \pi\text{-components}$$

$$m \begin{array}{l} \nearrow = m+1 \\ \\ \searrow = m-1 \end{array} \qquad \sigma\text{-components}$$

Space-Quantisation—Stern and Gerlach's Experiment

From the above theory of Zeemann effect it follows that when an atom magnet is placed in a magnetic field its axis is not orientated at random but are inclined at the angles

$$\mathrm{Cos}^{-1} \frac{1}{j} (j,\ j-1,\ j-2,\ ..\ -j) \text{ to an arbitrarily fixed}$$

external axis.

The schematic picture of these oriented axes are shown in the following diagram:

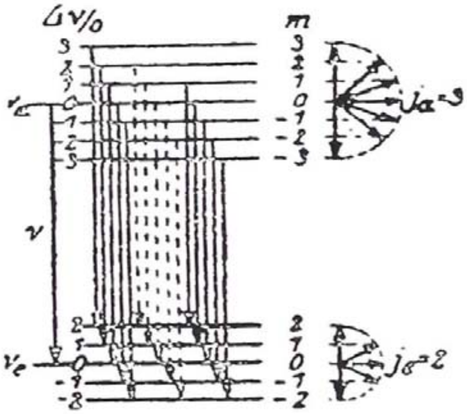


Fig. 40.—Zeemann effect for Triplets ($p_2\ d_3$)

(From Handbuch der Experimental Physik, Vol. XXII, p. 85.)

The terms have the inner quantum numbers 3 (top), and 2 (bottom). The orientation of the atom-axis is shown by the arrows and corresponds to 0, $\cos^{-1}(\frac{2}{3}, \frac{1}{3}, 0, -\frac{1}{3}, -\frac{2}{3})$, π. The magnetic levels 'm' are shown by horizontal lines. The allowed transitions ($m \rightarrow m \pm 1$) giving rise to σ-components are shown by heavy lines, the transitions ($m \rightarrow m$) giving rise to π-components are shown by dotted lines.

The deduction is rather surprising, for it signifies that the atom-axis can point only to certain privileged directions as indicated by arrows in Fig. 40,—any haphazard direction is not possible. Stern and

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*The symbol 'm' has been used to denote magnetic quantum number as well as mass of the electron: the confusion is regrettable, but can scarcely be avoided.

Gerlach however devised an ingenious method for verifying this paradoxical deduction experimentally (see Fig. 41).

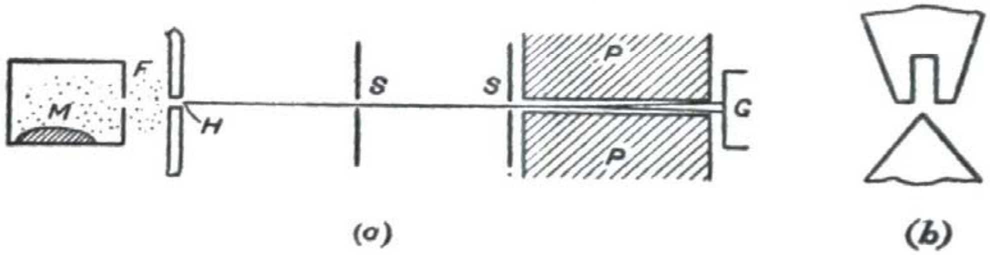

Fig. 41

Stern and Gerlach's apparatus for investigating the space-quantisation of atom-magnets (from Andrade's *Structure of the Atom*).

A beam of silver-atoms produced by heating silver in a small oven M, and rendered parallel by a number of fine slits SS is allowed to pass through a non-homogeneous magnetic field PP. If the atom-magnet possesses the magnetic moment μ, and its axis is inclined at an angle θ to the field it can be shown that it will be subjected to an acceleration $f = \frac{\mu\cos\theta}{m}\frac{dH}{dz}$ perpendicular to their line of motion. They are then allowed to be deposited on a plate placed normally to their path. The deflection can easily be calculated and comes out to be

$$d = \frac{1}{3kT}\frac{dH}{dz}\mu\cos\theta,$$

where k is the Boltzmann constant, T=absolute temperature of the atom-stream. Calculation shows that d is just measurable.

If the angle of tilt θ can have any value, the trace will be continuous, but we have postulated that $\cos\theta = \frac{m}{j}$, hence the trace will consist of a number of paralled lines. For silver, $j=\frac{1}{2}$ for the normal orbit, $m=\frac{1}{2}$ or $-\frac{1}{2}$, hence the trace will consist of two parallel lines on both sides of the geometrical image of the slit. This was actually found to be the case.

Stern and Gerlach's experiments confirmed the results in a brilliant manner, and placed the theory of space-quantisation on a secure basis.

Lande's Table of Inner Quantum Numbers

The determination of the value of 'j', the inner quantum number which was at first merely formally introduced, thus acquires a great significance, for the nature of atomic magnetism is seen to depend wholly on 'j'. The magnetic moment of the atom-magnet is given by "$\mu g j$", where μ is the Bohr-magneton, 'g' is a factor depending on k, j, and s, and is known as the Lande-factor.

Lande arrived at the final system of 'j-'values for terms of multiplets of different order which is reproduced in the Table, from an examination of the empirical data arising out of the results of classification of spectral lines of elements and of Zeemann patterns of different multiplets. As a discussion would involve a survey of the whole of this enormous data, I have merely contented myself by reproducing the

Lande's Table of j-values

Odd Multiplets								Even Multiplets							
$k-1$ \ j	0	1	2	3	4	5		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$		i / i
$s=0$	0						Singlets $=0$	$\frac{1}{2}$						Doublets $=\frac{1}{2}$	$s=0$
$p=1$		1						$\frac{1}{2}$	$\frac{3}{2}$						$p=1$
$d=2$			2						$\frac{3}{2}$	$\frac{5}{2}$					$d=2$
$f=3$				3						$\frac{5}{2}$	$\frac{7}{2}$				$f=3$
$s=0$		1					Triplets $=\frac{2}{2}$		$\frac{3}{2}$					Quartets $=\frac{3}{2}$	$s=0$
$p=1$	0	1	2					$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$					$p=1$
$d=2$		1	2	3				$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$				$d=2$
$f=3$			2	3	4				$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$			$f=3$
$s=0$			2				Quintets $=\frac{4}{2}$			$\frac{5}{2}$				Sextets $=\frac{5}{2}$	$s=0$
$p=1$		1	2	3					$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$				$p=1$
$d=2$	0	1	2	3	4			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$			$d=2$
$f=3$		1	2	3	4	5		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$		$f=3$

Table. A few empirical rules will enable the reader to write out the Table off-hand. It may be noted that the 'j-'values for even multiplets are half-integral, while 'j-values for odd-multiplets are whole numbers. The j-value of the s-term is just s or $\frac{r-1}{2}$, and for any other term in a multiplet,

'j' is the vector sum of $k-1$ and s. Let us consider the doublets. We find that for any group of terms:

$$j=k-1\pm\tfrac{1}{2} \quad \text{giving} \left.\begin{array}{ll} \frac{1}{2},\ \frac{3}{2} & \text{for P-terms} \\ \frac{3}{2},\ \frac{5}{2} & \text{for D-terms} \end{array}\right\}$$

Similarly for triplets:

$$j=\lvert k-1+1\rvert \quad \text{giving} \left.\begin{array}{ll} 0,\ 1,\ 2 & \text{for P-terms} \\ 1,\ 2,\ 3 & \text{for D-terms} \end{array}\right\}$$

$j=\lvert k-1+1\rvert$ denotes the vector sum, *i.e.*, $\lvert a+b \rvert$ denotes the group of integral or half integral values ranging from $a+b$, to $-(a+b)$ and differing successively by unity.

We have generally:

$$j=\lvert k-1+s \rvert$$

Let us now consider the mechanical interpretation of this most interesting result. '$\mu g j$' represents the magnetic moment of the atom, and the fact that the js for a group of associated terms are the vector sums of $k-1$ and s point to the conclusion that the magnetism arises from two distinct causes: (*i*) from the motion which gives rise to the k-quantum number *viz.*, orbital motion; (*ii*) from the motion which causes the multiplicity.

But the magnetism associated with orbital motion turns out to be proportional to $k-1$. This is rather opposed to the results of the Bohr-Sommerfeld theory, for when the electron is in an s-state, the magnetism should be nil, whereas according to the orbital theory it is one Bohr-magneton. But this deduction is supported by wave-mechanics.

Interpretation of Multiplicity Quantum Number

We shall next take the interpretation of the multiplicity quantum number. From the fact that 'r' increases with the complexity of the atom, it was first thought that 'r' depends on the atomic residue, *i.e.*, the system of electrons minus the one directly involved in the production of light. But Pauli brought conclusive evidence to prove that, 'r' is *an attribute of the electron itself*, and the multiplicity observed must be due to a superposition of the effects due to the number of valency electrons, which are involved in the production of line spectra.

According to Pauli, the motion of each electron is distinguished by four quantum numbers, n, k, s, and m. For any electron s is always fixed and equal to half. This gives rise to a mechanical difficulty. We have been so far accustomed to regard the electron merely as a point charge, hence more than three degrees of freedom (corresponding to three independent quantum numbers) would be incomprehensible. What is then the origin of the fourth?

The fourth must be due to some further degree of freedom which the electron possesses, and Goudsmit and Uhlenbeck traced it to the rotation of the electron about some axis fixed in itself. They thus revived an old theory due to Parsons and Compton that the molecular currents giving rise to atomic magnetism may be due to the fact that the electron is rotating rapidly round an axis. The quantum number $s = \frac{1}{2}$ is therefore now also known as *the spin-quantum number.*

It was originally Abraham who worked out a theory of the *rotating electron* from classical-electro-magnetism. He showed that if a spherical charge 'e' occupies a volume of radius 'a' and rotates with the angular velocity ω about an axis fixed in itself we get the following results:

$$\text{Electromagnetic Mass} = \frac{2}{3}\ \frac{e^2}{ac^2}$$

$$\text{Mechanical moment, } \Omega = \frac{2}{9}\ \frac{ae^2}{c^2}\ \omega$$

$$\text{Magnetic moment } \mu = \frac{a^2e}{3c}\ \omega$$

$$\text{Ratio } \frac{\mu}{\Omega} = \frac{e}{mc}$$

But if $\mu = \dfrac{eh}{4\pi cm}$, a Bohr-magneton, we can calculate $a\omega$, the surface velocity. It comes out to be very nearly thousand times the velocity of light.

In spite of the difficulty that the surface has to rotate with a speed which is about thousand times the velocity of light, the rotating electron has some very recommendatory features. The ratio of the magnetic moment to the mechanical moment comes out to be $\dfrac{e}{mc}$ which is more in accord with the results of the Einstein-De-Haas experiment on the ratio between the two moments. It also removes a mechanical difficulty. According to the orientation hypothesis, the atom-magnet can be in equilibrium at any tilt to an external axis given by $\cos^{-1}\left(\frac{m}{j}\right)$. But according to dynamical principles only the position $\theta=0$ (the atom-axis parallel to the magnetic field) is one of stable equilibrium. The position $\theta = \pi$ (atom-axis antiparallel to the field) is one of unstable equilibrium. The others are not positions of equilibrium at all. But if we suppose the electron to rotate rapidly, it behaves more or less like a gyroscope and hence the orientation of the electron-axis at any angle does not present an insuperable mechanical difficulty.

The idea of the rotating electron thus provides a very suggestive picture of mechanical processes involved in the production of series lines. If it is correct the elementary spectrum, *i.e.*, the spectrum produced by the motion of an electron round a bare nucleus (as in H-atom) should be a doublet spectrum as in alkalies. In other words, the hydrogen spectrum should be exactly analogous to the spectrum of sodium.

This gives a new interpretation to the fine structure of Balmer lines. According to Sommerfeld the fine structure was due to difference in values of k of orbits having the same total quantum number, *i.e.* between 2_2 and 2_1. But now the difference is seen to be due to difference in the value of j, k remaining the same. It so happens that for hydrogen value of 2_{11}, and 2_{21}, are identical, and $2_{21}—2_{22}$continues to be given by Sommerfeld's formula.† The separation observed in hydrogen is therefore of magnetic origin and not of relativity origin, though the observed separation continues to be correctly given by the relativity formula.

Lande's '*g*' -factor

Further support to the view that magnetism is due to the superposition of two distinct motions of the valency electrons, *viz*., 1) due to rotation denoted by s. . . 2) due to orbital motion denoted by $k-1$. . . . is provided by an examination of the g-values, and of *Paschen-Back effect*. The last result, which is very important for atomic physics, was discovered by Paschen and Back in the year 1912. They

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*See Stoner, Theories of Magnetism.

†The mathematical proof is due to Heisenberg and Jordan, see Birtwhistle, New Quantum Mechanics.

found that when a gradually increasing magnetic field is applied, the anomalous Zeemann patterns undergo a most curious transformation. For example, the D_1 and D_2-lines tend to coalesce into a single line at the centre of gravity of the two lines with three normal components given by the original Lormor-Lorentz formula.

Lande explained this, and the '*g*'-values from the hypothesis that the observed magnetism is the resultant of '*s*' and '*k*'. When the field is weak, the spin-axis, and the orbital axis are strongly coupled to each other, and in calculating the change in energy when the atom is placed in a magnetic field, we must take the coupling between '*s*' and '*k*-1' into account. We then get the '*g*'-values. In a strong field, this coupling is broken, and the energy-changes due to spin and orbital motion are integral multiples of $\frac{eH}{4\pi cm}$, and are added vectorially, giving rise to normal pattern (For details see Lande and Back, *Zeemann-effect*).

Bohr's Principle of Atom-structure

While Sommerfeld with his students was engaged in unravelling the structure of complex spectra, Bohr with his pupils was occupied in evolving the principles of atom-structure. The two sets of studies are complementary to each other. Bohr was mainly guided by results of X-ray analysis, and chemical properties of atoms, though full use was made of spectroscopic results wherever needed. He pictured to himself a nucleus of Z-charges, and constructs the atom by bringing the Z-electrons one by one and studying their quantum-mechanical characteristics. The preliminary studies of Moseley had shown that the electrons are arranged in the K, L, M shells, and these shells are characterised by the total quantum numbers 1, 2, 3, ... etc. Further experiments on the absorption as well as the emission spectra of X-rays showed that while the K-shell is single,

the L-shell is threefold . . . . denoted by L_1, L_2, L_3,
the M-shell is fivefold . . . denoted by M_1, M_2, M_3, M_4, M_5,

The absorption-edges are similar to the absorption-edges appearing at the limit of principal series of the optical spectrum of sodium. This, as we know, corresponds to the ionisation of sodium, *i.e.*, splitting off of the valency electron from the sodium-atom. We shall see that the X-ray absorption-edges correspond to a similar phenomenon, *viz.*, the tearing off of an electron from the K-or some one of the K,L,M . . . shells as the case may be.

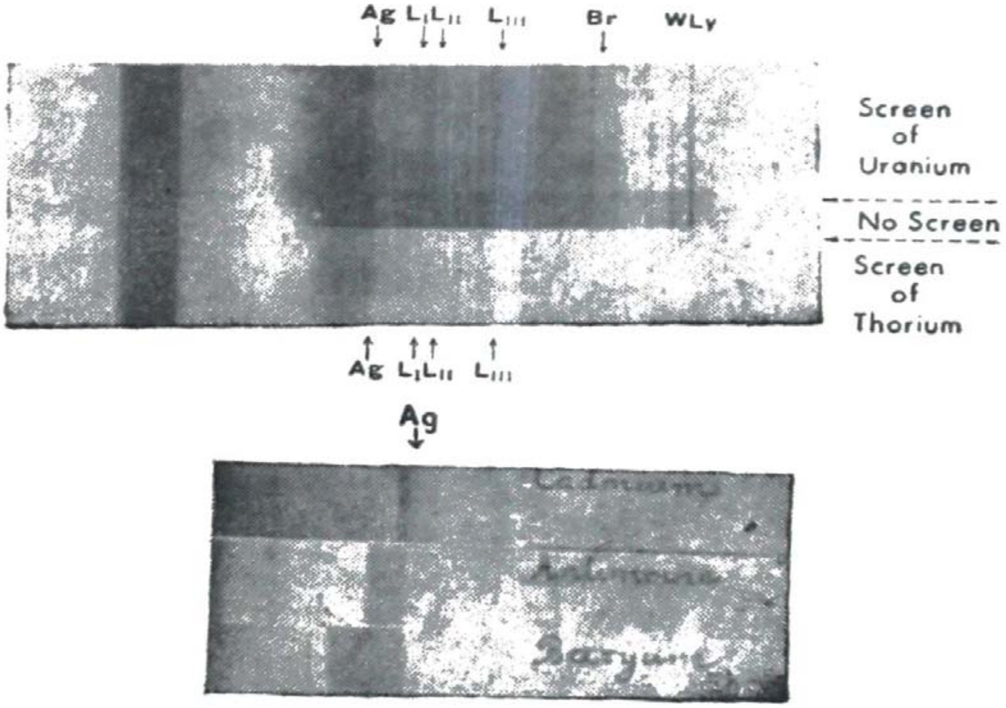

Fig. 42—(From Andrade's *Structure of the Atom*, p. 380.)

(The absorption spectra of X-rays were first studied by Wagner, and De Broglie. A white beam of X-rays as is obtained from the tungsten anti-cathode of an X-ray tube, falls upon the reflecting face of a rotating crystal. The spectrum formed is allowed to pass through a thin metal foil to the photographic plate. The nature of the absorption spectrum is quite different from what is obtained in optical absorption. There are no monochromatic absorption corresponding to the characteristic K_α or K_β-lines, but an absorption edge appears in the position of the limit of K-series. The K-absorption edges for the elements Cd (48), Sb (51), and Ba (56) are shown at the top-picture. Note that the absorption edges recede to the short-wavelength side with increasing atomic number. In the lower picture, the L-absorption edges of the U are shown. They are three in number denoted by L_1, L_2, L_3, in order of decreasing frequency.)

It was found that the K-series of emission-lines can be represented by transition of the electron between the K and two of the three L-shells and the L-series by transition of the electron between the L and M-shells, as represented in Fig 43.

The study of the transitions determine the quantum-characteristics of the levels.

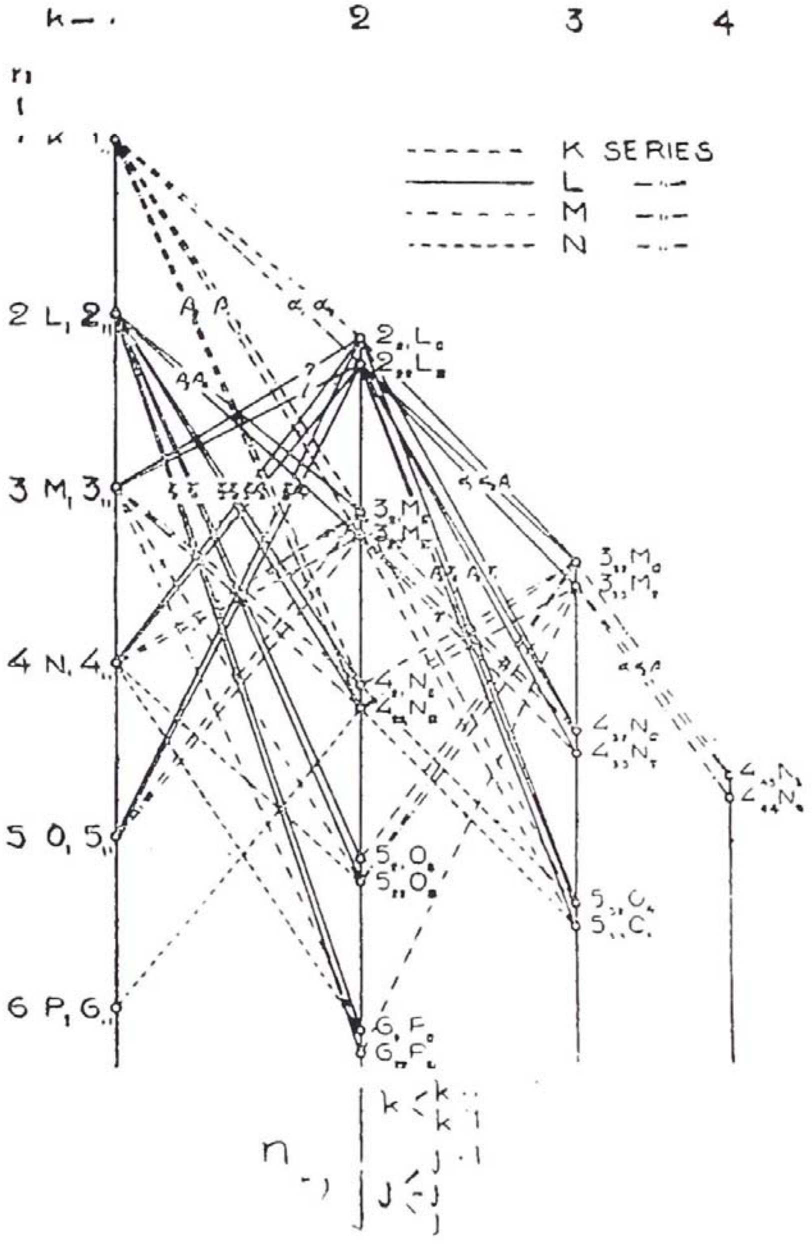

Fig. 43.—(From Siegbahn's *X-rays*)

For the K-shell, $n=1$, and hence $k=1$. It may be denoted, in terms of the n^{r}_{kj} nitation by 1_{11}, is it similar in nature to the ${}^{2}S_{\frac{1}{2}}$-term of Sodium.

The line K_{α} is due to the transition $K_1 \leftarrow L_3$, and K_{α}' arises from $K_1 \leftarrow L_2$. L_1 does not combine with K_1. Hence L_1 must be 2_{11}, and L_3 and L_2 are respectively 2_{22} and 2_{21}. L_3 and L_2 must have their $k=2$, and differ in their inner quantum numbers. The L-levels are similar in nature to the $2s$ (L_1), $2p_1$ (L_2), $2p_2$ (L_3)-terms of Sodium.

There are really three L-groups of lines, and analysis shows that the quantum characteristics of the M-shells can be denoted by:

M_1	M_2	M_3	M_4	M_5
3_{11}	3_{21}	3_{22}	3_{32}	3_{33}
$3s$	$3p_1$	$3p_2$	$3d_2$	$3d_3$

The L-lines are

$(L_2, L_3) \leftarrow M_1$	. .	n, l	$2p_{12}-2s$
$L_1 \leftarrow (M_2, M_3)$	. .	$\beta_3\ \beta_4$	$2s-3p_{12}$
$(L_2\ L_3) \leftarrow (M_4, M_5)$	. .	$\alpha_1\ \alpha_2\ \beta_1$	$2p_{12}-3d_{23}$

The analogy with the alkali-spectrum is therefore complete. This analogy is in fact far-reaching.

For finding out the full number of electrons required to fill up a level completely, Bohr made use of the periodic classification, not as originally formulated by Mendeleef and Lothar Meyer, but as modified by Julius Thomsen:

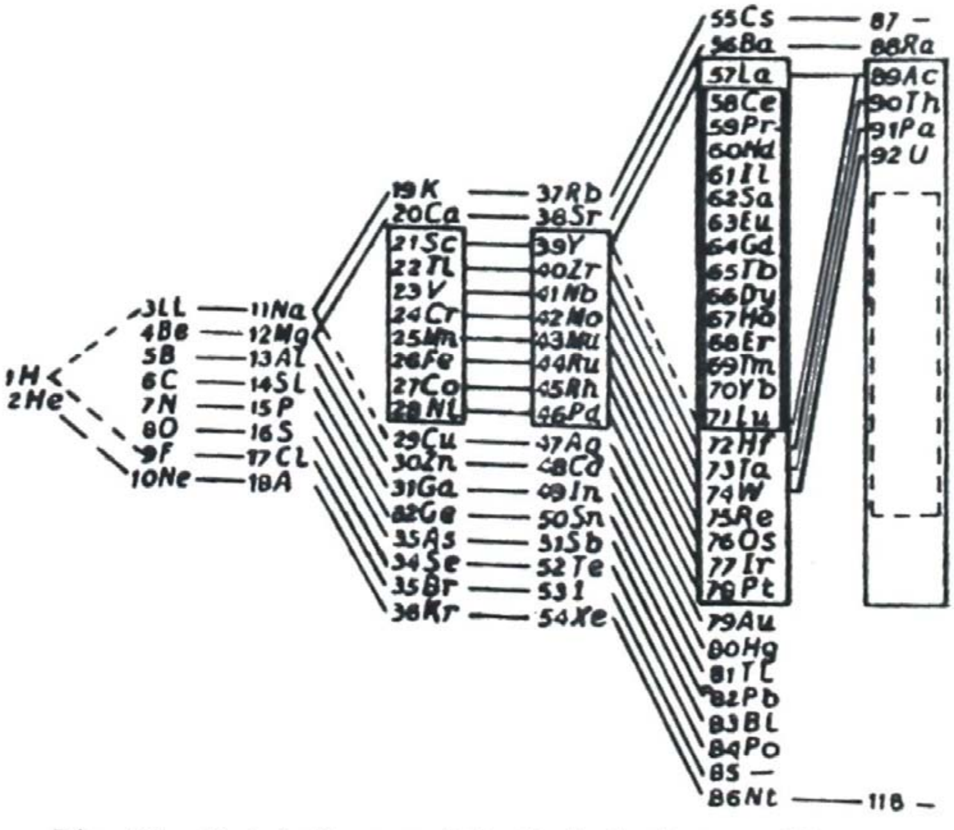

Fig. 44.—Bohr's Survey of the Periodic System. (From Andrade's *Structure of the Atom*, p. 429.)

The above diagram in substance due to J. Thomsen, was drawn up by Bhor to illustrate his principles of atom-structure. Each vertical column corresponds to a horizontal row of the usual Mendeleef

Table. Hydrogen and Helium stand apart, and constitute the first period. The second and the third period are constituted by the groups Li (3) . . . to Ne, and Na (11) . . . to A.

Elements with similar properties are placed opposite each other, as (Li-Na), (Be-Mg), and the valency goes on increasing by one as we follow each period vertically downwards. The periods are closed by inert gases (10Ne—18 A). But when we come to the fourth period (fourth vertical column), the first two elements are monovalent and divalent respectively (11 Na—19K), (12 Mg—20 Ca) but then we come across a group of elments from (21 Sc to 28 Ni) in which the properties are not repeated. They constitute a new group of elements with new chemical properties and extremely complicated spectra, and are generally denoted as a '*Transitional Group*'. From (29 Cu to 36 Kr) we again get a regular group, in which the valency goes on increasing one by one, *viz*., (11 Na—29 Cu) monovalent. (12 Mg—30 Zn) divalent . . . (18 A—36 Kr) inert gas.

Bohr now postulates that similarity in chemical properties and in structure of spectra arise from the similar quantum characteristics of the electrons outside of the closed shells. Hence it becomes necessary to find out how the K -and L-shells are filled up.

Two electrons are necessary to fill up the K-shell, giving rise to He, an inert gas. The next electron must be lodged in L (Li). Since Li and Na are alike, the valency, electron of Sodium must be in a similar level which can be only M . Hence the L-sehlls must accommodate the eight elements between Li and Na.

$$\begin{array}{cccccccc} K_1 & L_1 & & \underbrace{L_2\ \ L_3} & M_1 & \underbrace{M_2\ M_3} & \underbrace{M_4\ M_5} \\ 2 & 2 & & 6 & & & \\ \text{He} & \text{Li} & \text{to} & \text{Ne} & \text{Na to A} & & \end{array}$$

We assign two electrons to L_1, since we have assigned two to K_1. This leaves 6 for L_2L_3. The M-levels up to M_3 are similarly filled up by 8-electrons, giving rise to elements from Na to A.

The next elements, K and Ca, are monovalent and divalent, and they are essentially similar to Na and Mg. Hence the valency electrons must occupy similar shells. These cannot be (M_4 M_5), but N_1, which just requires two electrons.

Next we have the elements Sc to Ni forming the Transitional Group 1, with different chemical as well as spectral properties. Scandium is quite dissimilar to Al, hence the valency electron is not in N_2. Bohr postulates that it must be in $(M_3\ M_4)$, and the process will continue till the $(M_3\ M_4)$—levels are filled up giving rise to elements from Sc to Ni.

But from Cu 29 to Ar 36 we have again a regular group. This is easily explained if we assume that 10 electrons are required to fill up $(M_4\ M_5)$, and when this is done in the last element of the transitional group *viz.*—Ni 28, the $(N_1\ N_2)$ levels begin to be formed giving rise to a fresh regular group.

The number of electron required to fill up a sub-group:

We find that two electrons are required to fill up a s-shell, $(K_1\ L_1\ M_1 \ldots)$, 6 for the combined p-shells $\overbrace{L_{21},\ L_{22}},\ \overbrace{M_{21},\ M_{22}}, \ldots\ldots$, 10 for the combined d-shells $(M_{32}\ M_{33} \ldots\ldots)$. Stoner observed that the number of electrons is just double the inner quantum number of each shell,* *e.g.*

L_{11}	L_{21}	L_{22}	M_{11}	M_{21}	M_{22}	M_{32}	M_{33}
2	2	4	2	2	4	4	6

The electron-composition has be illustrated in Fig 45.

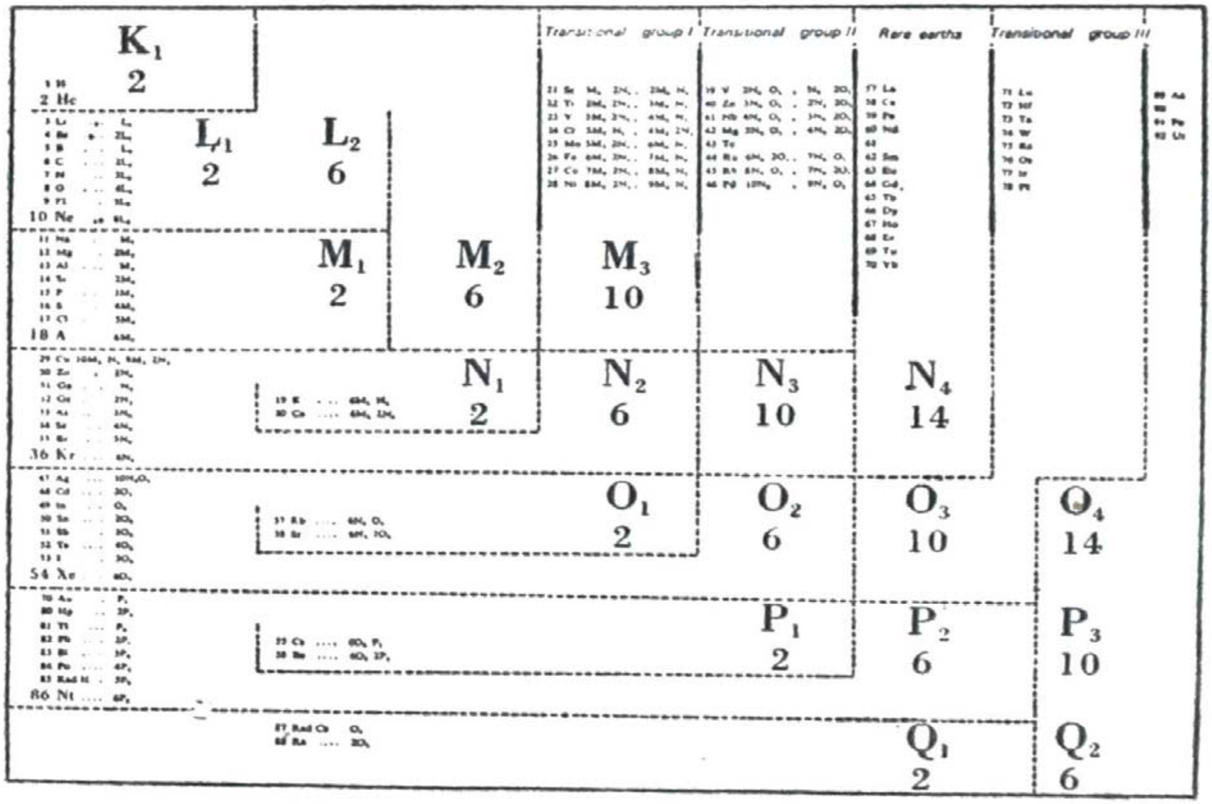

Fig. 45.—(From Volta-centenary Volume.)

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*The inner quantum number in the old sense. They exceed Lande's *j*-vaules by $\frac{1}{2}$.

In this diagram, we have written the levels with the same k diagonally (K_1, L_1 ..... L_2 M_2 .....). Again, the sub-levels of L_2 *viz.* L_{21}, L_{22}..... have been combined, as the record of complex spectra shows that the splitting up of the two levels is rather artificial. The splitting observed in X-rays will be explained later. The chart visualizes the electronic composition of atoms. Thus let us take the elements O and S: they have the compositions:

O ..... $2K_1\ 2L_1\ 4L_1$ ..... or $(1s)^2\ (2s^2)\ (2p)^4$

S ..... $2K_1\ 2L_1\ 6L_2\ 2M_1\ (4M_1)$ or $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^4$

The inert gases end in closed shells of $(xp)^6$, $x=2$ for Ne. 3 for A. . . etc., ... The composition of the regular groups is shown in the sides. The electronic composition of a transitional element like Ti can be written down from a glance at the chart:

$$\text{Ti}\text{—}(2K_1\ 2L_1\ 6L_2\ 2M_1\ 6M_2)\ \left.\begin{matrix} 3M_3\ N_1 \\ 2M_3\ 2N_1 \end{matrix}\right\}$$

or alternatively as

$$(1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^6)\ \begin{matrix} 3d\ 4s^3 \\ 3d^2\ (4s)^2 \end{matrix}$$

The chemical and spectral properties depend entirely on the electron-combination

$$\begin{matrix} 3d^2\ 4s \\ 3d^2\ 4s^2 \end{matrix}$$

lying outside the closed shells.

Higher Periods

It is now quite easy to follow the formation of the fifth period (*vide*) consisting of

	37 Rb 38 Sr	
Transitional Group II	39 Y to 46 Pd	$(4d)^x\ 5s$ $(4d)^{x-1}\ (5s)^2$
Regular Group IV	47 Ag to 54 Xe	$(5s)^2\ (5p)^x$

Explanation of Complex Spectra : Principle of Superposition of Quantum Numbers

The Principle of superposition of quantum numbers which gives a unitary explanation to complex spectra, to Bohr's theroy of periodic classification, and to the origin of X-ray spectra was arrived at by different workers, almost simultaneously, proceeding along quite different lines. Saunders and Russell proceeded from a deep, and significant study of the anomalous terms of Ca, Sr, and Ba. Pauli and and Heisenberg proceeded from an examination of the spectral terms of two-valence elments. The basic ideas are the following (some have been already foreshadowed):

(1) It is only the electrons outside a closed shell which determine the nature of the spectrum.

(2) The quantum-characteristics of each electron is of a doublet type and is determined by the shell in which it is palced.

The second part simply means that the electron is also a magneton, and has four quantum numbers n, k, s, m. The values of these quantum numbers for an electron in M_1 are

$$n=3,\ k=0,\ r=\tfrac{1}{2}\ j=\tfrac{1}{2},\ \text{hence } m=\tfrac{1}{2} \text{ or} -\tfrac{1}{2}.$$

The value of 's' is always $\frac{1}{2}$. For the k-values, we assume for an s-orbit, $k=0$, for p-orbit $k=1$, for d-orbit, $k=2$, etc.

These k-values are less than Sommerfeld's k's by one.

For an electron in N_2,

$$n=4,\ k=1,\ j=\tfrac{1}{2}, \text{ or } \tfrac{3}{2} \text{ giving } P_{\frac{3}{2}} \text{ or } P_{\frac{1}{2}}$$

and we have $m=\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$, or $m=\frac{1}{2}, -\frac{1}{2}$.

There are six different m-values. The $\pm\frac{1}{2}$-values for $P_{\frac{1}{2}}$ and $P_{\frac{3}{2}}$-terms really arise from different relative orientations of the spin axis and the orbit-axis (k) and are really different in spite of their numerical agreement.

Probably these m-values are better explained if we make use of the diagrams shown in Fig 46.

(3) When there are more than one electron outside of the closed shells, the observed spectral terms are obtained by the vectorial addition of each of the quantum numbers pertaining to each electron.

To illustrate these principles, let us first consider the spectrum of an one-valence element, *e.g.* Na. We write out the structure diagram as shown in Fig. 47.

Sodium contains 11 electrons. Of these 2 fill up the K-level and 8 the L-levels completely. The remaining electron is normally at M_1 ... the normal level is ${}^2S_{\frac{1}{2}}$. The next transitions are shown by the symbol (1). We get successively the ${}^2P$, ${}^3D$-terms. All terms arising from a diagonal displacement from the successive members of a Rydberg sequence. This is indicated in the structure diagram. If we take any other alkali element, say Li, K, Rb or Cs, we find the same story repeated hence there spectra are identical, vide supra.

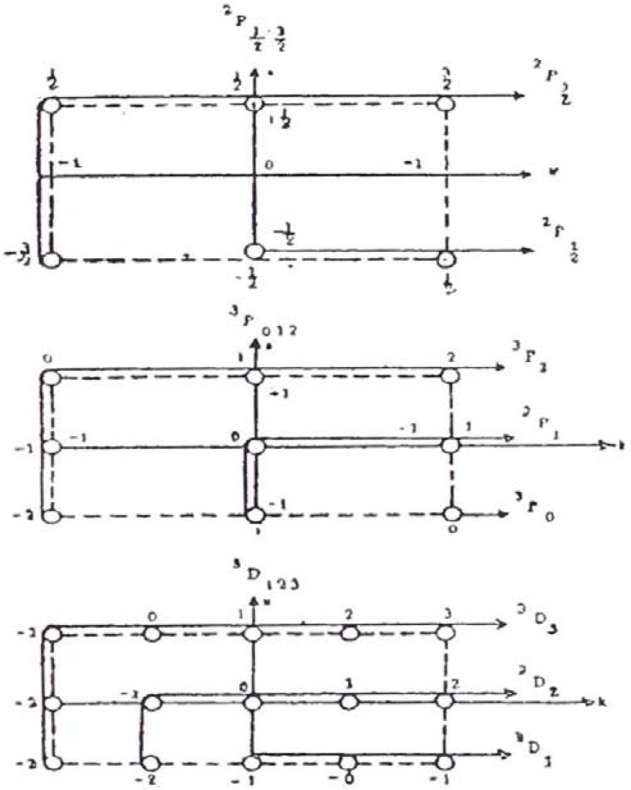

Fig. 46.

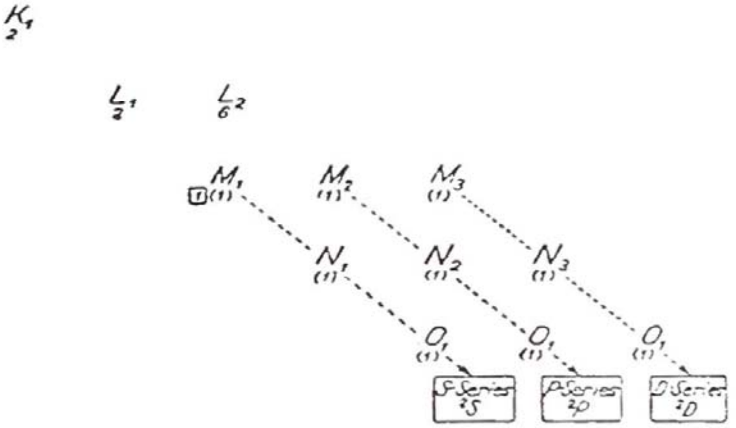

Fig. 47.—Structure diagram of Na.

Rules of Transition.—We know that the *s*-terms can combine with *p*-terms only, and cannot generally combine with another *s*-term or a *d*-term. To come from an *s*-term to a *p*-term we must displace the electron (horizontally or vertically, both being regarded equal : but not diagonally) an odd number of times. To come from an *s*-term to another *s*-term or *d*-term, the number of displacements required is even. So we may formulate a general principle: *Only such transitions of the electron are possible which involve an odd number of displacements. An even number of displacements is forbidden.*

We shall see that this rule is of universal application.

It should be noted that there is a difference in the designation of the spectral terms as done by spectroscopists, and as formulated by Bohr. In Na, the largest term $M_1=41449=\dfrac{N}{(1+s)^2}$ is denoted by spectroscopists by the symbol 1*s*, the total quantum number being taken unity. According to Bohr, this should be 3*s*. The term in the M_2-level are $2p$, $2p_2$ according to the notation of Paschen, but this should be $3p_1$, $3p$, according to Bohr. The superiority of the Bohr-notation will be evident when we come to a discussion of the *irregular doublet law*. Spectroscopic notation changed too rapidly in course of the last few years; it has now been thought necessary to introduce some notation which will be more representative of new facts. Russell, Saunders, Shenstone and other spectroscopists introduced the folliwing symbols which have been adopted by general consent :

Old symbol ...n_{kj}^{r} ... New ... ... $^2S_{\frac{1}{2}}$

The central capital letter indicates the k-nature of the term. The subscript denotes the inner quantum number. The small figure to the left hand shoulder of S indicates multiplicity. The total quantum number is not usually given. When necessary, it is indicated by a numerical figure before the capital letter.

Thus $5^2S_{\frac{1}{2}}$.... denotes that the total quantum number is 5. A transcription of the spectral terms of sodium in terms of the new symbols is shown in earlier.

Periodicity of the Spectrum

We adopt a similar procedure to denote the spectrum of any other alkali. Thus for Potassium we get ($2K_1$ $2L_1$ $6L_2$ $2M_1$ $8M_2$). . N_1 . . There is only one electron in the N_1—orbit (4^2S) outside of the closed shell, in the normal condition. The excited orbits are obtained by allowing the electron to run through the higher levels N_2 N_3 O_1 . . etc. . .

It is clear that the spectrum of Potassium should be quite alike that of Na. Similarly for Rb, Cs, and to a certain extent for Cu, Ag, Au.

Spectra of Two Valence Elements.—Under the heading, we include the spectra of Be, Mg, Zn, Cd, Ca, Sr, Ba. But for the sake of

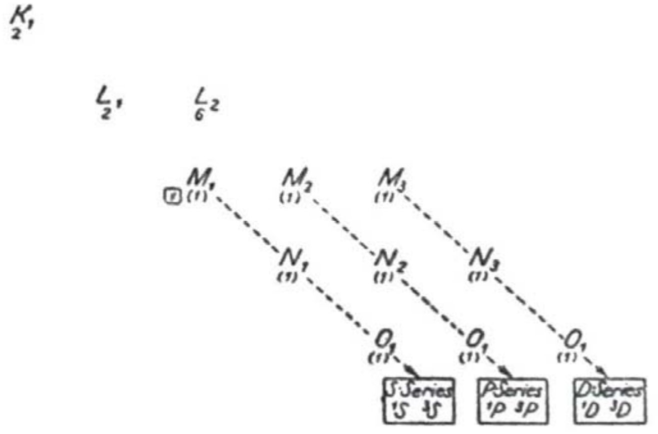

Fig. 48.

convenience, we shall begin with the spectrum of Mg. Let us write out the structure diagram.

We see that after the K and L-levels have been completed, there are two electrons at M_1. The normal orbit of Mg arises when both electrons are at M, the higher terms arise when one is kept permanently at M_1, the other is allowed to run through the higher levels.

The observed spectroscopic terms of Mg are:

^1S_o		.. .. spectroscopic	$n=1$, largest term
$^1P_1$	$^3P_{o.1.2}$	.. }	$n=2, 3..$ with Rydberg sequences
$^1D_2$	$^3D_{1.2.3}$	.. }	$n=3, 4..$
^1S_o,	$^3S_1$ ..	.. }	$n=2, 3..$

The largest ^1S_o-term is due to M_1M_1.. The next terms (^1P, ^3P) are due to M_1M_2. (^1D, ^3D) are due to M_1M_3. M_1N_1 gives us (^1S_o, $^3S_1$) etc. ..

All terms except the largest ^1S_o are explained by the rules of vectorial addition. We have for the combination $M_1M_{,2}$

$$\begin{array}{llll}
\text{for } M_1 & \ldots\ \ldots & s_1=\tfrac{1}{2}, & k_1=0 \\
\phantom{\text{for }} M_2 & \ldots\ \ldots & s_1=\tfrac{1}{2}, & k_1=1 \\
\text{for } M_1\,M_2 & \ldots\ \ldots & s=|s+s_1|=0 \text{ or } \tfrac{3}{2} \ldots \text{singlets, triplets.} & \\
 & & k=|0+1|=1 \qquad P\text{-terms.} &
\end{array}$$

Similarly we get the D-sequence from the combination $M_1\ X_3$. The *s*-sequence is obtained from the combination $M_1\ X_1$.

We have now to explain *why in the combination* M_1N_1, *we get only* ^1S_o *and no* $^3S_1$.

For explaining this fact, we have to see how the *j*-values of the resultant terms arise.

Let us take the M_1M_2 or *sp*-combination.

$$\begin{array}{llll}
\text{For } M_1, & \ldots \quad j=\tfrac{1}{2}, \quad \ldots & m=\tfrac{1}{2}, -\tfrac{1}{2} & \\
\phantom{\text{For }} M_2, & \ldots \quad j=\tfrac{1}{2}, \tfrac{3}{2} \quad \ldots \Big\} & m=\tfrac{1}{2}, -\tfrac{1}{2} & \text{for } {}^2P_{\frac{1}{2}} \\
 & & =\tfrac{3}{2}, \ \tfrac{1}{2}, -\tfrac{1}{2}, -\tfrac{3}{2} & \text{for } {}^2P_{\frac{3}{2}}
\end{array}$$

For the combination

$$S_{\frac{1}{2}}\ P_{\frac{1}{2}}, \quad \ldots \qquad \begin{array}{rrr}
m= & \tfrac{1}{2} & -\tfrac{1}{2} \\
 & \tfrac{1}{2} & -\tfrac{1}{2} \\ \hline
1 & 0 & \\ \hline
 & 0 & |-1
\end{array}$$

The resultant m's arise from $j=1$, $j=0$, *i.e.*, the terms are $^1P_1$, ^3P_o.

For the combination:

$$S_{\frac{1}{2}}\,P_{\frac{3}{2}},\quad \ldots \qquad \begin{array}{rccccl} m_1= & & \frac{1}{2} & -\frac{1}{2} & & \\ m_2= & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} & \\ \cline{2-5} & 2 & 1 & 0 & -1 & \\ \cline{2-5} & & 1 & 0 & -1| & -2 \end{array}$$

The resultant m's correspond to $j=2$, $j=1$, *i.e.*, the terms are ($^3P_1$, $^3P_2$).

In the (M_1N_1)-combination

$$\begin{array}{rlccc} \text{for } M_1 & \ldots\ S_{\frac{1}{2}}\ \ldots\ \ldots\ m= & \frac{1}{2}, & -\frac{1}{2} & \\ N_1 & \ldots\ S_{\frac{1}{2}}\ \ldots\ \ldots\ m= & \frac{1}{2}, & -\frac{1}{2} & \\ \cline{2-4} & & 1 & 0 & \\ \cline{3-5} & & & 0 & -1| \end{array}$$

The j-values are 1, 0, we get $^3S_1$, ^1S_o. But in M_1 M_1 we get only ^1S_o.

Pauli explains this by enunciating his famous Exclusion Principle:—*No two electrons can have all their four quantum numbers n. k. j, m identical.*

In M_1N_1 the n's were 3 and 4. Hence k, r, m could take all possible values. But in M_1M_1, the n's are identical, as well as k and r. Hence the m's should be different. Hence if $m_1=\frac{1}{2}$, $m_2=-\frac{1}{2}$, resultant $m=0$, we get only ^1S_o.

Thus in the closed shell, the electrons have their magnetic axes in the opposite directions, forming an astatic system with the resultant magnetic moment zero.

But Pauli's principle goes much further than explaining the spectrum of two-valence elements. It explains almost the whole of complex spectra as well as the periodic classification.

LECTURE V

(CONTINUATION OF LECTURE IV)

Total number of atoms required to fill up a level

We have seen that according to the Bohr-Stoner-Mainsmith scheme, 6 electrons are necessary to fill up a *p*-level, 10 to fill up a *d*-level, 14 for an *f*-level. This fact turns out to be a simple deduction from Pauli's Principle: The full number to fill up a level is given by the number of different *m*-values in that level, for since *n*, *k*, *r* are the same, the *m*'s should be all different. The level is completely filled up when there is one electron to each *m*-level. For a *p*-level (M_2), the *m*-values are:

$$\begin{array}{cc} {}^2P_{\frac{1}{2}} & {}^2P_{\frac{3}{2}} \\ \frac{1}{2}, -\frac{1}{2}, & \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}. \end{array}$$

Similarly, 10 electrons are required to fill up a *d*-level (M_3) corresponding to the 10 magnetic levels of ${}^2D_{\frac{3}{2}}$, ${}^2D_{\frac{5}{2}}$. Pauli's Principle thus explains the periodic classification in a most elegant way.

Spectra of Three-Valence Elements

After Magnesium, we come to Aluminium, with the structure diagram .. .. ($2K_1$ $2L_1$ $6L_2$ $2M_1$) M_2 .. . The normal terms are therefore those corresponding to M_2, *i.e.*, ${}^2P_{\frac{1}{2}}$ ${}^2P_{\frac{3}{2}}$. The next terms are given by M_3, ${}^2D_{\frac{3}{2}, \frac{5}{2}}$ .. N_1 .. ${}^2S_{\frac{1}{2}}$ etc.

If the two electrons in M_1 formed too inert a shell, aluminium would be monovalent. It is found that $2M_1$ does not form, so rigid a shell as helium. We get lines corresponding to M_1 $2M_2$, *i.e.*, one M_r electron passing to M_2.

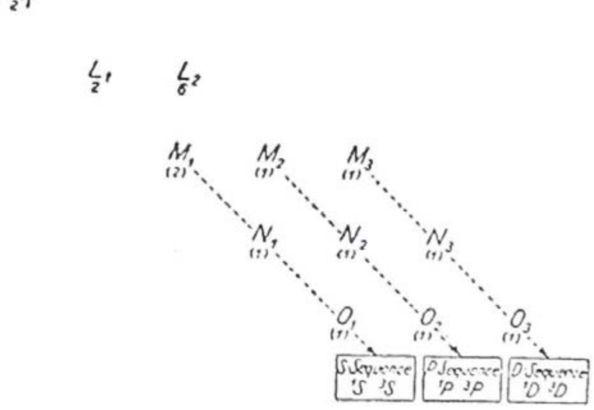

Fig. 49.—Structural diagram of Al.

The term values and their origin are shown below.

Combination	Terms	Term-values	Remarks
b_0) M_2	$^2P_{1,2}=$ and sequence	$\left.\begin{array}{l}48168{\cdot}87\\ \ldots 280{\cdot}88\end{array}\right\}$ $\left.\begin{array}{r}15316\\ 331\end{array}\right\}$ etc.	Normal terms
c_1) M_3	$^2D_{2,3}=$	$\left.\begin{array}{r}15845{\cdot}5\\ 844{\cdot}2\end{array}\right\}$ etc.	$b_0{}^2P-c_1{}^2D$ roughly follows the irregular doublet law, because the total quantum number is the same.
a_1) N_1	$^2S_1\ =$	$\left.\begin{array}{r}22933{\cdot}3\\ 10592{\cdot}6\end{array}\right\}$	$b_0{}^2P-a_1{}^2S_1$ does not follow the irregular doublet law Total quantum number different.
a_1) $M_1{\cdot}2M_2$	$^4\overline{P}$ $^2\overline{P}_{1,2}$ $^2D_{2,3}$ $^2S_1$	? $\left.\begin{array}{r}-8361\\ -8249\end{array}\right\}$? ?	Combination $P\overline{P}$ corresponding to the inner transition $2M_1M_2-M_1{\cdot}2M_2$ has been discovered by Millikan and Bowen in case of Al, and by Kichlu in case of Si^+. So this transition is possible in all three-valence spectra.

Spectra of Four-Valence Elements

Coming to the next element Si, we find that there are two electrons in M_2 or the structure is p^2. For the next elements P, S, Cl, A . . the structures are p^3, p^4, p^5, p^6. We have to find out, with the aid of the Exclusion Principle, the nature of terms arising out of the combination p^n. This was first done by Hund, and afforded the explanation to the whole of complex spectra.

If Pauli's principle were not operative, pp would give us:—

$$\begin{array}{llll} s=\lvert s_1+s_2 \rvert = \lvert \tfrac{1}{2}+\tfrac{1}{2} \rvert = 0, & \ldots\ \text{Singlet};\ \tfrac{3}{2} & \ldots & \text{Triplet} \\ k=\lvert k_1+k_2 \rvert = \lvert 1+1 \rvert = 0,\ 1,\ 2 & \ldots & \ldots & s.p.\ d\text{-terms} \end{array}$$

$$\text{i.e.}\qquad \left.\begin{array}{lll} {}^3D_{1\,2\,3}, & {}^3P_{0\,1\,2}, & {}^3S_1 \\ {}^1D_2 & {}^1P_1 & {}^1S_0 \end{array}\right\}$$

$$\text{i.e.}\qquad \text{10-terms with}\ \left.\begin{array}{l} (3+5+7)\ +\ (1+3+5)\ +\ 3 \\ \quad +\ \ 5\ \ +\qquad 3\qquad\ +\ 1 \end{array}\right\}$$

altogether 36 magnetic levels. This is just equivalent to 6×6, *i.e.*, the number of levels obtained by combining any one of the 6*m*-levels of one electron with 6 *m*-levels of the other. But while this occurs in a '*pp*' combination where the *n*'s are different, as in M_2N_2; in a 'p^2' combination, *i.e.*, where *n*'s are the same the resulting terms should be such that their magnetic levels number only ${}^6C_2$ *i.e.*, 15. Hund showed by a detailed calculation in accordance with the Pauli Principle that the following terms remain :—

$$^3P_{012}\,,\quad ^1D_2\,,\quad ^1S_0.$$

In a similar way, Hund calculated the terms due to the p^3, p^4, p^5, p -combinations. They are shown below:

Number of p-Electrons	Terms		
1	^2P		
2	$^3P_{0,1,2}$	$^1\overline{D}_2$	$^1S_0$
3	$^4S_2$	$^2D_{2,3}$	$^2\overline{P}$
4	$^3P_{0,1,2}$	$^4D_2$	$^1\overline{S}_c$
5	$^2P_{1,2}$		
6	$^1S_0$		

As regards this table, we call attention to the fact that p^4 gives the same levels as p^2, and p^5 gives us the same levels p^1. This is partly a consequence of the theorem that ${}^nC_r={}^nC_{h-r}$. But the terms are inverted *i.e.*,

in p^2 . . . $^3P_0 > {}^3P_1 > {}^3P_2$
but in p^4 $^3P_0 < {}^3P_1 < {}^3P_2$.
similarly in p^1, $^2P_{\frac{1}{2}} > {}^2P_{\frac{3}{2}}$
but p^5, $^2P_{\frac{1}{2}} < {}^2P_{\frac{3}{2}}$

In the p^6-combination as in Ne and A, we have the full quota of electrons occupying the 6 levels $\frac{1}{2}, -\frac{1}{2}\,;\ \frac{3}{2}, \frac{1}{2}, -\frac{1}{2} -\frac{3}{2}$. Hence resultant $m=0$. The level has no magnetic moment. Thus a closed shell gives us a $^1S_0$-term.

VALUES OF TERMS

From a scrutiny of spectroscopic data, Hund showed that generally the largest terms are those which have the highest multiplicity and the highest *k*-value.

Thus in the spectrum of carbon,

$^1P_{0,\,1,\,2,} > {^1D_2} > {^1S_0}$, all arising out of the combination L_1L_2 or p^2.

The ^3P-terms are known as the normal terms, $^1D_2$, $^1S_0$ are known as meta-stable terms.

The composition of the spectrum of four-valence elements can now be very easily written out. It is shown below for Silicon.

GROUP IV—FOUR-VALENCE ELEMENTS

Under this group, the following elements are included:

Atomic Number	6	14	32	50	82
	C	Si	Ge	Sn	Pb
	N^+	P^+	As^+	Sb^+	Bi^+
	O^{++}	S^{++}	Se^{++}	Te^{++}	Po^{++}
	Fl^{+++}	Cl^{+++}	Br^{++++}	I^{+++}	
	etc.				

They have almost identical spectral structure. The constitution of the structure of the spectrum of Si is indicated below:

THE SPECTRUM OF Si.

THE SPECTRUM OF Si.

$^2M_2$		$^3P_0$	$^3P_3$	$^3P_2$ (6076) $^1D_2$ (9095) $^1S_0$		
M_2N_1		64275	64198	64051	57975	48880
24592	$^3\bar{P}_0$	—	(8) 39606	—	—	—
24515	$^3\bar{P}_1$	(7) 39760	(7) 39683	(9) 39537	(5) 33461	(5) 24366
24320 24320	$^3\bar{P}_2$	— —	(9) 39878	(10) 39732	—	—
23823	$^1\bar{P}_1$	40998	40914	40768	(10) 34152	(9) 25057

Dashed and Undashed terms.—Some explanatory remarks may be made here regarding the dashing of terms in the foregoing Table. The rule is that if a number of terms arise from a particular combination of electrons, they must have all the same combinatory properties, provided the selection rule for the inner quantum number j is obeyed. Supposing now that from a particular combination, say p^2 above, S, P, and D terms arise, they must have all the same combinatory powers, and cannot combine amongst themselves. But if they are all denoted merely as S, P, D, then according to the usual convention, the P-can combine with S or D-terms. To express that this is not possible, we provide S and D with a bar (some authors prefer to dash them). Thus P and D have the same combinatory powers, and cannot combine amongst themselves, except under exceptional circumstances. We can express the same fact by dashing P, and keeping S and D undashed. It is purely a matter of convention in which we have to be guided by our previous knowledge of the spectrum of the element.

Thus in the spectrum of all four-valence elements, we have ^{3}P-terms in a normal p^2-combination, and a set of ^{3}P-terms in the excited *ps* (L_2M_1 in carbon) combination. The latter $^{3-}\overline{\mathrm{P}}$-terms (due to L_2M_1) are dashed, or barred, to signify that they can combine with the fundamental ^{3}P's, giving rise to the resonance lines of carbon. The combination does not violate the selection principle $\triangle k = \pm 1$ because this principle applies only to *electron-transition*. In giving rise to the $^3\mathrm{P}\overline{\mathrm{P}}$-lines, the electron passes from $(ps) \rightarrow (pp)$ or $(L_2M_1) \rightarrow (L_2L_2)$ or $M_1 \rightarrow L_2$. Hence the rule is strictly obeyed.

Inner Transition:—According to chemists, Silicon is a tetravalent element, but in the picture given above the composition is given as $2M_1$ $2M_2$. The two electrons in M_1 form a closed shell. There are only 2 electrons in the incomplete shell L_2. Hence strictly speaking, Silicon ought to be divalent. But experience shows that the electrons in L_1 do not form a very rigid structure. With moderate stimulus, they can easily be made to pass to L_2 giving rise to combinations $L_1 3L_2$ and $4L_2$. The existence of such transitions has been proved from lines arising from the combinations,

$$\begin{array}{cc} (2L_1\ 2L_2) & \leftarrow (L_1\ 3L_2) \\ L_1 & \leftarrow L_2 \\ (L_1\ 3L_2) & \leftarrow (4L_2) \\ L_1 & \leftarrow L_2 \end{array}$$

in carbon and silicon, and probably they exist in the other elements of the group, and in the spectra of ionised elements having normally the composition s^2p^2. Such transitions may be called *inner transitions*. Their existence justifies the treatment of carbon as a tetravalent element.

They are also present in the spectra of higher valency elements, *viz*., those having the compositions s^2p^3, s^2p^4, s^2p^3, (*e.g.*, N, O, Fl).

Calculation of spectral terms due to presence of several electrons in the same shell

Table, page 287 given above, represents the nature of spectral terms arising out of the combination p^x. It has been merely quoted. We shall briefly discuss how it can be derived from an application of Pauli's Principle.

Pauli's Principle tells us that in calculating the spectral terms due to a number of electrons in the same shell, the magnetic quantum numbers should be all different. Now we have

$$j = | k + s, |$$

hence m, the projection of j, can also be written as

$$m = | m_k + m_s |$$

Where m_k is the part of the magnetic quantum number arising from the projection of 'k', m_s is the part arising from 's'. Of course, m_s has only two values $(\frac{1}{2}, -\frac{1}{2})$. m_k is 0 for S-terms, $(1, -1)$ for P-terms and so on. The way in which m_k and m_s combine to give us the ${}^2P_{\frac{1}{2}}$, ${}^2P_{\frac{3}{2}}$ terms has been shown in diagram (Fig. 47, page 282).

In calculating the terms due to a p^x-combination, it is more convenient to use m_k and m_s as independent variables in place of 'j' and s. Pauli's Principle tells us that no two electrons should have identical m_k's and m_s's.

The calculation of terms due to a p^2-combination is shown below:

We find that the most fundamental terms are obtained by choosing the highest values of m_s, and adjusting m_k's in accordance with Pauli's Principle. Thus if we choose $m_s = \frac{1}{2}$ and $\frac{1}{2}$, the m_k's should be different, and the highest possible values are 1 and 0, giving rise to ${}^3P$. This group of terms possesses $(5+3+1)=9$ magnetic levels, whereas we require ${}^6C_2$ or 15-levels. The remaining 6 are obtained by taking m_k's

p^2....NUMBER OF MAGNETIC SHELLS $^6C_2=15$

Electron	(1)	(2)	Σ	Terms	Magnetic Levels
m_s ..	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{2}$		
m_k ..	1	0	1	^3P	9
m_s ..	$\frac{1}{2}$	$-\frac{1}{2}$	0		
m_k ..	1	1	2	$^1D_2$	5
m_k ..	0	0	0	$^1S_0$	1
					Total 15

different. Then we take the highest possible value of m_k, i.e. 1 and 1.

It should be remembered that in all these calculations, only the highest possible values of m_k, m_s should be used.*

Calculation of terms due to p^3-combination are shown in the following table:

p^3....Number of magnetic shells $^6C_3=20$.

Electron	(1)	(2)	(3)	Σ	Terms	Magnetic levels
$\begin{cases} m_s \\ m_k \end{cases}$ ..	$\frac{1}{2}$ 1	$\frac{1}{2}$ 0	$\frac{1}{2}$ -1	$\frac{3}{2}$ 0	$^4S_{\frac{3}{2}}$	4
m_s ..	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$		
m_k ..	1	0	1	2	$^4D_{\frac{5}{2}\frac{3}{2}}$	10
m_k ..	1	0	0	1	$^2P_{\frac{3}{2}\frac{1}{2}}$	6
						Total 20

---

*Vide Sommerfeld, *Zeit F Physik* Vol 40

As remarked above, terms due to p^4 and p^5 are respectively identical with those due to p^2 and p^1.

It is now merely a matter of algebra to write out the spectral terms due to five valence (*e.g.*, . . .N), six-valence (*e.g.*, O), seven valence (*e.g.*, F) elements, and to inert gases (p^6). They are illustrated below:

ELEMENTS OF GROUP V

Atomic Number ..	7	15	33	51	83
	N	P	As	Sb	Bi
	O^+	S^+	Se^+	Te^+	Po^+
	Fl^{++}	Cl^{++}	Br^{++}	I^{++}	At^{++}
	Ne^{+++}	A^{+++}	Kr^{+++}	Ne^{+++}	Nt^{+++}

All these elements have identical structure of spectra. The principal lines are shown below for Nitrogen which has been very completely investigated by Compton and Boyce:—

NITROGEN

$3L_2$ \ $2L_2M_1$	$^4P_{\frac{4}{2}}$	$^4P_{\frac{5}{2}}$	$^4P_{\frac{5}{2}}$	$^2P_{\frac{1}{2}}$	$^2P_{\frac{3}{2}}$
$^4S_{\frac{3}{2}}$ ..	83283	83318	83369		
117345 ..					
$^2D_{\frac{3}{2}}$ ..	104864	104890	105007	66900	66987
$^2D_{\frac{5}{2}}$ ..	110323	110351	110399		
98143 ..					
$^2P_{\frac{1}{2}}$ ..				57298	57381
$^2P_{\frac{3}{2}}$ ..					
88537 ..					

The group of lines arising from the transition $2L_2\ (M_1 \leftarrow M_2)$ lie in the infrared and were first obtained by Kiess and Kiess. $2L_2M_1$ . . gives us 9-terms (^4P, ^2P, ^2D, ^2S) and $2L_2\ M_2$ gives us $\left.\begin{matrix} ^4D\ ^4P\ ^4S \\ ^2D\ ^2P\ ^2S \end{matrix}\right\}\ \left.\begin{matrix} ^2F\ ^2D\ ^2P \\ ^2S \end{matrix}\right\}$ . . . altogether 21-terms. Not all of these have yet been obtained.

No intercombination has yet been obtained between the quartet and doublet spectra, in Nitrogen. But as pointed out by Kronig, the strength of the intercombination lines increases with atomic weight, and they are found quite strong in the analogous spectra of Bi, Sb and As.

ELEMENTS OF GROUP VI

This group includes

Atomic Number	8	16	34	52	84
	O	S	Se	Te	Po
	Fl^+	Cl^+	Br^+	I	
	Ne^{++}	A^{++}	Kr^{++}	Xe^{++}	
	etc.				

The structure of their spectra is illustrated in the following table for Oxygen,

OXYGEN

From $^2S_2$ of O^+, from ^2D; from ^2P

L_2M_1 $4L_2$	$^5S_2$	$^3S_1$	^3D	^1D	^3P	^1P
$^3P_0$ . .		76562				
$^3P_1$ . .	73601	76630				
$^3P_2$ . .	73760	76788				
$^1D_2$ . .						
$^1S_0$ . .						

The group of lines arising from the transition $3L_2$ ($M_1 \leftarrow M_2$) mostly lies in the infrared.

Now $3L_2$ of O^+ gives us $^4S_2$ ^2D ^2P.

In Oxygen, when we couple an outer electron to O^+-shell, we get different groups of terms according as the O^+-atom is in the normal ^4S or metastable ^2D or ^2P-states.

Thus in the $3L_2$ M_1-combination, we get

$\left|{}^4S+{}^2S\right|$ . . .${}^5S$ and ${}^3S$ from normal ${}^4S$-state

Also

$\left|{}^2D+{}^2S\right|$ . . .${}^3D$ . . . . ${}^1D$ from metastable ${}^2D$

$\left|{}^2P+{}^2S\right|$ . . .${}^3P$ . . . . ${}^1P$ . . . ${}^2P$.

in the $3L_2M_2$-combination, we get

$\left|{}^4S_2+{}^2P\right|$ . . .${}^5P$ . . . . ${}^5P$. . . . .

etc.

The complications are therefore too intricate and too vast to be explained in a short compass. But attention should be drawn at one point. If we take the terms arising from $(3L_2X_1)$-combination, we find that corresponding terms will form a Rydberg sequence. Thus the successive ${}^5S$ or ${}^3S$-terms arising from $\left|{}^4S_2+{}^2S\right|$ . . . will form a regular Rydberg sequence. But not so in the case of the terms which arise from the metastable states of O^+, *viz.*, the ${}^3D$-terms from $\left|{}^2D+{}^2S\right|$ coupling which arise from the metastable ${}^2D$-state of O^+. These terms will form a Rydberg sequence only if the difference $({}^4S_2-{}^2D)$ of O^+ is added to them. This point will be dealt with more elaborately when we come to the anomalous terms of Ca.

Metastable Levels

Two, three, and four-valence electrons all give metastable levels arising out of normal combinations p^2 p^3 p^4. We have for

p^2	. .	${}^3P$	${}^1D$	${}^1S$
p^3	. .	${}^4S$	${}^2D$	${}^2P$
p^4	. .	${}^3P$	${}^1D$	${}^1S$

Generally the differences ${}^2P-{}^1D$ or ${}^4S-{}^2P$ are large, *viz.*, . . . of the order of 10000∼20000. No transition is usually expected between metastable or normal terms, *e.g.*, between ${}^4S$ and ${}^2D$ of N or O^+, as there is no electron transition. But still they are observed under exceptional circumstances.

For example, in Pb, the normal terms arise from a p^2-combination just as in C, or N^+, and the lines corresponding to the differences:

$${}^3P_1-{}^1\overline{D}_2 \ldots \lambda\ 7330{\cdot}3$$
$${}^3P_1-{}^1\overline{S}_0 \ldots \lambda\ 4618{\cdot}2 \ldots$$

occur faintly in ordinary arc, and more strongly in heavy current arcs as observed by Dr. N. K. Sur (Phil. Mag. Vol. 3; 1927, page 736). We obtain lines due to similar transitions in the spectra of Bismuth and other heavy elements.

But in lighter elements, lines due to such transitions have never been observed, at least in the laboratory. But Bowen recently showed that certain lines of unaccountable origin, which are observed only in the spectra of Nebulae and used formerly to be attributed to a hypothetical element, Nebulium, are really due to similar 'forbidden' transitions amongst the metastable levels of O^{++}, N^+, O^{+++}. He has thus brilliantly solved one of the outstanding puzzles of astrophysics.

Lines due to 'Forbidden' Transitions.

FOUR-VALENCE ELEMENTS

		${}^3P_0-{}^1D_2$	..	${}^3P_1-{}^1D_2$	..	${}^3P_2-{}^1D_2$	..	${}^1D_2-{}^1S_0$
O^{++}	..	..		(20160)	193	(19967)	..	(22911)
				4958·9		5006·8		4363·2
N^+	..	..		(15267)	82	(15185)	..	(17372)
				6548·1		6583·6		5754·8
C	..	..						

FIVE-VALENCE ELEMENTS

		${}^4S_2-{}^2D_2$		${}^4S_2-{}^2D_3$		${}^2D\cdot-{}^2P$
O^+	..	(26830)	19	(26810)	..	
		3725·1	..	3727·8	..	7325
N	..					

All these lines are observed in the spectra of Nebulae.

SIX-VALENCE ELEMENTS

			${}^3P_1-{}^1D_2$	${}^3P_2-{}^1D_2$	${}^1D_2-{}^4S_0$
O	..	..	15710	15869	17932

The line 'λ 5577' which occurs prominently in the spectrum of Aurora Borealis and used formerly to be ascribed to a hypothetical element "Geocoronium" has been proved by McLennan, Paschen, and Sommer to be due to a metastable transition between two metastable levels $^1D_2-{}^4S_0$.

The lines belonging to the forbidden combination $3P_1-{}^1D_2$, $3P_2-{}^1D_2$ have been found by Paschen and Sommer.

ELEMENTS OF GROUP VII

9	17	35	53	85
Fl	Cl. .	Br. .	I	. .
Ne^+	A^+	Kr^+ . . .	Xe^+	Nt^+
Na^{++}	K^{++}	Rb^{++}	Cs^{++}	

etc.

The structure of their spectra is illustrated below in the case of Fl.

FLUORINE

$^4L_2M_2$	$^2\bar{P}_1$	$^4\bar{P}_2$	$^4\bar{P}_3$	$^2\bar{P}_1$	$^2\bar{P}_3$	$^2D_2$	$^2D_3$	$^2S_1$	Remarks
	(160)	(274·5)		(325)					
$^5L_2$ $^2P_1$				104654	104331	123928	(?)		Fundamental terms
409									
$^2P_2$				105063	104736		123518		
$^4L_2M_1$									
$^4D_1$	(20) 14468	(3) 14712							
83 $^4\bar{D}_2$	(18) 14552	(18) 14628	(1) 14903						
177 $^4\bar{D}$		(30) 14484	(20) 14758						
144 $^4\bar{D}_2$			(40) 14582						

The above analysis is due to Bowen, De Bruin, and Dingle. We have shown only one multiplet due to the $4L_2$ $(M_1 \leftarrow M_2)$ transition.

ELEMENTS OF GROUP VIII

Ne	A	Kr	Xe	Nt
Na^+	K^+	Rb^+	Cs^+	. .
Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}	

etc.

The structure of the spectra of this group is illustrated in the following table for Neon:

EXPECTED TERMS AND COMBINATION OF THE SPECTRUM OF NEON

NEON

$5L_2M_1$ \ P_5S_1	$^3P_0$ 39111	$^3P_1$ 39470	$^3P_2$ 39888	$^1P_1$ 38041	Remarks
b$_0$) $6L_2{}^1S_0$ 173970	—	(743·5) 134500	—	(735·7) 135929	Normal state
b$_1$) $5L_2M_1$	—	—	—	—	
$^3D_1$ (23808)	(6) 15303	(12) 15662	(15) 16080	(9) 14233	
$^3D_2$ (23614)	—	(8) 15798	(12) 16220	(10) 14427	
$^3D_3$ (24272)	—	—	(20) 15615	—	
$^3\bar{P}_0$ (23012)	—	(10) 16458	—	(7) 15029	
$^3\bar{P}_1$ (22891)	(12) 16220	(10) 16579	(20) 16997	(15) 15150	
$^3\bar{P}_2$ (23071)	—	(8) 16399	(8) 16817	(9) 14970	
$^3S_1$ (25672)	(8) 13439	(10) 13798	(10) 14216	(8) 12369	
$^1D_2$ (24105)	—	(15) 15364	(10) 15782	(10) 13935	
$^1\bar{P}_1$ (23157)	(15) 15954	(6) 16313	(12) 16730	(2) 14883	
$^1S_0$ 20959	—	(50) 18511	—	(50) 17082	

The full analysis of the spectrum of Neon was achieved by Paschen in 1920, before anything was understood of the structure of complex spectra, and forms a landmark in the development of method of spectroscopic classification. Paschen denoted the four terms $^3P_0$ $^3P_1$ $^3P_2$ $^1P_1$ arising from $5L_2$ M_1 by s_3 s_4 s_5 s_2 and the ten terms (^3D, ^3P, ^3S) from $5L_2$ M_2 by p^x, where x varies from 0 to 10.

There are twelve terms ^3F, ^3D, ^3P arising from $5L_2$ M_2. These were denoted by *d*'s, *d* varying from 1 to 8, and s s_1 s_1 s_1

Though this classification was nothing short of a feat, it would have seemed almost hopeless for even experts in spectroscopy to attempt a full grasp of the work. But now thanks to development of theories of complex spectra, we can very simply explain these terms. We have

$$\begin{array}{ccccc} 5L_2M_1 & & 5L_2M_2 & & 5L_2M_3 \\ 4s\text{'s} & \leftarrow & 10p\text{'s} & \leftarrow & 12d\text{'s} \\ M & \leftarrow & M_2 & \leftarrow & M_3 \end{array}$$

Thus the transitions are the same as in the spectrum of Na.

The fundamental terms $6L_2 \leftarrow 5L_2$ M_1 were obtained by G. Hertz.

Other important works are the classification of Argon-lines by Meissner, of Na^+ lines by K. Majumdar, and Bowen.

The inertness of these elements is due to the fact that in the normal state the six *p*-electrons form a completely closed shell with the spectral term $^1S_0$. The magnetic moment is zero, and the shell cannot receive any further electron, nor can be easily excited.

Spectra of Elements Belonging to the Transitional Groups

As is apparent from Chart page 279, the outer shell of the transitional group of elements has the constitution:

$$d^x\, s^1 \text{ or } d^{x-1}s^2$$

[*e.g.*, Sc. . . d^2s, ds^2; Ti . . d^3s, d^2s^2;. . . . . .Ni . . d^9s, d^8s^2;].

To calculate the nature of spectra given by these elements we must first calculate the spectroscopic terms arising out of a number of electrons in the *d*-shell, *viz.*, due to the d^x-combination. This was first done by Hund, and is shown in the Table below. The way in which these calculations have been made will be discussed later.

TABLE

Number *d*-of electrons	Terms
1	^2D
2	^3F ^3P, ^1G ^1D ^1S
3	^4F, ^4P, ^2H, ^2G. ^2F, ^2D, ^2D, ^2P
4	^3D ^3H, ^3G ^3F, ^3D, ^3P
5	^6S, ^4G, ^4D ^3F, ^4P
6	^5D ^3H, ^3G. ^3F, ^3D, ^3P
7	^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P
8	^3F, ^2P, ^1G, ^1D, ^1S
9	^2D
10	^1S.

With the aid of this table the calculation of spectroscopic term of the Transitional Elements is merely a matter of Algebra. For example, let us calculate the terms due to Ti (24). This has the composition:—

$$\left.\begin{matrix} d^3s \\ \text{or } d^2s^2 \end{matrix}\right\}$$

Now a glance at Table above shows that

$$\left.\begin{matrix} d^2 \text{ gives us} & \ldots & ^3F\ ^3P\ ^1G\ ^1D\ ^1S_0. \\ \text{and } d^3 & \ldots & ^4F,\ ^4P,\ ^2H \text{ etc}\ldots \end{matrix}\right\}$$

Hence owing to (d^2s^2) we get .. ^3F, ^3D, ^1G, ^1D, $^1S_0$.

and owing to (d^3s) we get .. ^5F, ^5P, ^3H, ^3G, ^3F, ^3D. ^3P.
^3F, ^3P, ^1H, ^1G, ^1F, ^1D. ^1P.

for (s^2) forms a closed shell and introduces no further complication, while 's' convert the ^4F of d^3 to ^5F and ^3F, and similarly for the rest.

The next combination is

$$\left.\begin{matrix} d^2s\,p \\ \text{or } \quad d^3p \end{matrix}\right\}$$

An application of the Principle of Superposition tells us that $d^2s\,p$ will give us the terms:

$$^5G,\ ^5F,\ ^5P \quad \ldots \quad ^3G,\ ^3F,\ ^3P\ldots$$

The resonance lines of Titanium arise from the transition:—

$$\left\{\begin{matrix} d^3s \\ d^2s^2 \end{matrix}\right\} \longleftarrow \left\{\begin{matrix} d^3p \\ d^2sp \end{matrix}\right\}$$

$$s \longleftarrow p.$$

The above analysis shows that the number of terms is enormously large, and the spectrum will be complicated beyond imagination. Yet H. N. Russell has been able to classify the lines of Titanium almost completely and establish the existence of almost all the terms predicted by Hund's Theory. As regards the other elements of this group or any other transitional group, the procedure is identical, and the predictions of the theory have been verified in every case. But owing to the extreme complexity of terms, Rydberg sequence has been traced only in a few cases (Cr and Mn where s-terms form fundamental levels). The value of the ionisation potential can therefore be calculated only roughly, except in the case of Cr and Mn.

We have now to explain how Table, page 300, has been compiled. This is shown below:

d^2.... Number of Magnetic Levels .. ${}^{10}C_2=45$.

Electron	1	2	Σ	Term.	Magnetic levels
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$		
m_k	2	1	3	${}^3F$	21
m_k	1	0	1	${}^3P$	9
m_s	$\frac{1}{2}$	$-\frac{1}{2}$	0	..	..
m_k	2	2	4	${}^1G_4$	9
..	1	1	2	${}^1D_2$	5
..	0	0	0	${}^1S_0$	1
..	..	..	..	..	45

d^3......Number of Magnetic Levels .. ${}^{10}C_3=120$.

	(1)	(2)	(3)	Σ	Term	Magnetic Levels
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	..	..
m_k	2	1	0	3	${}^4F$	28
m_k	..	..	..	..	${}^4P$	12
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	..	..	..
..	2	1	2	5	${}^2H$	22
..	..	..	1	4	G	18
..	..	..	0	3	F	14
..	..	..	-1	2	D	10
..	..	..	-2	..	P	6

d^4......Number of Magnetic Levels......${}^{10}C_5=210$

	(1)	(2)	(3)	(4)	Σ	Terms	Magnetic levels	
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{4}{2}$	..	..	..
m_k	2	1	0	-1	2	${}^5D$	25	25
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{2}{2}$	..	..	..
m_k	2	1	0	2	5	${}^3H$	33	..
..	2	1	0	1	4	${}^3G$	27	..
..	..	..	..	0	3	${}^3F$	21	..
..	..	..	..	-1	2	${}^3D$	15	..
..	..	..	..	-2	1	${}^3P$	9	105

and some singlet terms.

d^5......Number of Magnetic Levels ${}^{10}C_5=252$.

	(1)	(2)	(3)	(4)	(5)	Σ	Term	Magnetic level	
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{5}{2}$	..	..	..
m_k	2	1	0	−1	−2	..	${}^6S$	6	..
m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{2}$	..	..	..
..	2	1	0	−1	2	4	${}^4G$	36	..
..	..	..	..	..	1	3	${}^4F$	28	..
..	..	..	..	..	0	2	${}^3D$	20	..
..	..	..	..	..	−1	1	${}^4P$	12	..
..	..	..	..	..	−2	0	${}^4S$	4	..

In addition, we get a large number of doublet terms.

It is unnecessary to calculate for the remainder because d^6 gives the same combinations d^4, d^7 the same as d^3, etc., only the terms are inverted.

Normal Terms

In Transitional Group 1, the highest multiplicity terms arising out of the combination $d^{x+1}\ s^2$ form the normal terms, (except in the case of Cr) but in the ionised elements, terms due to $d^x\ s^1$ or d^{x-1} form the normal terms. The normal terms with the combination they arise from are shown in the next page.

In the normal elements, the terms arising from $d^{x+2}s^2$.. are generally deeper than the terms arising from $d^{x-1}s$, and form the normal levels. Note the exception in the case of Cr, where the normal term arises from $d^{x-1}s$. In the singly ionised element, there are terms corresponding to $d^{x-1}s$, and d^x, but generally the $d^{x-1}s$-terms are deeper. In the doubly-ionised elements the normal shell-formation is d^x. Note that when $x>5$, the terms become inverted.

In the formation of compounds like $FeCl_2$.., the chlorine atoms are supposed to attract two electrons from Fe, thus reducing it to the state Fe^{++}. Since the chlorine ions form closed shells, the magnetism of such compounds is entirely due to Fe^{++}. The electron composition is d^x, and magnetism may be calculated from Lande's rule, . . . mag-

	Element	Outer shell	Highest Term	Element	Outer shell	Highest Term	Element	Outer shell	Highest Term
20	Ca	s ..ds^2	$^1S_0$	Sc^+	ds..d^2	^3D	Ti^{++}	d^2	$^3F_2$
21	Sc	ds^2..d^2s	^2D	Ti^+	d^2s..d	^4F	V^{++}	d^3	$^4F_{\frac{3}{2}}$
22	Ti	d^2s^2..d^3s	$^3F_2$	V^+	d^3s..d^4	^5F	Cr^{++}	d^4	$^5D_0$
23	V	d^3s^2..d^4s	$^4F_{\frac{3}{2}}$	Cr^+	d^3s..d^4	^6D	Mn^{++}	d^5	$^6S_{\frac{5}{2}}$
24	Cr	d^5s..d^4s^2	$^7S_3$	Mn^+	d^4s..d^5	$^7S_3$	Fe^{++}	d^6	$^5D_4$
25	Mn	d^5s^2..d^6s	$^6S_{\frac{5}{2}}$	Fe^+	d^6s..d^7	^6D	Co^{++}	d^7	$^4F_{\frac{7}{4}}$
26	Fe	d^6s ..d^7s	$^5D_4$	Co^+	d^7s..d^8	^5F	Ni^{++}	d^8	$^3F_1$
27	Co	d^7s^2..d^8s	$^4F_{\frac{7}{2}}$	Ni^+	d^8s..d^9	$^4F_{\frac{7}{2}}$	Cu^{++}	d^9	$^2D_{\frac{5}{2}}$
28	Ni	d^8s^2..d^9s	$^3F_4$	Cu^+	d^9s..d^{10}	$^3D_3$	Zn^{++}	d^{10}	$^1S_0$
29	Cu	$d^{10}s$..d^9s^2	$^2S_{\frac{1}{2}}$	Zn^+	$d^{10}s$	$^2S_{\frac{1}{2}}$	Ga	$d^{10}s$	$S_{\frac{1}{2}}$

netic moment $=\mu gj$, where g is the Lande factor, j=inner quantum number of the deep-lying term. But actual conditions seem to be more complicated.

Anomalous Terms in Calcium

The constitution of the outer shell of Ca has been given as ($6L_2.2N$) and the spectrum should be strictly analogous to that of Mg. But important differences in the two spectra were observed early by spectroscopists. The nature of the differences will be clear from the comparison of the structure diagram of Mg from that of Ca.

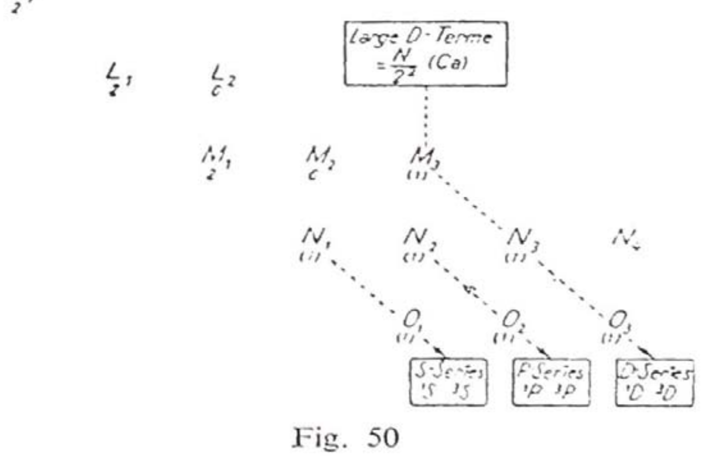

Fig. 50

Comparing this with the structure diagram of Mg, we find that in Mg, the electron runs as:

$$\text{from } M_1 \longrightarrow M_2 \longrightarrow M_3$$
$$^1S_0\ [^1P, {}^3P]\ (^1D, {}^5D)$$
$$\downarrow$$
$$N_1$$
$$4^1S_0,\ 4^3S_1.$$

3^4P_3 is approximately $\frac{R}{2^2}$, $3^1D = \frac{R}{3^2}$. But in Ca, there is an empty M_3-level, lying diagonally opposite N, and hence equal in energy value to N. Actually the first *D*-term 3^1D or M_3 is found to be approximately $R/2^2$. These large D-levels form the characteristic feature of the spectra of Ca and also of Sr and Ba, while Cd and Hg are perfectly analogous to Mg. These levels are really metastable compared to the normal levels. According to Bohr's enumeration, the total quantum number corresponding to this D-term viz. 3, is less than even that of the first *s*-term, viz. 4. When we come to Sc^+ or Ti^{++}, which have an analogous structure, these D-terms become fundamental.

Anomalous Terms: The influence of these metastable levels is clearly seen in the "anomalous terms" obtained in the spectra of Ca, Sr and Ba. They were first thoroughly investigated by Saunders and Russell and the attempt to obtain a theoretical explanation to their origin led to formulation of the Principle of Superposition of quantum numbers. To obtain the anomalous terms, we have to keep the fixed electron at M_3 (for Ca), and allow the running electron to pass through the higher levels. The terms expected and observed are shown in Table given in the next page.

It is clear that these terms are due to an incipient formation of the transitional group-shell.

Mathematical Proof of the Origin of Anomalous Terms

This view of the origin of anomalous terms was proved by Russell and Saunders from their Rydberg sequence. Thus let us take the terms M_3X_3.

They give for $M_3\ M_3$ .. ^3F, ^3P, etc., and for M_3X_3, in general.. ^3G, ^3F, ^3D, ^3P, etc., the ^3P-terms form a Rydberg sequence. Now let us

TABLE

State	Present notation	Russell & Saunders' notation.	Term vzlues					
			Ca		Sr.		Br.	
(*a*) M_3M_3	$^3\bar{F}_{4,3,2}$	..	....		....		19077·9 19510·1 19990·3	 432·2 480·2
	$^3\bar{P}_{2,1,0}$	*p*·	10753·0 10839·8 10887·1	 86·8 47·3	10250·7 10525·5 10731·8	 247·8 206·3	18115·5 18548·3 18828·3	 438·8 271·0
	$^1S_0$ $^1D_2$ $^1G_4$	X	8584·9		8964·9		9929·0	
(*b*) M_5N_2	$^3F_{4,3,2}$	*f*	13407·6 13485·9 13573·9	 78·3 88·0	12006·0 12335·7 12658·5	 329·7 322·8	18372· 19082· 19964·	 709·5 882·7
	$^3D_{3,2,1}$	*d*	11045·3 11085·3 11112·0	 40·0 26·7	9365·9 9543·4 9661·1	 177·5 117·8	17049·8 17498·1 17837·6	 444·3 339·5
	$^3P_{2,1,0}$	*p''*	9964·3 9969·1 9971·0	 4·8 1·9	8588·5 8622·2 8633·0	 33·7 10·8	16073·1 16325·5 16337·8	 252·4 62·0
	$^1F_3$ $^1D_2$ $^1P_1$	Y	8767·0		9836·1		15213·4 13475·2	
(*c*) M_5O_1	$^2D_{0,2,1}$ $^1D_2$		....		....		4526	

compare their values with those of the ^3D-terms arising from N_1X_3-Combination. The comparison is shown below:—

$$\begin{array}{ccccc} M_3M_3 & M_3N_3 & M_3O_3 & M_3P_3 & M_3Q_3 \\ {}^3P & {}^3P & {}^3P & {}^3P & {}^3P \\ (1) & (2) & (3) & (4) & (5) \\ N_1M_3 & N_1N_3 & N_1O_3 & N_1P_3 & N_1Q_3 \\ {}^3D & {}^3D & {}^3D & {}^3D & {}^3D \end{array}$$

The numerals (1), (2), (3), etc., denote the spectroscopic total quantum number, *i.e.*,

$$4^3D = \frac{N}{(4+\delta)^2} \text{ approximately.}$$

Now $(M_3Q_3)-(N_1Q_3)=(M_3-N_1)Q_3$
$=(M_3-N_1)$ of Ca^+, Q_3 being far off, may be neglected.
$=-13711$

i.e., the ^3P-terms from any M_3X_3 will be less than the ^3D-terms from N_1X_3 be about 13711. The actual values of the sequence, as obtained by Russell and Saunders are:—

^3P	10840	767·7	−4983	−8313	−10063
$^3D-13711$	15306	−2097	−7090	−9359	−10649

i.e. ^3P-terms from M_3X_3 form a Rydberg sequence only if 13711 be added to them. Hence the higher terms from a combination M_3X_3 may become negative. Such lines are sometimes known as double transition lines because the fixed electron is at M_3, but the designation appears to be faulty because actually there is only one transition.

Spectrum of Copper—The Anomalous Terms

A glance at the structure diagram, page 279, shows that the constitution is $10M_3N_1$ giving rise to normal $^2S_{\frac{1}{2}}$-terms and a spectrum similar to that of the Alkalies. But actual investigation showed that while a part of the Cu-spectrum is like that of the alkalies, there are many lines which remain outside of it. The most prominent of these are the characteristic lines which impart to the copper flame its characteristic green colour.

It has recently been shown, by Turner, Shenstone and Kichlu that the structure $9M_32N_1$ is also alternatively possible. This gives $(^2D_2.D_2)$ terms, $^2D_3$ being about 11204 frequency units lower than the fundamental $^2S_1$ and $D_3>D_2$. The $9M_3$ shell gives rise to these non-alkaline lines. Thus Copper has some of the properties of the transitional group, and probably the double valency is also due to this structure $(9M_3)$.

Spectra of Rare Earths

A glance at Chart, page 279, shows that the Rare Earths from La(57) to Yb(70) have the general composition

$$\left.\begin{array}{l} xN_4, yO_3, P_1 \\ \text{or } (x+1)\,N_4,\ (y-1)\,O_32P_1 \end{array}\right\} \qquad \begin{array}{c} y=2, \\ x \text{ varies from 0 to 14.} \end{array}$$

The singly ionised elements will have their shells normally constituted as

$$\left.\begin{array}{l} xN_4,\ yO_3, \\ (x+1)\ N_4,\ (y-1)\ O_3, \end{array}\right\} \qquad \begin{array}{l} y=2. \\ x \text{ varies from 0 to 14.} \end{array}$$

Doubly and trebly ionised elements are expected to be constituted as

xN_4....thus Gd^{+++} has the constitution................f^7.

The spectral terms due to such shells will be extremely complex. This accounts for the extreme complexity of the spectra of rare earths. Most of them have not yet been classified. We give in Table below the highest terms due to f_y-combination.

	$2\ \Sigma m_s$	$\Sigma\ m_k = \Sigma 3+2+1+0$	Element	'J' for Highest term	N_4 4f	O_3 5d	P_1 6s
f^1	1	^2F	Ce^{+++}	..	1	2	1
f^2	2	^3H	Pr^{+++}	4	2	2	1
f^3	3	^4I	Nd^{+++}	$\frac{9}{2}$	3	2	1
f^4	4	^5I	..	4	4	2	1
f^5	5	^6H	Sm^{+++}	$\frac{5}{2}$	5	2	1
f^6	6	^7F	Eu^{+++}	0	6	2	1
f^7	7	^8S	Gd^{+++}	$\frac{7}{2}$	7	2	1
f^8	6	^7F	Tb^{+++}	6	8	2	1
f^9	5	^6H	Ds^{+++}	$\frac{15}{2}$	9	2	1
f^{10}	4	^5I	Ho^{+++}	8	10	2	1
f^{11}	3	^4I	Er^{+++}	$\frac{15}{2}$	11	2	1
f^{12}	2	^3H	Tu^{+++}	6	12	2	1
f^{13}	1	^2F	Yb^{+++}	$\frac{7}{2}$	13	2	1
f^{14}	0	$^1S_0$	Cp^{+++}	0	14	2	1

Σm_k is calculated from the rule that we have to begin from the highest value of m_k, *viz.*, 3, and then take values successively less than 1 from 3 and add up. Thus for f^3, ... $\Sigma m_k = 3+2+1 = 6$ giving us a ^3H-term. The last three columns illustrate the electron composition of the normal element.

The formation of the electron shells of the doubly, singly ionised, and normal shells are illustrated below:—

			Normal Terms
Gd^{+++}	......$4f^7$	...	...^8s
Gd^{++}	......$4f^7.5d$	...	...^9D
Gd^{+}	......$(4f)^7$	$(5d)^2$. $(5d).(6s)$	...^{10}D
Gd	......$(4f)^7$	$(5d)^2$. $(6s)$. $(5d)(6s)^2$	...^{11}D

These hypotheses are still to be proved, but the spectroscopic work will entail colossal labour.

Paramagnetism of Compounds

The application of the theories of electron composition of atom to explain the magnetic behaviour of elements and their compounds has been attended with very conspicuous success, but there is scarcely any opportunity to talk of these works. The reader may refer to Stoner's Theories of Magnetism and the later short volume on Magnetism by the same author. Nor shall I have time to refer to certain empirical rules which have been found to be of great use in the classification of spectral lines, *viz.*, the regular and irregular doublet laws, and the horizontal comparison method. For these, the original sources must be consulted.

LECTURE VI

RECENT IDEAS ON THE STRUCTURE OF MATTER

In the last lecture, I shall follow the usual practice of reviewing the ground which has been covered in the previous lectures, and placing before you a brief account of certain recent ideas on the structure of matter. I have unfortunately to cut down my programme of a discussion on "Subatomic Thermodynamics."

The impressions of the last Great World War must be vivid in the minds of many of my audience. One of the after-effects of the Great War was that it set the thinking sections of mankind reflecting on the future of civilisation. One of the most thought-provoking post-war publications was Oswald Spengler's *Untergang des Abendlandes*—*Decline of the West*. The title is rather misleading—as the book is a comparative study of the civilisations which have flourished and decayed in this globe of ours, *e.g.*, Egyptian, Minoan, Babylonian, Hellenic, Roman, Indian, Chinese and Islamic—and of the present West-European. If I have understood Spengler properly, his main theme has been to prove that the same types of Man are periodiaclly recurring throughout ages, but his activities take different turns according to the prevailing attitude of the *contemporary human mind*. Each civilisation carries within itself, not only the germs of its growth and maturity, but also the virus of its decay, and it is probably not unprofitable to survey the past progress of mankind with a critical outlook.

One of the prides of what we call Modern Civilisation has been that it has given us the Natural Sciences, and therewith the power over the Forces of Nature. It is certainly true to some extent, and is the result of the new attitude which the human mind took with respect to Nature about 1500 A.D. I will illustrate by a few concerete examples.

When Thales of Miletus, the first of the seven sages of Greece, discovered that amber, when it is rubbed with a piece of silk, develops a force which attracts small bits of paper, he ascribed this force to a spirit residing in the Electrum, that is the Greek name for amber, and described this spirit as Electricity. He did not certainly set up an altar to the spirit of Electricity and worship it after the manner of Egyptians or Hindus, but certainly neither did he nor his contemporaries attach much importance to this observation. If the observation was pursued with modern spirit, it might have given us the science of electricity two thousand years ago, with consequences on human history of which we can only dream now. The Eastern Civilisations suffered from still cruder mentality. The Vedic Indians were conscious of the mighty forces of Nature only as manifestations of passion on the part of their God, could do no better than write beautiful hymns for His propitiation But the spirit of the type of soul which is at present dominating human culture may be understood from that of the prosaic Benjamin Franklin who flies a kite and demonstrates that the thunder of clouds is identical with the electricity which we get by rubbing amber with silk. But this spirit of searching enquiry after natural phenomena is not the only characteristic of the human mind (the Faustain Soul, as Spengler puts it) responsible for modern culture. When he has sufficiently formed his impressions over a class of nature-phenomena, he tries to refer then "to a single structurally and numerically measurable order." This tendency to an intellectual conquest of Nature by precise formulation and by measurement, and the tracing of time-changes was aided by the discovery of new sciences which we call Infinitesimal Calculus, and Dynamics. These sciences are essentially creations of the modern type of the human mind. The Greek mind created Statics and Geometry—the Hindu mind created Trigonometry, Algebra and Arithmetic. And the Arabians blended the two but probably did not evolve an independent type. But these sciences contain no notion of motion or changes—in fact with their ahistoric time-sense, the ancient nations were incapable of creating sciences involving time-changes.

The science of Dynamics was discovered by Galileo while blind and infirm and shut up in prison by the bigoted clergy who were afraid of the new knowledge. The symbols for the new knowledge of Dynamics were created by Descartes, Leibnitz and Newton, and Newton in particular showed that the mysterious motion of the planets which troubled the sages of Chaldea and of Greece for several millenniums and the medieval Europeans for about thousand years can be very easily explained with the aid of the law of gravitation, and the dynamical equations.

So great was the impression created by the methods of the new science that Huygens, writing in 1680, says "In true philosophy, we should conceive the cause of all natural phenomena in terms of mechanics. This we must do, or for ever renounce the hope of understanding anything of physics."

The spectacular success of the dynamical methods in their application to the problem of motion of the heavenly bodies was followed, for about a century, by efforts at consolidation of the ground won, and the formulation of more general principles. Maupertuis, a religiously minded mathematician who lived in the corut of Frederick the Great of Prussia, showed by rather obscure reasoning that the laws of dynamics followed from a more general minimal principle—the Principle of Least Action. This law says that bodies move in such a way that a certain dynamical quantity. . . energy × time . . . should have the minimum value during motion. The pious gentleman saw clearly in this law, the Hand of God—a Divine Dispensation! Somewhat earlier, another mathematician, Fermạt, showed that light travels in such a way that the path is traversed in the minimum time and of course being a sincere religious man, discovered in this fact that all laws in Nature are determined by the Divine Will! In these investigators, the medieval mind of religiosity was mixed up with the modern mind of rationalism. But very different was the attitude of Laplace, the typical product of the French Revolution. who on being asked by Nepoleon why he had not mentioned God in his Macanique Celeste, bluntly replied, 'Sire, I did not feel the necessity of such a hypothesis!'

When the human mind first turned its serious attention to the long neglected study of the natural sciences (chemistry, physics and biology —which event really took place during the French Revolution) and Nature began to yield up, one after another, her precious secrets to the gaze of a wondering humanity, the potency of the methods of dynamics and of infinitesimal analysis, for the analysis and exploration of the newly discovered domain was at first not very apparent. But in course of the nineteenth century, dynamical methods were applied with great advantage to all branches of physics—acoustics, hydrodynamics, electricity and magnetism, and light and the kinetic theory of matter, and chemistry also followed suit with the development of the branch known as physical chemistry. Only the principles of thermodynamics, developed from empirical facts, seemed to lie outside the domain of dynamics, till Boltzmann showed that it really formed a branch of the calculus of probabilities.

The triumph of dynamical methods in handling these new sciences was so striking that Helmholtz, summing up the situation in 1869, says in an oft-quoted passage, which is a repetition of Hyugen's remarks made two centuries earlier:—

"The aim of Natural Science is to discover the motions underlying all alteration, and the motive forces thereof:—that is to resolve itself into mechanics."

I have told you in the previous lectures how this mechanical concept of the world had been applied to the study of one important question agitating ancients and moderns alike, namely the ultimate nature of things—atomic theories. You will see that even this conception has its limitations and *probably some new attitude* of the human mind is necessary for the further exploration of Nature. I have told you how the belief of the ancients that this polyglot world is built up of five hypothetical elements—Earth, Water, Air, Fire, Ether, received its deathblow when Volta discovered his pile, and Nicholson and Carlisle showed that the so-called element 'water' could be decomposed into two simpler gases—hydrogen and oxygen—by the passage of electricity. Lavoisier gave a precise meaning to the terms 'elements.' But the elements seemed to be coming one upon other without any particular regard for pet human theories. But the human mind refuses to believe in complexity. So even as early as 1850, Prout tried to show that the so-called elements were really compounds of some primordial elements. But this theory was rather still-born. The whole of the nineteenth century was spent in perfecting our notion of atoms, in getting estimates of their size, weight, and chemical and physical properties.

ATOMIC PHYSICS

Amongst the many important discoveries which were made in the nineteenth century in Chemistry and Physics, two stand out as the most significant for further development of atomic theories. The first is the discovery of the periodic classification by Mendeleef and Lothar Meyer which showed that though the number of elements was large, and their properties widely different, yet the position was not so chaotic as was first thought. The elements showed certain periodicity in their properties and can be arranged in groups of elements having similar properties.

The second great discovery is that of spectrum analysis by Kirchoff which showed that every element, when excited, gives characteristic line spectra, by which it can be identified just as any musical instrument can be identified by the note it emits. The spectrum analysis also revealed that the atom must be a more complex structure than the lead bullet type conceived by the physicists, and chemists of those days.

I have told you how, in course of the last century and the beginning of the present century it was discovered chiefly as the result of the work done at the Cavendish Laboratory under the leadership of Sir J. J. Thomson and his successor Sir Ernest Rutherford, that matter is electrical in nature, and all atoms are really compounds of only two primordial elements—the *proton* or the atom of positive electricity, and the *electron*, the atom of negative electricity. The proton, and the electron have the same amount of electricity on them, but for some reason not known to us, the proton is as heavy as the hydrogen atom, and two thousand times heavier than the electron.

The application of dynamics to the world of the atom was first taken up by Niels Bohr of Copenhagen in the year 1913. Up to the time of Bohr, the conception of the atom had been static, but Bohr showed that it is full of life and movement. He followed, in the treatment of the problem, the same dynamical principles which were discovered by Galileo, over three hundred years ago, and applied with such conspicuous success by Newton for explaining the motion of celestial bodies. As I told you, Bohr showed that an atom is a miniature solar system. In the solar system, the sun occupies the central position, and the planets revolve round it in orbits which as Newton showed can be easily calculated from the law of universal gravitation, provided the initial conditions are once known. Bohr applied the same ideas to calculate the motion of the electron but a difficulty was felt in finding out the initial condition. The atom is such a submicroscopic body that we can never expect to see it, or follow the motion of its electrons at any particular instant. Hence, some other device must be sought to obtain the initial conditions of dynamics. Bohr found it in the so-called "Quantum Theory of Energy."

About two thousand and five hundred years ago, there lived a philosopher in Greece named Pythagoras who believed in the magical value of integral numbers. His idea was not wholly chimerical. He observed that two strings which are under the same tension, produced concordant music, if their lengths were to each other as some simple integral numbers, say 3 and 4. If the ratios were 3·1 to 4, the concord would be destroyed, we get noise. Pythagoras believed that God has made Creation according to some principle of simple integral numbers, and it is even said that he could listen to the music of numbers!

I might say that this is a form of the Quantum theory but, as I told you, to the modern world it was first given by Planck, the celebrated Berlin Physicist who said, in 1900, that energy is atomic in structure like matter, and occurs in integral multiples of a quanta.

Einstein made the position clearer a few years later. He said that light is propagated in unitary cells in space, which are not subdivided in course of their flight until they encounter matter.

The picture which Bohr constructed of the inner mechanism of the atom with the aid of Galilean dynamics and of the quantum conception of light has been sufficiently described in my previous lectures. We have seen that an atom may be compared in its inner structure to a kind of ceremonial show. Round the centre or the nucleus are grouped successive rows of seats which are labelled K, L, M, N, etc. The rows are arranged according to priority and are distinguished by the numbers 1, 2, 3, 4.... (principal quantum numbers). In any one level, there are again further subdivisions which are again denoted by the numbers 1, 2, 3,....(azimuthal quantum numbers). The number of seats in any one of these levels is perfectly fixed according to Pauli's Law and can each be occupied by only one electron. When any of these electrons is ejected, an electron from the outer levels will jump to fill up its place, and energy will be emitted. You must have noticed that some fundamental assumptions of Bohr's Atom-dynamics are a bit mysterious, for example, the hypothesis of the quantum. But if we examine the situation closer, we find that use has been made of ideas which are contrary to the mechanical concept of Nature. On Bohr's model, the electron exists in a number of definite quantised states characterised by integral numbers. Suppose it is in orbit No. 5; experience tells us that it cannot remain long there, but will jump back to some lower orbit. To which particular one will it fall? Is it the 4th, or the 3rd or the 2nd? This question cannot be decided on dynamical grounds. Hence we introduce an element of probability. We say that there is an element of chance in this process, just as a boy, left to himself in a meeting, will go on jumping from one seat to another in a quite arbitrary way with a strong preference for seats close to the chair. But in making this picture, we are sacrificing the Law of Causality. We are endowing the electron with a certain amount of Will-power of its own, which enables it to determine its own Destiny. This conception is contrary to all the canons which the philosophers have tried to establish since the days of Galileo.

The dynamical model, therefore, becomes insufficient in dealing *with atomic phenomena*. The failure of Dynamics to deal with physical problems particularly optical has been previously pointed out by Einstein. In dynamics, we work with three fundamental concepts—

space, time and mass. All others are derived units. We have been fortifying ourselves in our faith by such principles or phrases as Conservation of Mass. Time as a *universal flux*, and the logical completeness of the Euclidean method of measuring space.

All these concepts have been, as you know, very seriously challenged by the "ruthlessly cynical theory of Relativity." Like an iconoclast, Einstein demolishes the foundation of dynamics. Supported by the experiments of Michelson, which show that the velocity of light remains unaffected by the motion of the medium, he teaches us that Æther is only Maya, there is no absolute frame of reference, there is no absolute standard of time. Time and Space forms a sort of four-dimensional continuum and we are called upon to trace the time-changes of world-phenomena, both microscopic, and macroscopic, according to some new basis.

The only principle which escapes, in some measure, this general cataclysm, is the Principle of Least Action already referred to, enunciated by the theologian Maupertuis about a hundred and fifty years ago, and as remarked before, interpreted by him as a divine dispensation for the guidance of Nature. The hypothesis was later on elevated by the mathematicians Lagrange and Hamilton to the dignity of a guiding dynaminal principle. But Einstein's way of treating the Principle of Least Action is similar only in form, but differs greatly in essence. It synthesised dynamics with four-dimensional Geometry, in which Euclid's principles are to some extent sacrificed, and aims at deducing not only the Laws of Motion but also the Physical Laws of Nature such as the Law of Universal Gravitation from one single principle. It has succeded wonderfully well in accounting for gravitation, but has not yet been able to deal successfully with electromagnetic phenomena, though a solution is said to be just in sight.

One of the most striking results of the Principle of Relativity has been the establishment of the identity of mass and energy. Einstein showed that mass and energy are different names for the same physical quantity, in fact they become identical if we choose our units of length and space in such a way that the velocity of light becomes unity. You will then ask me how are we to express the variation of energy? The answer is by the variation of mass. Energy is mass multiplied by square of the velocity of light.

This is a most surprising deduction, for here we are sacrificing the law of conservation of mass, so sedulously established by philosophers in the last century. It means that a substance weighs more when it is moving than when it is at rest. But however much we may dislike to see our fond beliefs shattered, we cannot help it, for Einstein's theory has stood the most rigorous experimental tests and hostile criticisms. But Einstein's theory of equivalence of mass and energy introduces further complications. It shows that all forms of energy must have 'mass.' According to Planck, radiant energy occurs in pulses $h\nu$, hence the equivalent mass is $h\nu$, divided by c^2. This theory has received very brilliant confirmation from astrophysical phenomena, as well as from more direct experiments of Compton. It also opens up a new way for accounting for atomic phenomena. I have told you that according to modern theories, all matter is composed of protons and electrons. A helium atom is composed of four protons and four electrons. The proton and the electron have been very carefully weighed, and so has been the helium atom. We should therefore expect that the mass of the helium atom should be the sum total of the mass of its constituents. This is found to be very nearly true, but not quite true. In packing the electrons and protons, we invariably find that a certain amount of mass is lost. Where does this mass disappear? Einstein answers that this mass disappears as radiation.

Failure of Infinitesimal Calculus

The difficulties pointed above and the fact that the Bohr-Sommerfeld method did not afford numerical satisfaction in accounting for the spectra of more complex elements particularly helium led Heisenberg to raise the standard of revolt against the application of dynamical methods, and methods of infinitesimal calculus to atomic phenomena. In Heisenberg's method, the dynamical variables are supposed to vary discontinuously though connected by the still mysterious Planck constant. But a more suggestive way was pointed out by the talented Frenchman, De Broglie, who strated from an entirely fresh point of view. I have already called your attention to controversies regarding the nature of light. According to one conception, light is a wave motion, according to the other light is corpuscular. The two views appear to be as diametrically opposite, as the politics of the French and the Germans, but like a skilful diplomat, De Broglie suggests a solution which amounts to admitting that both views are correct. Let us see how this is done.

Those of us who have visited the sea-beach must have watched the phenomenon of breakers. As the waves approach shallow water, a solitary crest is observed to separate from the rest, and advance over the beach, while waves in the rear die cut. This phenomenon was first explained by the late Lord Rayleigh in the following way:—

In shallow water, wave velocity varies from point to point, and induce waves always occur in groups differing slightly in wavelength and velocity. As you all know, when two waves combine, they may either strengthen or destroy each other. The bundle of waves in shallow water is continuously destroying each other at one point and intensifying each other at other points. The points where they intensify is the crest. Lord Rayleigh shows that the velocity with which the crest moves is very different from wave velocity, the crest velocity representing transportation of energy.

This analogy was made use of by De-Broglie in a very elegant way. In explaining the apparent difference between the corpuscular theory and the wave-theory of light, he remarked that light is of course a wave-motion, but we have to deal with not one single wave but a bundle of waves. The transport of energy may be compared to the motion of the crest of a wave group. Thus light is simultaneously a wave as well as a particle. In the particular case of light, the wave velocity and the crest velocity are the same.

But this suggestion by itself does not carry us far. With masterly intuition, De Broglie extends the conception to matter as well; in other words he conceives of matter as a bundle of waves. The considerations, which led him to this conception have been already discussed—equivalence of energy and mass. De Broglie argues that energy is the main thing, and instead of distinguishing between matter and radiation as being fundamentally different, he includes them under the general heading 'particles of energy.' Now one type of particles of energy, *viz.*, radiation, is characterised by wave-nature. Why should we stop here—to be consistent logically, we should expect that the other type of particles of energy, *viz.*, matter should also exhibit a wave-nature.

Thus De Broglie arrived at the conception of matter as bundles of waves. If matter moves with some velocity that corresponds to the crest velocity of the waves—what gives us the wave velocity? De Broglie arrives at the result by a most ingenuous application of the Principle of Relativity. In Relativity, as you know, we compare two systems moving relatively to each other with the velocity v.

It is found, by very simple calculation which we need not repeat, that a stationary wave of frequency ν, when viewed from a moving system, appears like a progressive wave moving with the velocity $\frac{c^2}{v}$. The wave of matter therefore,appears to move with a velocity larger than that of light, in fact, the smaller the velocity of transport, the larger is the velocity of the wave representing matter.

This deduction, though it appears at the first sight a bit fantastic, appears to be borne out by experimental facts. From De Broglie's calculation, it can be shown that the length of the matter-wave is $\frac{h}{mv}$, and as you can easily perceive, it varies inversely as the velocity, You are also probably aware of another property of wave-motion, *i.e.*, when a large wave passes past a small obstacle. it takes no notice of the obstacle, but passes straight on. Something like this seems to take place in the motion of electrons. We can give to the electron any velocity we desire, and if we then hurl a swarm of electrons against atoms and study how many of them succeed in making their way through, most surprising results occur. It is found that when the velocity is extremely small the electron is not at all stopped, but passes straight on. It takes no cognizance of the presence of swarms of atoms in its path. This curious effect, discovered some years before De Broglie's hypothesis, by Dr. Ramsauer in Germany, seems to support his view of matter-waves though at the first they seem rather fantastical.

The wave view of matter was found to be supported by certain experiments of Davisson and Germer, but most straightforward confirmation was obtained from the experiments of G. P. Thomson (referred to in the first lecture) and of Rupp and of Nishikawa and Kikuchi.

Wave Mechanics

A great impetus to De Broglie's hypothesis was given by Schrödinger in the year 1926. Schrödinger set to himself the following question: If electrons are to be regarded as waves, in what domain is the conception likely to be most useful? He made use of an analogy which is well-known to students of Physics:—I have repeatedly told you that we can explain the phenomenon of light by the conception that light consists of flight of swarms of particles, or of a bundle of waves. As long as light has to pass round large obstacles, the corpuscular theory can be made use of. But in studying the passage of light round obstacles which are as small as the wavelength of light. the wave conception must be used otherwise we cannot explain the phenomena of diffraction and polarisation. Schrödinger showed that the same considerations apply to the wave theory of matter. A particle must be replaced by its wave, whenever it has to move in regions of the same dimension as its corresponding matter wave.

Schrödinger shows that this is exactly the case in all motions of the electron inside the atom, and hence we must replace the electron by its wave. But this means a recasting of the whole of mechanics. Already steps for this end were taken by De Broglie. but Schrodinger went much further.

It is known to everybody that light travels in a straight line. in a homogeneous medium. In heterogeneous medium the path is deflected and is given by Snell's law. But as I told you previously Fermat wanted to go deeper. and to find out if God has ordained some general principle for the guidance of light-rays. He discovered what is known us the Principle of Least Time which means that light takes such a course that requires the minimum expenditure of time in its passage.

De Broglie argued that since light and matter are essentially of the same nature, their motion must be governed by the same general principle. Now the motion of matter is governed by the principle of Least Action—the motion of light is governed by the principle of Least Time. De Broglie argues that the two must be identical. and deduces very interesting relations regarding the mechanics of wave-motion by introducing detailed comparisons between the two principles.

Starting on De Broglie's speculations. Schrödinger writes out the wave equation of the electron round the nucleus. He arrives at the surprising result that the equation has a solution only when the energy-values of the electron are discrete. as given by Bohr's hypothesis. This at once removes the arbitrariness of Bohr's method of calculating hydrogen orbits by using the mysterious quantum conditions. They come out automatically from the nature of the problem itself.

To the mathematician, this was a great achievement. But Schrödinger went still further, and reconstructed the whole system of mechanical quantities in terms of the new wave conception of the electron. We call this science—hardly three years old—by the name Wavemechanics. Schrödinger's method also enables one to find out the transition probabilities, *i.e.*, the chance of an electron for passing from one state to another.

When we review the whole situation, we find that we have gradually sacrificed most of our cherished notions of the last two centuries. But the work has not been merely destructive, we have learnt to build fresh structures on the debris of older theories, and though much of this must be of a very transient nature, there is no doubt that we are penetrating more and more into the mysteries of Nature. Much of the new conceptions has been contradictory to each other—for example in one breath we are talking of the electron as a wave, and then again as a rotating gyroscope. In this connection, the history of the fine-structure problem is very interesting. As we pointed out in Lecture 3, according to Bohr's elementary theory, the levels of the electron in the H-atom turn out to be single, while actual observations show that they are double, so that an H-line is found to be composed of a number of closely situated lines when high resolving power is used. Sommerfeld showed that since the electron is moving with high velocity, the Einstein expression for kinetic energy must be used in place of the usual $\frac{1}{2}mv^2$; applying this correction, he obtained a formula for the doubling of spectral levels, which agreed exceedingly well with the experimental results. According to this view, the doubling is of relativity origin, and arises from different values of E in n_k orbits. But though the formula was mathematically found to be quite correct, Lande showed that the physical explanation was wrong, as the splitting was shown to be of magnetic origin and was connected to the inner quantum numbers, and not to the k-quantum number of Sommerfeld. An alternative view of splitting was given by Goudsmit and Uhlenbeck by assuming that the electron should be considered as a sort of gyroscope, rotating rapidly round an axis fixed in itself. This combined with our knowledge of complex spectra has led to the recognition of the important fact that the electron should be regarded not merely as a point charge of electricity, but also as an elementary magnet. How are these facts to be fitted up into a wave mechanical treatment of the problem? Schrödinger naturally followed in Sommerfeld's wake, but failed to obtain the correct expression for the splitting up of levels. It was left to Pauli to remove this defect by introducing the spin-coordinates in the wave mechanical treatment of the H-atom, but Dirac showed that the whole structure can be built out of the principles of the Special Theory of Relativity. But it is next to impossible to give anything like a popular account of this work—the impression left on one's mind after the perusal of this work being that one is put blindfolded in a railway train, and brought to the destination being thus deprived of the opportunity of getting acquainted with the route traversed. Probably as Fraenkel and Mie have pointed out, the analogy between light-waves and matter-waves have to be worked out in greater detail on the lines of the Maxwellian equation.

From the above sketch, you will probably realize that the human mind is gradually emancipating itself from the time-honoured dogma that the cause of all natural phenomena should be sought in terms of mechanics. As described in the present sketch, this profound change in our outlook has been forced upon us from the study of the microcosmic world of atoms, during the last fifteen years, but the insufficiency of mechanical methods was clearly brought out nearly thirty years ago, when Rutherford and Soddy explained the phenomenon of radioactivity by the Theory of Successive Disintegration. As is well-known, they had to introduce an element of chance in accounting the observed breaking up of the nucleii, but it was probably not realized at the time that this hypothesis was against the mechanical concept of natural phenomena. The point was absolutely untouched in all the developments which took place in Atomic Physics during the last twenty years, because the nucleus was regarded merely as a point charge of electricity. It is only in recent years, thanks to the works of Aston, Rutherford and others, that the problem of constitution of the nucleus is promising to become the absorbing topic of the times. But the modern philosophers are much more modest than the ancients; (they rarely seek after the First Causes, they are careful to give their problem a mathematically definite formulation.) based on existing knowledge.* Our problem is to prove that all nucleii are compounds of the proton and the electron (and such simpler combinations of them as can be definitely proved to exist *e.g.* the α-particle, the neutron), and to account how large numbers of such particles can be compressed within the very small dimension of 10^{-13} cm without violently exploding. The ideas of wave mechanics are likely to be of great value for such problems *e.g.* witness the partial success of Gamow, Gourney and Condon and others in explaining the Geiger-Nutall Law regarding the life of radioactive atoms.

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*This remark is not quite true of all current attempts, for example Eddington's attempt to explain the origin of the electron and its mass in sixteen dimensional tensor calculus, and Dirac's attempt to explain protons as negative energy holes.

1. 2. 3. SPECTROSCOPY IN THE SERVICE OF CHEMISTRY*

Introduction

THERE was a tendency, amongst the philosophers of early times, to deduce every problem with which mankind comes across, regarding life and nature, from a First Principle, or from a small number of simple principles. Experience of centuries showed the futility of such attempts. Nature is *diverse* and every one of her phenomena must be studied separately. So it happened that when scientific studies of nature were revived in Europe, contemporaneously with the French Revolution, every branch of science began to be studied by itself. Thus modern chemistry, the different branches of physics, the biological sciences were all studied and developed in separate closed compartments. The result of such intensive studies was a rich harvest of profound discoveries of facts and phenomena in each branch of science, which revealed the unsuspected diversity of natural phenomena. But the human mind refuses to believe in complexity and before long, active minds were busy in finding out whether some unifying principles do not exist beneath the superstratum of all these apparent diversities. The formulation of the atomic theory, the discovery of the electro-magnetic theory of light, the modern theories of electrical structure of matter are the fruitful results of such enquiries.

The connection between the phenomena of light, and chemical phenomena has been long suspected, Sir P. C. Ray, in his monumental History of Hindu Chemistry quotes from a iatro-chemical treatise of the eighth century how the ancient Indian savants could find out the elements occurring in an ore from the coloration which they imparted to flames.

"Copper yields a blue flame. . . . . that of tin is pigeon coloured . . . . . that of lead is pale tinted . . . . . that of iron is tawny . . . . . that of "peacock ore is red." (Rasaratna Samuchhaya, History of Hindu Chemistry, Vol. I. P. 38.)

No notice was taken of this observation for twelve hundred years, but it is well-known that seventy years ago, a scientific investigation of this fact of observation led Kirchoff to the great discovery of Spectrum Analysis. Kirchoff and Bunsen, and other chemists and physicists like L. de Boisbourdan, Urbain, Lockyer, Nielson and Ramsay

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* Sir P. C. Ray 70th Birthday Commemoration vol. of the Indian Chemical Society, 1933, p 293.

were quick to grasp the great importance of this discovery, and seek for new elements in minerals, as well as in heavenly bodies. Today not less than 40 elements out of a total of 92 stand to the credit of spectrum analysis.

For a long time it appeared that excepting its application to discovery of new elements, spectroscopy would not have much use for the chemist, and would not help him in the solution of such problems as those of valency, origin of chemical forces, explanation of photochemical actions, characteristic colours shown by organic or inorganic salts. Recent events have however shown that such is not the case. The previous attitude prevailed for a long time because the chemist and the physicist had a dread for the complexity of spectral data. An element like Fe gives no less than 6000 lines in the visible region and to report the whole information regarding the spectra of atoms alone, even eight bulky volumes of Kayser and Runge have not been found sufficient. The spectra of molecules with which the chemist is more concerned are still further diverse and complex. Hence it is not a matter of surpirse that the chemist would find it extremely difficult to make any use of spectroscopy, and would look upon such attempts with horror and dismay.

But in recent times, thanks to the recent developments in physics, the situation has entirely changed. Due to the discovery of the quantum theory of radiation, the development of the nuclear theory of atoms, and the theories of spectra of atoms, it has been found possible to reduce the whole mass of data in the spectra of atoms to a few simple rules. The application of the new theories to explanation of the problems facing the chemist has also been started and it has already yielded such fine results that it is hoped that in a short time, *a student of chemistry will find a knowledge of modern theories of spectroscopy as valuable as the knowledge of the different methods of group analysis*. It is impossible to give a complete account of all the attempts, but I shall try to indicate a few lines in which very fruitful results have been achieved.

On the Nature of Chemical Forces

The nature of the forces which bind two or more atoms to give rise to the molecules which are ordinarily met with have taxed the ingenuity of chemists and physicists for a long time. Since the times of Berzellius the forces in compounds of the type NaCl have been thought to be of electrical origin. It is supposed that when an atom like Na which contains one electron which it can easily lose, and another like Cl which shows an affinity for an electron, come together, the valency electron leaves Na and goes over to Cl. Thus the molecule really consists of (Na^+, Cl^-). The forces of binding are therefore of electrostatic origin. Such compounds are known as polar or ionic compounds. This hypothesis has been put on a scientific foundation by the spectroscopic work of Franck[1] and his students. They have shown that the absorption spectra of these compounds are continuous, beginning from a long wave-length limit. Franck interprets this result in the following way:—When a quantum of energy $h\nu$ falls on a molecule, it acts on an electron, and raises it to a higher orbit (if such an orbit exists) or removes it altogether from the anion to the cation. In the present case, Cl^- ion has the most loosely bound electron, and this has no further stable orbit. So provided the incident light has the proper energy, it detaches itself completely from Cl^- and attaches to Na^+. So the absorption limit ν , corresponds to the process

$$(Na^+ Cl^-)+h\nu=Na+Cl \qquad .. \quad (1)$$

If this theory be correct, $h\nu$ should be equivalent to the energy of formation of NaCl vapour out of gaseous Na and Cl atoms. In thermochemistry, the heat of formation is usually determined by taking the substances in the forms in which they are usually available. Thus we have

$$[Na]+\tfrac{1}{2}Cl_2=[NaCl]+Q \qquad .. \quad (2)$$

where [Na] denotes sodium in the solid state, Cl_2 denotes a chlorine molecule, and Q is the heat of formation. From this the atomic heat of formation, defined by the relation

$$Na+Cl=NaCl+R \qquad .. \quad (3)$$

is obtained with the aid of the thermochemical relationship

$$R=Q+L_{Na}+\tfrac{1}{2}D_{Cl_2}-L_{NaCl} \qquad .. \quad (4)$$

Calculation shows that $R=118$ Cal for NaCl; L_{Na}=latent heat of evaporation of Na; L_{NaCl}=latent heat of NaCl. The value of λ_0, the beginning of absorption can be calculated from the relation

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[1] Franck, *Trans. Faraday Soc.*, 1925.

$$\lambda_0 = \frac{286000}{\text{R in Cal}} \qquad .. \quad (5)$$

For NaCl, λ_0 was found to be 2428 Å which corresponds to R= 118 Cal. The agreement is therefore very satisfactory. Similar agreement has been found in the case of all the alkali halides.

Excitation of Higher States

Further proof of the essential correctness of Franck's hypothesis is afforded by the idea that the electron from Cl may separate from it in such a way that the Cl atom is left not in the normal Cl ($^2P_{\frac{3}{2}}$-state) but in the metastable Cl ($^2P_{\frac{1}{2}}$-state).
If ν_2 is the beginning of absorption in the second process it is found that this beginning is shifted according to the following relation

$$\nu_2 = \nu_1 + ({}^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}) \text{ of the halogen atom} \qquad .. \quad (6)$$

For Cl, Br and I atoms, the $^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$ values are 880, 3700, and 7600 respectively. Hence the absorption curves for the two kinds of splitting will be very close to each other for Cl but should be separable for Br and I. Actually the absorption curves for bromides and iodides show two maxima, which are roughly separated by the ($^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$)-separations. This affords a further confirmation of Franck's theory. So as regards the alkali halides, the correctness of Franck's hypothesis seems to be well established.

Origin of Chemical Forces in Homopolar Compounds

But there are a certain class of compounds like H_2, I_2, ICl...... where the attraction between constituent atoms cannot be of electrical origin. For example in H_2, we cannot conceive that one constituent is H^+, the other is H^-. The constituents must be H and H. What is the origin of chemical forces of attraction in such a case ? Both constituents are electrically neutral, hence the force of attraction must arise from some other cause. The discovery of the origin of this force is due to Heitler and London.[2] They showed that the force arises from the resonance interaction of the electrons in each atom. As the expression stands, it is probably unintelligible to the majority of chemists, but it becomes clear when we bear in mind the fruitful discovery, that the electron is not merely a point charge of electri-

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2. Heitler and London, *Z. Physik*, 1927, **46**, 455.

ity, but is also a magneton, *i.e.*, electrons possess magnetic moment f definite values. Thus though the two H-atoms exert no attractive orce of electrical origin on each other, the electrons in each, accordng to Pauli's principle, have their magnetic axis in opposite direcions, and so attract each other. This is probably not quite a correct lescription of the Heitler-London force, but this may serve to convey ome idea of it. When the electrons have their spin axes in the pposite directions, they form a state known as $^1\Sigma_1$; when they are in he same directions, they form the state $^3\Sigma$. Heitler and London howed that in the first state, the potential energy of two atoms runs through a minimum as the distance between them varies while in the second case, it continuously diminishes with increasing distance. The first state is therefore one of stable equilibrium giving us the normal H atom, while the second is an unstable configuration. The energy of this H atom as calculated from quantum mechanics by Wang and others, exactly agrees with the energy of dissociation of the H_2 molecule, obtained from actual experimental data. Heitler and London have shown that in all cases (*e.g.*, O_2, N_2. .) where molecules are formed of non-polar constituents, the forces are to be ascribed to resonance interactions of pairs of electrons in each atom.

Spectra of Nonpolar (Atom) Compounds

The spectra of atom compounds have been studied by a large number of workers, and Franck[3] has given a general theory of their prominent features. The absorption spectra usually consist of bands, sometimes followed by continuous absorptions. For example, the absorption spectra of halogens consist in the visible region, of bands, which all terminate on the short wave-length side in continuous absorption. According to Franck, the molecule in the unexcited state consists of two atoms in the normal state, *e.g.*, in the case of I_2, both atoms are in the $^2P_{\frac{3}{2}}$ state. When light falls on it, one atom changes to the metastable state $^2P_{\frac{1}{2}}$, attended with the usual vibration-rotation disturbances; the continuous absorption corresponds to the splitting of the molecule into atoms with the states $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$. From this theory, Franck deduces the important conclusion that if ν_0 be the limiting frequency of absorption

$$h\nu_0 = D + h(^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}) \quad .. \quad (7)$$

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[3] Franck, Kuhn and Rollefson, *Z. Physik*, 1927, **43**, 155.

where D is the heat of dissociation of the halogen. From this relation, since ν_0 ${}^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$ are all known from spectroscopic data, it is possible to deduce the heat of dissociation D. The values obtained from such considerations agree remarkably well with the heats of dissociation of halogens as actually determined by Bodenstein and Strack[4] from thermochemical data.

Franck's relation (equation 7) has been extended to the case of other atom-compounds besides H_2.[5] Wherever the spectroscopic data are well-known, the relation has been found to lead to correct results.

Intermediate Compounds

There are compounds like the hydrogen halides, and silver halides which were found to satisfy none of the above conditions laid down either for atom-compounds or polar compounds. The three hydrogen halides HCl, HBr, HI[6] and (probably also HF) show no trace of band-absorption, but perfectly continuous absorption beginning from a long wave-length limit. But the long wave-length limit does not apparently satisfy Franck's relation (equation 7) which was written in the case of NaCl. On account of this discrepancy, Franck was led to believe that the hydrogen halides were atom-compounds. But this hypothesis is inconsistent with two well established facts. (1) that all the halides are diamagnetic. . . .this can happen only if the molecule consists of constituents with inert gas shells (*e.g.*, of H^+Cl^- in HCl). If they consist of H and Cl, then the ${}^2S_{\frac{1}{2}}$-term of H cannot be compensated magnetically by the ${}^2P_{\frac{3}{2}}$ or ${}^2P_{\frac{1}{2}}$ state of Cl, hence the molecule would be paramagnetic: (2) the absence of band absorption throughout the whole quartz and probably fluorite region, which is difficult to understand if the substances are atom-compounds.

On account of these doubts and as a study of the current literature showed that the works on which Franck's conclusions were based were not probably carried out with much care, I directed A. K. Dutta in my laboratory to make a quantitative study of the absorption spectra of these halides at different pressures, and find out their extinction coefficient for light of different frequencies. The wavelength at which this quantity just vanished was taken as Franck's limit ν_0. This was found in the case of HB and HI to be widely different from the values assumed by Franck from eye-estimation, but

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[4] Bodenstein and Starck, *Z. Electrochem.*, 1910, **16**, 910.

[5] Sponer, *Ergebnisse der exakten Naturwissenschaften*, 6.

[6] See Photoprocesses, etc., by Griffith and Mckeown, p. 232.

instead they perfectly agreed with formula for ionic compounds, thus proving that HBr and HI are ionic compounds like the alkali halides. The absorption curves in HBr and HI are found to be very gradual while in the case of alkali halides they are rather steep. Hence eye-estimation in the case of the hydrogen halides leads to great error.*

Silver and Thallium Halides.—The halides of silver and thallium have been found to give band absorption, as well as continuous absorption. The band-absorption of silver halides has been studied with great care by Brice[7] and thallium halides by Butkow,[8] but as yet no satisfactory explanation of their spectra has been found.

The Polyatomic Compounds.—Not much work has yet been done on the polyatomic compounds. Their spectra, in emission as well as in absorption, have for the most time remained unstudied. For this reason, and with a view to collecting information, a number of experiments was carried out in my laboratory and some of them appear to be quite promising. A few are reported below.

Absorption Spectra of Saturated Oxides

Next to halides, one would naturally try the oxides and sulphides, but these are for the most part very refractory, and attention was therefore confined to saturated oxides like SO_3,[9] N_2O_5, TeO_3, MoO_3, which are either gaseous or can without much difficulty be obtained in the vapour form. It is known that unsaturated oxides like SO_2, NO, NO_2, . . . give band absorption. As their spectra were well studied they were not taken up. A. K. Dutta[10] (in some works in collaboration with P. K. Sen Gupta) has shown that all these saturated oxides give continuous absorption. The result in the case of SO_3 is typical and promises to be quite interesting. It partially decomposed into SO_2 at ordinary temperature, but the proportion of SO_2 can be reduced by using an excess of oxygen. The absorption spectrum of SO_3 shows a sharp cut at λ 3300 Å followed by a patch of retransmitted light with a second cut at λ 2300 Å. Beyond this it was not possible to proceed as a fluorite vacuum spectrograph was

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[7] Brice, *Physical Rev.*, 1930, **35**, 232; 1931, **38**, 658. "On the absorption spectra of silver halides."

[8] Butkow, *Z. Physik*, 1928, **49**, 865.

[9] A. K. Dutta, *Proc. Roy. Soc.*, 1932, **137**, 366. "On the abxorption spectra of SO_3 and heat of dissociation of oxygen."

[10] A. K. Dutta, and P. K. Sengupta (Comm. to P.R.S.) "Absorption spectra of higher oxides of nitrogen, molybdenum etc."

* The work on HCl could not be completed owing to Mr. Dutta's transference to Benares.

not available. Dutta interpretated the results as follows: the first cut corresponds to the process,

$$SO_3 + h\nu_1 = SO_2 + O\ (^3P) \qquad \ldots \quad (8)$$

Normal SO_3 is supposed to consist of (SO_2) and O^{--}. When light falls on the molecule, the electron absorbs the energy and leaves O in the normal state (^3P), and the result is dissociation into SO_2 and O (^3P). If this idea be correct, the heat of dissociation of O_2 can be easily calculated from the value of ν_0 with the aid of thermochemical data as follows:

λ3300 Å corresponds to 86·7 Cal, hence

$$SO_3 + 86{\cdot}7\ \text{Cal} = SO_2 + O. \qquad \ldots \quad (8')$$

From thermochemical determinations, we have

$$SO_3 + 91{\cdot}9\ \text{Cal} = [S] + \tfrac{3}{2}O_2 \qquad \ldots \quad (9)$$
$$SO + 69{\cdot}3\ ,, = [S] + O_2 \qquad \ldots \quad (10)$$

From equations (8′) to (10) we get $Do_2 = 128$ Cal, which as Dutta shows is in good agreement with other reliable determinations of this quantity from other sources. A further support in favour of the hypothesis is afforded by the interpretation of the second cut. This is interpretated as,

$$SO_3 + h\nu_2 = SO_2 + O\ (^1D_2)$$

i.e., the pulse $h\nu_2$ decomposes SO_3 into SO_2 and an oxygen atom in the next excited state of the O-atom, *viz.*, $^1D_2$. If this hypothesis be true, $h(\nu_2 - \nu_1)$ should be O ($^1D_2$)—O (^3P). The latter value has been found very exactly from spectroscopic data by Frerichs and Paschen, and is equal to 1·90 volts. $h(\nu_2 - \nu_1)$ in SO_3 is found to have the value 1·70 volts. The agreement is not quite exact, but this is probably because the beginning of absorption has not yet been fixed with the accuracy needed for the purpose. There are other theoretical arguments to account for the discrepancy, but these are not reproduced here as the treatment will be too long.

Possibility of getting Auroral Radiation from Post-dissociation Radiation of Irradiated SO_3.

From the above interesting work on the spectrum of SO_3 and other saturated oxides, which are quite similar, Dutta has drawn a conclusion of the highest importance. If SO_3, on being irradiated with light frequency ν_2, breaks up into SO_2 and an oxygen atom in the $^1D_2$-state, what will happen to the excited oxygen atom ? It will either dissipate its energy by collisions of the second type with other atoms and molecules present, or if collisions be prevented by lowering the pressure, the only thing it can do is to revert back to the normal state after radiation of the line $\lambda = (^3P_{0,1,2} - {}^1D_2)$. These lines have the wavelengths λ6300, 6363 Å and have been obtained in the laboratory by Paschen and Frerichs[11] from pure discharge through a vacuum tube containing pure oxygen. They have been called "Red Auroral Lines" on account of their connection with the celebrated Green Auroral line λ 5577 Å which has been now definitely assigned to the transition $^1S_0 \rightarrow {}^1D_2$ of the oxygen atom. It may be mentioned here that the normal oxygen atom which has got electronic constitution $2p^4$ can, according to Pauli's Principle, take up five equilibrium states denoted by $^3P_{0,1,2}\ {}^1D_2,\ {}^1S_0$. In the triplet terms, the spins of three out of four electrons have the same direction, while the spin of the fourth has the reverse direction. In $^1D_2$ and $^1S_0$ two electrons have their spins in one direction, two others in the opposite direction. To go from $^1D_2$ or $^1S_0$ to ^3P-states, only one electron has to reverse its spin. Usually the transitions between these states are forbidden, but they do take place when the atom excited in the metastable state is under a strong electric or magnetic field, or is in such attenuated condition that collisions are rare, and the atom has nothing else to do than to revert back to its normal state by running its usual life.

The interest of these different states of the O atom lies in the fact that they have afforded an explanation of the green line λ 5577 Å which was observed in the spectra of aurora, and was at one time ascribed to a hypothetical element "Geocoronium"[12]. It has since been observed in the spectrum of the night-sky, and seems to be a general characteristic of the upper atmosphere. The origin of this line was a matter of controversy for a long time, till from a series of works, it was established beyond doubt that it is due to the $^1S_0 \rightarrow {}^1D_2$ transition of O. But the way in which it originates in the upper atmosphere has not yet been made clear. It is extremely probable that the $^3P_{0,1,2} - {}^1D_2$ lines, at least the first two of them should come in the auroral spectrum as well as in the spectrum of the night-sky, but

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11. Frerichs, *Phys. Rev.*, 1930, **36**, 398. "Singlet system of the oxygen arc spectrum and the origin of the green auroral line." Paschen, *Z. Physik*, 1930, **65**, 1, oxygen spectrum O_1.
12. Sommer, *Z. Physik*, 1932, **77**, 374. Uber den langwelligen Teil des sichtbaren Spectrum des Nachthimmellichtes.

this result, announced by Sommer[13] has been challenged by Grotrian[13]. Probably the intensities of the so-called red auroral lines are rather small compared with that of the green auroral line.

If Dutta's theory of the absorption spectrum of SO_3 and other higher oxides be true, then SO_3 illuminated with $\lambda < 2300$ Å should give us the red auroral lines; and when illuminated with $\lambda < 1700$ Å should give us the green auroral lines. These experiments have been tried by Dutta, and the appearance of one of the lines, *viz.*, λ 5300 Å seems to be fairly well-established. The experiments which are rather difficult to carry out, are being continued with greater effort.

Spectra of Polyhalides

No work seems to have been carried out so far on the spectra of the halides of Mg, Al and Si. A preliminary investigation in the Allahabad Physical Laboratory by S. C. Deb[14] has shown that all these halides give a continuous absorption spectrum beginning from a long wave-length limit. A. K. Dutta[15] investigated the absorption of CCl_4, $SiCl_4$ and $SnCl_4$ and found that they are exactly similar to the spectra of NaCl. From these experiments it appears that the frequency limit ν_0 is given approximately by the relation,

$$h\nu_0 = R/n \qquad .. \quad (11)$$

where R is the atomic heat of formation and n is the valency.

The quantity R cannot be directly determined but has to be deduced out of thermochemical data from the general formula

$$R = Q + L_M + \frac{n}{2} D_{Ha_2} \quad - L_{M_{Ha_2}}$$

where Q is the heat of formation, D_{Ha_2} = heat of dissociation of the halogen: and L = latent heat of vaporization.

Now L_M and $L_{M_{Ha_2}}$ the latent heats of vaporization of the element forming the cation, and of the halide are not known with certainty in most cases. For C it varies from 140 Cal to 280 Cal, unless these quantities are accurately determined, it is not possible to say whether the relation (11) is exact or not.

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[13] Sommer, Naturwissenschaften, 1930, 752; Grotrian, *ibid.*, 1931; Sommer, *Z. Physik*, 1932, 77, 375.

[14] S. C. Deb, *Bul. Acad. Sci.*, U.P. 1931, **1**, 92. On the absorption spectra of Saturated Halides.

[15] A. K. Dutta, and M. N. Saha, *Bul. Acad. Sci.*, U.P. 1931, **1**, 19.

In the course of these investigations it has appeared that in the case of those compounds where the molecule does not possess a spherical symmetry, the above generalisation fails to be true. The correctness of this statement is rendered probable from the fact, that in the case of spherical symmetry it can be supposed that the valency bond is distributed equally amongst the *n*-halogen ions, so that only 1/*n*th part of the total binding energy is required to break one of the halogen atoms from the molecule.

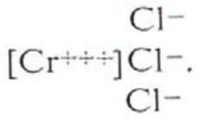
But where this spherical symmetry is wanting, we can suppose the Franck-Condon curves for these molecules to be shifted to the right according to the degree of assymmetry; the result is that the beginning of absorption shifts to the ultraviolet side. This is perhaps the case in the example of aluminium halide molecules. For aluminium halide, the thermochemical data are more or less accurately known. We find in this case that the value of R/*n* is in every case less than the value derived from L_M. Such is the case with the mercury halides as well, which is also studied by Deb and Mohanty in this Laboratory; in these cases thermochemical data are all available.

We thus find that the generalised Franck's relation, *hν* corresponding to R/*n* holds, only strictly for alkali halides and halides possessing a spherical symmetry in their structure. As we take $MgCl_2$, $AlCl_3$, $SiCl_4$ there is probably progressive departure from the relation (11).

Saturated Halides showing Bands in Absorption

Apparently band absorption in such cases is impossible from the considerations given above. But the absorption spectra of silver and thallium halides which are chemically similar to alkali halides show, as has been said previously, band absorption in addition to continuous absorption. It has been established in the case of silver halides in this laboratory that the continuous absorption phenomena can be interpreted as similar to those of saturated spherically unsymmetrical compounds. But the interpretation of the band absorption still remains obscure. Though no definite solution is yet available, it is clear that molecules whose metallic constituent possesses one or more metastable levels, always give rise to band absorption. To test this point I directed my scholars S. C. Deb and B. Mukherjee to investigate the nature of absorption shown by alkaline earth halides. It is definitely known that the metal constituent of these molecules have got a stable S^2 orbit and a metastable d^{10} orbit. So if the above generation be correct these compounds ought to show band absorption along with the continuous absorption which is common to every saturated molecule. Deb and Mukherjee[16] investigated several halides of these alkaline earth metals in the Heraus furnace of my laboratory. In every case there was a band absorption accompanied by continuous absorption similar to the well known case of silver halides.

Halides of the Transitional Group of Elements and Origin of Colours of the Inorganic Salts

Another entirely different class of compounds, chiefly poly-atomic are the halides of the elements of the transitional group. A study of the magnetic moment of these halides in solution shows that the compounds consist of an ionic metallic core surrounded by saturated inert gas type shells. If we take a compound like $CrCl_3$ we may suppose the picture of the combination as given by  $[Cr^{+++}]\overset{Cl^-}{\underset{Cl^-}{Cl^-}}$. Thus there are three Cl^- ions surrounding the nucleus. The magnetic action of these molecules is explained as due entirely to the Cr^{+++} core, the Cl^- ions contributing nothing to the moment. It is well known that to change a stable configuration such as that of an inert gas type, quite a large amount of energy is required; so the colour, *i.e.*, the absorption of light due to these compounds in the visible region, cannot be due to any change primarily occurring in the Cl^- ions. The probability remains that the colour arises from the reaction of light on Cr^{+++} ions. This contains in the free state an incomplete d^3-shell, giving rise to certain number of quartet ^4X and doublet ^2Y terms. '*l*' coupling in compounds ceases to be of importance in a molecular formation, which subdivides themselves along the figure axes, while S-vectors take up either parallel or antiparallel directions. We can therefore suppose that the action of light consists in changing the spin of one of the component electrons in the d^3 -shell. The energy required in this process is in every case small, and actually falls within the range indicated in the visible spectrum. This is the result with almost all ions of the elements of the transitional group.

A number of experiments may be designed to test this hypothesis. Owing to the limited capacity of this laboratory the absorption spectra of a few chlorides of the transitional group were tried. Due to various reasons chiefly among them the unstability of the compounds in

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[16] S. C. Deb, and B. Mukherjee, *ibid.*, p. 110.

vapour state at a high temperature, not many of these compounds could be satisfactorily investigated, but those investigated ($CrCl_3$, $FeCl_3$) showed without any ambiguity the presence of band absorption at the very position predicted by the hypothesis of the change of spin vector due to the action of light. S. C. Deb[17] working under my suggestion showed that in the case of $CrCl_3$, absorption bands were obtained in the blue violet region extending slightly into the ultra-violet, which is certainly due to reaction of light on the d^3 shell of Cr^{+++} ion, the spin moments of the electrons in the normal state for which level being parallel, give rise to a ^4x term. The action of light would be to turn the spin of one of the electrons in the opposite direction giving rise to band absorption; continuous absorption has also been observed, probably corresponding to the splitting of $CrCl_3$ into $CrCl_2$ and Cl but owing to absence of thermochemical data, *viz.*, heat of vaporisation of $CrCl_3$ and Cr the continuous absorption spectra could not be interpreted.

Thermochemical Data from Absorption Experiment

In cases where the theory is on safe grounds, the process can be reversed, and thermochemical data can be obtained from results of absorption experiments. As an illustration of this method, reference can be made to certain works which have been performed in this laboratory. M. S. Desai[18] has been able to determine the heat of dissociation of Fluorine by studying the absorption spectra of alkali fluorides and utilising relation (4). The value which he obtains, 78 Cal, is the first estimate of this important quantity. It has still to be confirmed by independent determinations. He also studied the absorption spectra of lithium halides, and determined the heat of evaporation of lithium[19] from equation (4). This was found to be 29·3 Cal. After his result was published, there came a paper by A. Bogros in the Annales de Physique (March, 1932, p. 200) where measurements of vapour pressure of Li are reported. The value of latent heat derived from these measurements is 28·2 Cal which is in very good agreement with Desai's value. Similarly, A. K. Dutta[20] determined the absorption spectra of N_2O and found it to be per-

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[17] M. N. Saha and S. C. Deb, same, p. 1. "On the colours of inorganic salts."

[18] M. S. Desai, *Proc. Roy. Soc.*, 1932, A. 136, 76. "On the absorption spectra of Alkali Fluorides and Heat of Dissociation of Fluorine."

[19] M. S. Desai, *Bul. Acad. Sci.*, Vol. II, 1932, Latent Heat of Evaporation of Lithium.

[20] A. K. Dutta, *Proc. Roy. Soc.*, 1932, **137**, 366. On the Absorption spectra of N_2O and heat of dissociation of N_2.

fectly continuous beginning from λ 2750 Å. From this, and using other thermochemical data he obtained a value of 204 Cal for the heat of dissociation of N_2. This is probably the best value of this quantity so far determined.

Conclusion

From the above short and imperfect sketch, the chemical reader will probably find that spectroscopy is making itself increasingly useful to the chemist. Space does not permit me to discuss the important contributions by Herzberg and on the theoretical side, of the works in recent years by Slater, Heitler, London, Born and Weyl[21] who are applying wave mechanical methods for finding out energy values of chemical bonds and explaining other features of chemical combination. These investigations are sure to throw much light on these time-honoured problems.

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21. See report on these works by M. Born, Ergebnisse der exakten Naturwissenschaften, 10.

1.3. NUCLEAR PHYSICS, COSMIC RAYS AND NUCLEAR ENERGY

1.3.1 ULTIMATE CONSTITUENTS OF MATTER*

THE task of science is not only the exploration of the mysteries of the inorganic and organic world by means of observations and experiments, but also the coordination of the facts of experience to an ordered system; for without this coordination, knowledge becomes too vast for human comprehension. Though struggle against nature has been found to be generally most successful when there is proper coordination between exploration and rational thinking, a number of psychological beliefs have sometimes directed human activities to the right direction. One of these is the belief in the ultimate simplicity of the laws of nature, and this belief has played a great part in the progress of science.

The Atomic Theories of Matter

As an illustration, we may take the theories concerning the ultimate structure of matter. You are aware that the ancients believed that this world is made up of five different elements, *viz.*, earth, water, air, fire and aether. The origins of this theory are shrouded in the mists of antiquity, but it must have rested on observations which it is not difficult to recall.

It is not surprising therefore, that the theory of five elements dominated the human mind during at least two millenniums during which period, further progress in this direction was arrested owing to insistence on blind obedience to scriptural authority and general lack of a spirit of exploration amongst mankind.

The theory became untenable towards the end of the eighteenth century before the onrush of modern discoveries in physics and chemistry; for Carlisle and Nicholson proved that by passing a current of electricity through water, one of these primordial elements, it can be decomposed into two simpler gases; hydrogen and oxygen. The other primordial elements like earth and fire could not stand the new test laid down for the characteristics of an element. This new test was that no chemical or physical processes should be able to decompose an element into simpler constituents. As a result of this new definition the atomic theory of matter was built up during the nineteenth century.

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* Lecture delivered at the Calcutta University under the Adhar Chandra Mookherjee Trust, in September, 1934. Sci & Cult 1, 12, 1935.

The general features of the atomic theory are so widely known that it is not necessary for me to go into the details but I shall only single out a few salient points to bring out its extraordinary complexity.

It was established that all matter in this world could be decomposed into 92 different elements, each having a definite weight, definite chemical properties and a characteristic spectrum. But the atomic weights stand in no simple integral ratio to each other: the spectrum of even the simplest element, *viz.*, the H-atom consists of infinite number of lines and in the case of an element like Fe the number and complexity of the lines are so great that it becomes difficult to believe that the atom could be such a simple thing as imagined by chemists, or physicists who regarded it as a mere mass-point. There is a saying due to the famous spectroscopist H. A. Rowland:—"The atom must be more complex than even the grand piano."

The chemical properties were also found to be extremely diverse. But intensive work by the investigators of the last century showed that underlying all these diverse and puzzling properties of the atom, there must be certain fundamental laws of great simplicity. Through the genius of Mendeleef and Lother Mayer, it was found that the elements follow certain periodicities having very deep significance.

The Rutherford-Bohr model of the atom

It is not my intention to tell you here in detail how within the last forty years the amazing complexity of physical and chemical facts received full explanation in the Rutherford-Bohr theory of the atom. It is now a matter of common knowledge that all different kinds of atoms can be shown to be composed of two fundamental atoms:

(*a*) the atom of negative electricity,
(*b*) the atom of positive electricity.

But a fundamental difference was noticed between the two primary constituents. While the atom of negative electricity was found to possess practically no mass (rather to be precise a mass amounting to $\frac{1}{1836}$ of the mass of the hydrogen atom) the atom of positive electricity was found to have the same mass as the hydrogen atom. No reason could be found for this marked dissymmetry, and later after some fruitless endeavours, scientific opinion was inclined to accept this dissymmetry in the behaviour of these two charges as a fundamental fact, inherent in the nature of things.

I need describe to you the essential features of the Rutherford-Bohr theory of the atom only in the barest outline simply for emphasising the essential difference in role played by the two primary atoms. On this theory, the atom is supposed to consist of a central nucleus which contains all the mass ascribed to the atom and a charge which is numerically equal to the ordinal position of the atom in the periodic classification. An equal number of electrons is arranged about the nucleus in successive layers: the characteristics of these electrons are defined by quantum mechanics.

It is quite true that the mechanics of the inter-atomic world is very different from the Galileo-Newton system to which mankind has been accustomed for three centuries and is therefore very difficult of comprehension by minds not familiar with the recent investigations in physics and chemistry. For the fundamental constituent, *viz.*, the electron, does not conform to the attributes of the mass-point of Galilean mechanics, for in this system mass is assumed to be constant whatever the velocity. But the mass of the electron is found to vary with velocity in a way which cannot be explained without introducing very artificial hypotheses about the structure and shape of the electron. This has necessitated the formulation of relativity mechanics. Secondly, the representation of the electron by a particle has been found to be faulty. It should be represented by a group of waves having the mean length $\lambda = h/m\,v$, and is subjected to a new kind of dynamics in which operations take the place of dynamical variables.

The Physics of the Nucleus

The Rutherford-Bohr model of the nucleus forms a self sufficient system. But the assumptions underlying this model themselves require critical examination. This critical attitude has been more marked in recent years. I shall talk only of one particular line of criticism. In the R. B. model of the atom, the nucleus is supposed to contain all the mass and the positive charge. But though for explaining the X-ray and optical spectra, the nucleus may be regarded as a mere point, it was quite clear to the early investigators that this picture was insufficient for the explanation of other phenomena, notably those of radioactivity. For in this class of phenomena, charged particles (α and β rays) and light quanta of very high energy content (γ-rays) are being spontaneously emitted from the nucleus, hence the nucleus must have an extremely complex composition.

The charge has been shown to be exactly an integral multiple of the elementary quantum of electricity and the mass was also shown by Aston to be very nearly an integral multiple of the mass of the proton. It was therefore believed that ultimately the nucleus may be shown to consist of merely protons and other types of positive particles which are formed out of the proton and the electron, e.g. the α-particle, the deutron etc. But the mass number is not equal to the atomic number. Thus for example the element uranium has got the mass number of 238 and the atomic number of 92. It is expressed by the symbol U_{92}^{238}. How are we to explain its composition on the basis that all matters can ultimately be referred to the proton and the electron ? The answer was that number of protons was equal to the mass-number 238, but there were besides in the nucleus (A-Z) electrons which reduced the net positive charge to Ze.

Before 1930, the assumption was made that the nucleus, though it ultimately could be decomposed into protons, and electrons, did not contain them in the free state, but mostly in a state of combination as α-particles. The α-particle has a mass of $4m_H$ and a charge 2e and can be written as He_2^4. But the hypothesis that there are free electrons inside the nucleus is beset with a number of difficulties. The electron as we know it outside the nucleus has got a magnetic moment, which is equal to $\frac{eh}{4\pi mc}$ and if there be some odd number of electrons inside the nucleus, it would possess a magnetic moment comparable with this quantity. Such a nucleus is not difficult to find out. In fact the common element N provides an example. Its composition may be taken to be

$$N_7^{14}=3He_2^4+2p_1^1+e$$

So we have to postulate that N_7^{14} contains an electron in its nucleus.

If this picture were true, the N-nucleus should possess a magnetic moment equal to $\frac{eh}{4\pi mc}$ the Bohr magneton. It is true that nuclei do possess magnetic moment which can be determined from the hyperfine structure of spectral lines, but they have been found to possess quite a different order of value which is generally $\frac{1}{2000}$ times smaller than this quantity and the nitrogen nucleus has been found to possess no magnetic moment at all. It thus appears that if the electron is a component of its nucleus its properties would be fundamentally different from those which we know about it in our investigations about the extra-nuclear electrons. Its magnetic moment must vanish. A second line of argument against the existence of free electrons inside the nucleus is as follows. The nucleus contains a large excess of positive charges. As we know from our ordinary experience charges of like sign repel each other. How can the nucleus be stable ? It was surmised that probably the force of repulsion might change into one of attraction at close quarters.

The Potential Barrier

A series of investigations by Rutherford and his students, however threw fresh light on the subject. They showed that the nucleus is surrounded by a potential barrier which accounts for its stability. Though the particles inside are repelling each other and are endowed with large kinetic energies inside the nucleus, they cannot jump over the barrier. The picture is just like that of a number of dangerous lunatics confined within a high walled enclosure over which they cannot jump, but must be content to remain inside. But according to modern conception all particles of energy (matter, radiation) are also waves, and these can perform feats which are unthinkable in particle dynamics, that though as particles the α-rays may not jump over the barrier, as waves they can leak through the barrier and thus give rise to the phenomenon of spontaneous disintegration as Gamow

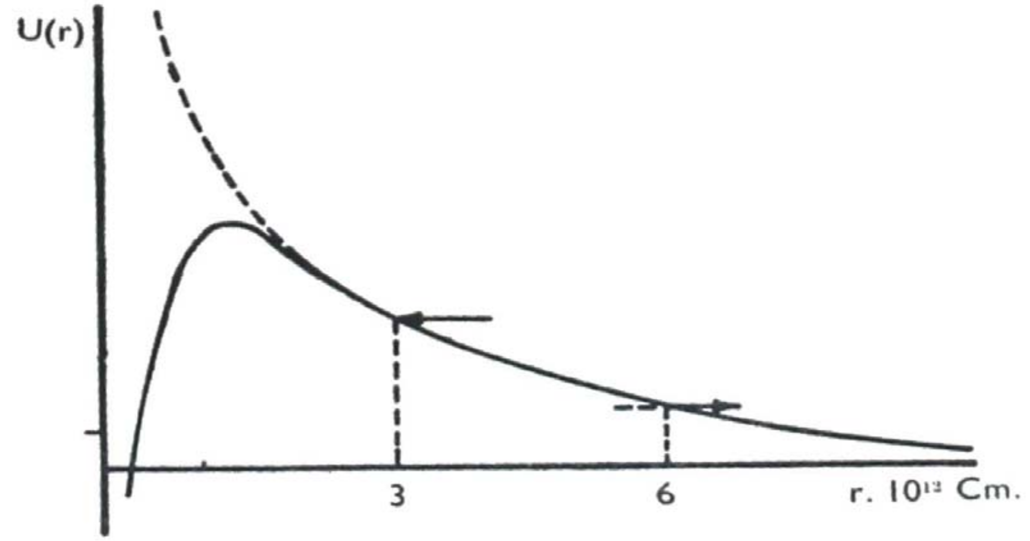

Fig. 1
Potential barrier

clearly demonstrated from wave mechanics. The presence of barriers about the atomic nuclei is thus well established and if we accept it, the natural consequence follows that an electron existing inside the nucleus will at once be ejected, for what is barrier to the positive particles is only a slope for the negative particles.

Our hypothesis about the structure of the nucleus therefore brings us to a very intriguing position. The investigations on the hyperfine structure and the stability of radioactive elements are clearly against the existence of any electron in the nucleus while the ejection of β-rays in radioactive disintegration is clear evidence for its existence. But on the whole the evidences against existence are too strong and Bohr tried to reconcile the two views by postulating that ordinarily the electron does not exist in the nucleus, but may be created in the process of radioactive disintegration in a way which is not yet fully understood.

Prediction about the Neutron

If the electron is definitely ruled out as a possible constituent of the nucleus, we have to postulate the probable existence of other particles to explain its composition. Rutherford has been assuming since 1919 the existence of neutron. It is simply the proton minus its positive charge. We are familiar with the Bohr theory of the H-atom. It consists of the proton round which the electron revolves in quantum orbits. The nearest orbit to the nucleus is defined by the quantum number one. Supposing that by some means electron be made to fall into the nucleus, the charges will be neutralised and we shall get a new body with the same mass as the hydrogen nucleus but with no charge. We may call this the *neutron*.

Discovery of the Neutron

Though the neutron was looked for, it could not be discovered for a long term presumably because on account of absence of charge it does not produce an effect which can be easily detected by ordinary physical instrument. But the detection came from investigation in unexpected quarters. In 1931, two investigators in Germany, Bothe and Becker, placed a radioactive body, polonium, in contact with a Be-plate. This device is very often used for studying the artificial disintegration of the nucleus. Some of the α-particles, by reason of their high velocities, can enter within the potential barrier of the nucleus of Be which thereby undergoes a profound change. The change generally consists in the breaking up of the nucleus with the ejection of new particles and radiation. This process is more feasible with lighter atoms, as the force of repulsion is smaller, and the particle has a greater chance of entering the nucleus. Bothe actually showed with the aid of the Geiger counter that in the process mentioned above, radiations of a very penetrating nature are ejected from Be which can pass through great thicknesses of matter. From the penetrating power, they made provisional estimate of their wavelength, and found them to be even shorter than the shortest γ-rays, known from radioactive sources, and possessed of an enormous amount of energy, *viz.*, 14 million electron volts. Curie and Joliot directed these radiations against paraffin and other substances containing hydrogen, and showed that they can liberate protons whose range can be determined and thus the energy can be calculated. They thought that the new radiation, on impinging against the hydrogen nucleus, imparts to it a velocity according to the principles of conservation of energy and momenta just as in Compton effect. The energy of the radiation obtained by this method was found to amount to 50 million electron volts, but the same experiment, repeated with Nitrogen, gave the energy of the same radiation as 90 million electron volts.

The energy of the radiation thus apparently varied with the nature of the particle with which it collided. Chadwick pointed out the apparent inconsistency between the two groups of measurements he introduced and to explain it the hypothesis that the Be-radiation was not γ-rays at all, but consisted of uncharged particles moving with large velocities which, colliding with the nuclei of other atoms, set them in motion according to the well-known mechanical laws of impact. In fact he showed that from the experimental results it was possible to arrive at a consistent value of the mass of the hypothetical particle. It was found to be very nearly equal to that of the H-nucleus. He concluded therefore, that the α-particles on entering a Be-nucleus ejects *neutrons*.

Track of Neutrons

The considerations regarding the nature of Be-radiations were further confirmed by the study of the tracks of the radiation in the Wilson chamber. If the radiations consist of neutrons, then since they have no electric or magnetic charge they can have little interaction with matter and are expected to pass through matter until they are stopped by some nucleus to which they will impart momentum and energy which can be calculated from ordinary mechanics. The tracks are thus expected to be of a kind which is quite different from that of any other known particle, α-rays, protons, electrons, recoil atoms or γ-rays. Chadwick argued that it would merely consist of two linear tracks inclined at a large angle to each other and emanating from a single point (the point where collision with the nucleus takes place). One would correspond to the track or the recoil atom, the other of the neutron which now probably captures a positive charge and becomes a proton. These experiments were carried out by Feather and Bee and the tracks came out as expected. Later it was found that many other light atoms on bombardment by high speed α-particles can be made to emit neutrons.

Occurrence of the Neutrons in Nature

The existence of the neutrons is thus definitely proved but its properties have not yet been completely elucidated. Heisenberg has shown that the neutron and the proton form probably the main constituents of the nucleus. Thus it used to be formerly thought that the α-particle consisted of four protons and two electrons. It is now thought that this consists of two protons and two neutrons.

α-particle$=4p_1^1+2e=He_2^4$ (former view)
α-particle$=2p_1^1+2n_0^1$ (present view)

Recently Urey and Brickwedde have succeeded in discovering heavy hydrogen which is an isotope of ordinary hydrogen with the nuclear mass two (deuton) $D_1^2=p_1^1+n_0^1$. The nucleus of this isotope, or of deuton, may simply consist of a proton and a neutron. The neutron also forms an important constituent of the heavier nuclei and its introduction has solved the old difficulty about the existence of the electrons in the nucleus. Thus the composition of U_{92}^{236} may be taken to be

$$U_{92}^{236}=45\ He_2^4+52\ n_0^1+2p_1^1$$

Characteristic of the Neutron

As far as known to the present time every fundamental particle is characterised by four attributes—mass, charge, spin and magnetic moment and further we have to specify the statistics it obeys. Thus

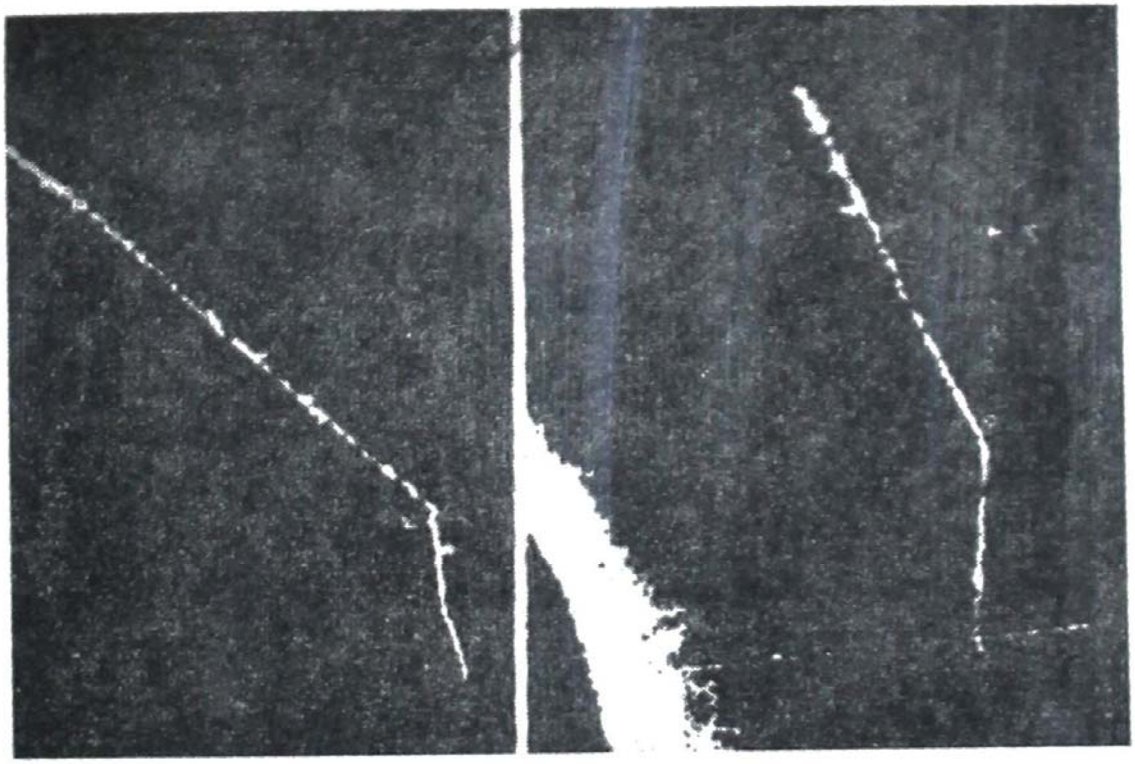

Fig. 2
Disintegration of Nitrogen nucleus by neutron

of the fundamental particles known to us, the electron has got $m = \frac{m_H}{1836}$, one quantum, spin moment $= \frac{1}{2}\frac{h}{2\pi}$, magnetic moment $= \frac{eh}{4\pi mc}$ and it obeys Fermi-Dirac statistics. The proton has the same but opposite charge, and the same spin, but its mass is equal to m_H and the magnetic moment has been found by Stern to be $\frac{5}{8}$ times $\frac{eh}{4\pi m_H c}$.

The proton too is found to obey Fermi-Dirac statistics. The α-particle is not fundamental but as it has not been broken up, we may regard it as fundamental up to a certain extent. Its mass is nearly 4 m_H, charge is 2e, spin=0, and it obeys Bose-statistics. What about the neutron ? Its mass is still uncertain though it is believed to be very close to that of the proton and the charge is zero. Heisenberg has shown that it has a definite spin moment which is of the same order as that of the proton and it obeys Fermi-Dirac statistics. We shall return to this subject later and now we shall pass on to a description of the discovery of another fundamental particle, the positron.

Discovery of the Positron

The electron as the fundamental atom of electricity and one of the ultimate constituents of all matter has been known since the last forty years. But in spite of all attempts, no corresponding positive unit of electricity was known until recently. Before 1933, the smallest positively charged particle discovered namely the proton, had the same mass as the H-atom which is 1836 times heavier than that of the electron. Thus nearly all mass is associated with positive electricity. This asymmetry in behaviour between positive and negative electricity has never been properly understood, for the classical equations of electricity and magnetism predict perfect similarity in the behaviour of the two kinds of electricity. So before 1932, the investigators had resigned themselves with respect to this question, to the philosophic attitude, *viz., that a fact is a fact.* Certain attempts were also made notably by Eddington to find out from wave mechanics an explanation for the difference in mass of the unit quantum of charges of different signs. I need give no account of this highly speculative work, as the discovery of the positron has probably undermined the whole basis of these speculations.

In 1932, a number of investigators working in different parts of the world (U.S.A. England, France and Germany) almost simultaneously announced the discovery of the positron which is the exact counterpart of the electron not only in charge but also in mass, and probably also in other properties. The discovery was made in the Wilson photographs of cosmic rays, the chamber being placed in a magnetic field. This method, which was first introduced by Skobelzyn in Leningrad, enables one to find out not only the track but in addition the charge, mass and velocity of the ionising particles.

Cosmic Ray Explorations

I have no time here to talk to you of the wonderful interest which has been created in recent years by the investigations on cosmic rays. You are certainly reading in the papers of the upper air ascents made in specially constructed balloons by European and American investigators. The chief object is to study the nature of cosmic radiation, a mysterious phenomenon which was first discovered about 30 years ago by certain investigators who found that even when their electrical measuring instruments were completely enclosed by heavy insulating material, they continue to lose their charge. Bit by bit, by almost an epic struggle, it was established that this leakage was due to a mysterious radiation coming from space which can penetrate through thick layers of matter and ionise the gas in the ionisation chamber. The extra-terrestrial nature of these radiations was first established by Hess, an Austrian worker, who was the first to put himself with his apparatus in a balloon and take observations at increasing heights. But in spite of enormous amount of work, it has not as yet been found possible to determine with certainty whether these radiations are particles of some kind, or γ-radiation of high energy. To determine its nature, scientific expeditions have been taken to all places from the poles to equator and observations have been taken from balloons reaching extraordinary heights of 25 km and down to depths of $\frac{1}{2}$ km in frozen lakes. But the problem is not yet solved and the lure of the unknown may still continue to attract fresh investigators and probably fresh victims.

A novel method of investigating these radiations was introduced, as mentioned above, by Skobelzyn who took Wilson photographs of the tracks of these rays in magnetic field. The tracks of the particles are now curved and from the nature and amount of curvature and of the nature of ionisation tracks produced, it is possible to determine the charge and the mass of the particles. The work was further taken up by Millikan and Anderson in California and Blackett in England.

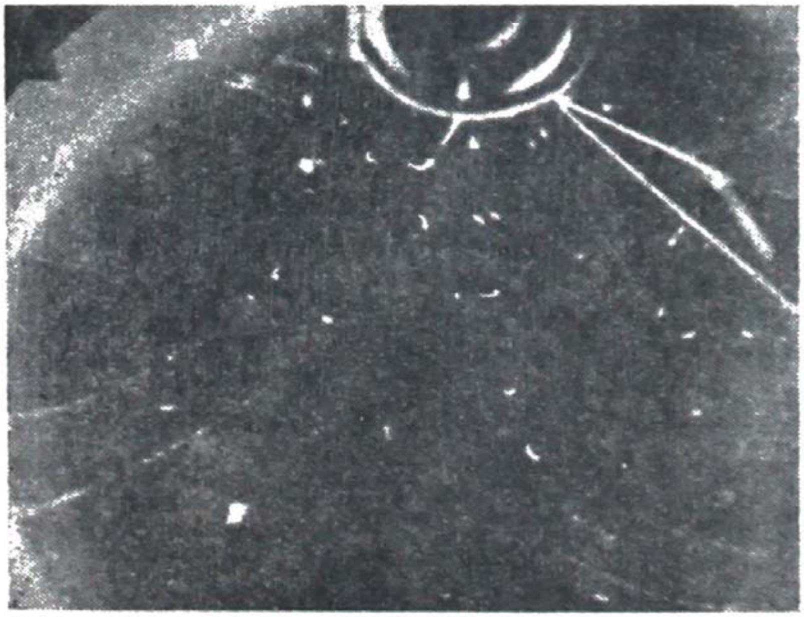

Fig. 3
Positron Tracks

The device is simple. The apparatus is exposed to the cosmic rays and whenever they happen to enter and fire the gas in the chamber, a photograph of the track is registered by automatic devices. These tracks are not actually those of the cosmic rays but of the particles produced by them when they encounter matter. The largest part of them can be identified as being due to high speed electrons possessing sometimes the extraordinary energy of thousand times their rest mass and moving very nearly with the velocity of light. Carl Anderson working with Millikan at Passadena in California made the fortunate discovery in October 1932 that a small percentage of these tracks curve in an opposite direction and can only be due to a particle having an opposite and therefore positive charge. Further from an examination of the ionisation tracks it was apparent that their mass was much less than that of the protons and of the same order as that of the electron. From these observations Anderson was emboldened to make the definite statement that he has made the discovery of the positive electron or the *positron*.

Electrofission of Quanta

The bold statement proved to be quite correct. One might ask how the positive electrons are produced by cosmic rays. If the cosmic rays are identical with rays of great energy, then even terrestrial γ-rays of sufficient energy should show the same effect. This was proved by allowing a beam of very penetrating γ-rays from ThC″ to fall on different kinds of matter (lead, aluminium, carbon) and observing the track of the particles ejected from them. In a small percentage of cases coupled tracks were obtained curving from the same point in opposite directions and it was shown by Anderson, Blackett, Curie-Joliot and others that sum of the energies of the two particles was exactly equal to the energy of the original γ-radiation. The relation by the way, throws light on the mechanism of production of the positrons. It appears, as Blackett pointed out, that the quantum of γ-radiation is split up, under the influence of the intense electric and magnetic field inside the nucleus, into a pair of positron and electron. This phenomenon has been termed by Curie-Joliot as the materialisation of quanta but probably a better term would be "*Electrofission of quantum*"[1] as suggested by the present writer and Dr. Kothari.

It is thus curious that a fundamental particle like the positron

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[1] This process is now known as pair prodution—*Ed.*

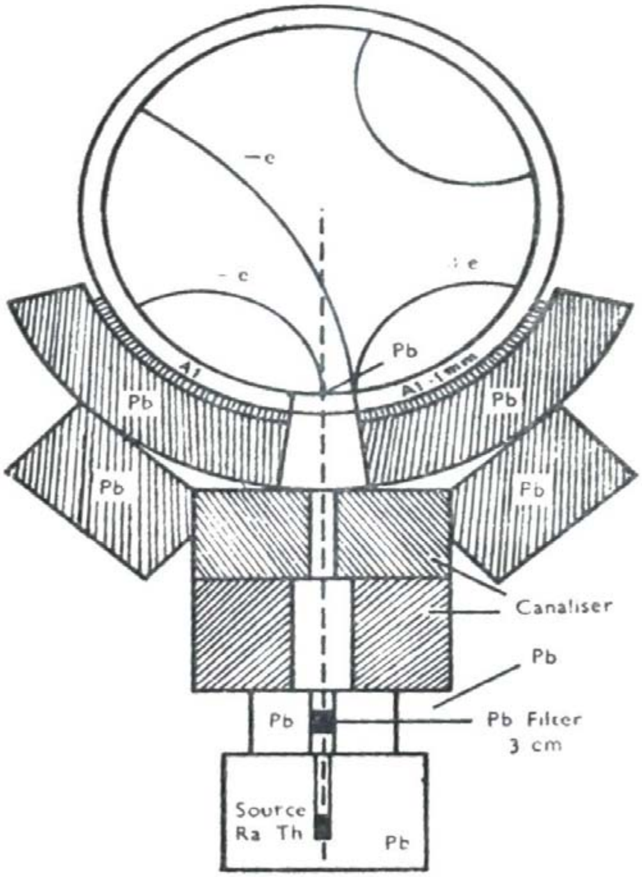

Fig. 4
Production of positron by bombarding Al with γ-rays

should be discovered in such a strange way. Other methods of its production have also been found. Skobelzyn has found that it probably occurs when a β-particle is allowed to collide with some nucleus. Curie-Joliot and Fermi have found that it is given out by unstable nuclei when radioactivity is induced in them by subjecting them to bombardment by α-particles and neutrons respectively. It thus seems to be a fundamental constituent of the nucleus and the fact that it is found to be so rare is due to the circumstance that it can be produced only in a nuclear process. But some of its properties are yet to be investigated. As it has got the same charge and mass as the electron its ionisation track should be similar to that of the electron. This has been found to be the case. But in one respect it should differ from the electron. On passing through matter, it should occasionally come into direct contact with extranuclear electrons and the electrical charge would be annihilated. This is the opposite phenomenon to *Electrofission* and would result in the formation of either one quantum of energy (larger than 10^6-electron volts). Anderson records one or two such cases and this has also been supported by Blackett and Chadwick, in their own Wilson ray photographs and by E. J. Williams indirectly by bombardment of matter with positrons, when *annihilation radiation* is given out.

We have as yet no definite evidence regarding the spin of the positron or its magnetic moment, neither of the statistics which it obeys. The perfect symmetry between two kinds of electricity, as given by the electro-dynamical equations, shows that all its properties should be the counterpart of those of the electron, i.e. it should not only have the same mass and charge as the electron which is well-established, but also the same spin and the magnetic moment. But these properties, as Bohr showed in the case of the electron, cannot be experimentally demonstrated but can be inferred only from indirect evidence, *viz.*, from the study of the behaviours of extra-nuclear electrons in producing spectra. But as far as our present knowledge goes, the positron is only confined to the nucleus, where the magnetic moment which it might have possessed in the free state, evidently disappears. The conclusion therefore seems to be irresistible that the equations which describe the motion of charged particles in outside space (including even the Dirac equation) cease to hold good in the nucleus.

FUNDAMENTAL PARTICLES

Particle	Mass	Electric charge	Mag. charge	Spin	Mag. moment	Statistics
Electron	0·00054	−1	0	$\frac{1}{2}$	1	F.D.
Positron	0·00054 (?)	1	0	?	?	F.D.
Neutron	1·0080	0	0	$\frac{1}{2}$	—	F.D.
Proton	1·0072	1	0	$\frac{1}{2}$	2·5	F.D.
Antiproton (Negatron)	?	−1	0	—	—	
Magnetron (Dirac free poles)	?	0	$\pm \frac{1}{\alpha}$			
α Particle	4·00108	2	0	0	0	B.E.
Deuton	2·01309	1	0	1	0·85	B.E.

Mass unit $1{\cdot}6490 \times 10^{-24}$ gram
Unit of electric charge $4{\cdot}770 \times 10^{-10}$ esu

Unit of spin moment $\frac{h}{2\pi} = 1{\cdot}042 \times 10^{-27}$ erg × sec.

Unit of magnetic moment $\frac{eh}{4\pi mc} = 0{\cdot}92 \times 10^{-20}$ erg/Gauss.

F.D.	Fermi-Dirac Statistics
B.E.	Bose—Einstein Statistics

1.3.2 CONFERENCE ON NUCLEAR PHYSICS*

[An attempt has been made to give a clear and connected account of all matters of importance discussed on this occasion. This has necessitated the inclusion of the historically or otherwise relevant matter which was presupposed on the part of those who attended the conference, and without which the account here would have been quite unintelligible. Mathematics has been altogether avoided, and only the general line of thought is stressed.]

FOR some years past, Professor Niels Bohr has been in the habit of calling a private conference of physicists at Copenhagen during summer. The last was held in 1934. This year's conference was held in the Institute for Theoretical Physics at Blegdamsvej 15, Copenhagen, from June 17 to June 20, and was attended by about one hundred physicists (most of them original workers in nuclear physics) from different parts of Europe and America. For four days the Institute was the scene of very lively and instructive discussions on this latest branch of physics. Among those who attended the following may be mentioned:

Profs. M. Born; Franck; von Hevesy; Stern; Pauli; Heisenberg; Meitner; Oliphant; Thomas; Jordan; Kramers; Weisskopf; Delbrück; Heitler; London; Placzek; Teller; Frisch; Mùller; Kalckar; Caisimir; Peierls; Weizsäcker; Amaldi; Wick; Koch; Holtsmark; Trumpy; Bhaba; Jakobsen; Saha; Richardson Jr.; Reiche; Uhlenbeck; Dunning; Hund; Rosenfeld; Euler; Ehrenfest Jr.; Hulme; Jehle; Rasmussen; Mrozowsky; Waller; etc.

Professor Bohr welcoming the guests said in an introductory speech that he was glad that so many eminent physicists working in different parts of the world and on different branches of nuclear physics had responded to his invitation and assembled at Copenhagen to discuss their work and exchange their ideas. Knowledge in this direction is progressing so rapidly that one does not often believe what he did two years ago. Within the last few years two new 'elementary' particles, neutron and positron, have been discovered, and the existence of two, neutrino and negative proton, has been postulated though not yet experimentally proved. He concluded by remarking that the conference had representatives from almost every school of workers—Cambridge, Rome, Paris, Berlin, and other places.

Dr. Jakobsen was the first to speak. He gave an account of the work which he had carried out at the Institute of Copenhagen on the scattering of γ-rays from Th C″. It is well known from the

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*With Pannalal Kapur—*Sci & Cult* **2**, 133, 1937 theory of Compton effect that encounters between electrons and photons (light quanta) can be treated mathematically according to the laws of conservation of momenta and energy. Such a treatment leads to a correspondence between the direction of the scattered quanta and the direction of the recoil electrons. Some years ago Bothe and Geiger established the correctness of Compton's theory by an experiment in which the coincidence between the scattered quanta and the recoil electron was established. This classical experiment has generally been taken to form the most rigorous experimental proof of the law of conservation of momenta and energy when applied to processes in which individual elementary particles are involved. The experiments had hitherto been done only with X-rays, and it was not quite sure whether similar results could be extrapolated for the γ-ray region.

Some months ago Shankland performed an experiment, which was reported in the *Physical Review*, with γ-rays from Ra C, and obtained rather startling results—results which could not be reconciled to the Compton theory. He found that there was no correspondence between the direction of scattered quanta and the recoil electrons and that the same number of coincidences were obtained in directions not predicted by the theory as well as in directions predicted by the theory. Thus the validity of the conservation laws was questioned. Dirac, in a short article in *Nature*, expressed the view that Shankland's experiment definitely proved the non-validity of the conservation laws when applied to individual encounters between particles and photons, and in the death of the basic principle saw the possibility of setting up a new system of quantum electrodynamics which would have better success in dealing with nuclear phenomena than the older quantum electrodynamics.

In view of the revolutionary nature of Shankland's experimental results and the support given to them by one of the most distinguished theoretical physicists, it was thought necessary to carry on further experiments with γ-rays. Many physicists in Europe and America have applied themselves to this task, and the results of Bothe in Heidelberg, Dee in Cambridge, and Jakobsen in Copenhagen are now known. All of them contradict Shankland's experimental findings. It was pointed out that the main defect in Shankland's experiment was that he used a beam of γ-rays that was not homogeneous and consequently obtained coincidences even in directions not predicted by the theory. Also the geometry of his experimental arrangement was insufficient. The new experiments favour the view that the Compton scattering holds for high-energy photons as well.

Prof. L. Meitner gave a detailed account of the work which she had carried out at Berlin on the transmutation of uranium by neutrons and the consequent formation of elements of atomic numbers greater than 92. The work was first carried out by Fermi, who claimed the formation of elements 93 and 94. This was contradicted by Gross, and a later work again confirmed Fermi's view. It was held that a new rarer group begins to be formed after the atomic number 92, and therefore it was not chemically possible to separate the various elements formed and investigate their properties separately. Prof. Meitner showed that according to her experiments the new elements formed correspond to a *new transitional group*. She was almost definite of the production of Eka Re (93) and possibly also of the elements Eka Os (94), Eka Ir (95), and Eka Pt (96) as a result of the β-ray disintegration of the uranium nucleus when bombarded by neutrons.

Next Amaldi and Wick gave an account of the work carried out at Fermi's Institute in Rome on the increased efficiency of the production of artificial radioactivity by slow neutrons. It is well-known that neutrons on account of being chargeless particles are able to penetrate much further into the nucleus than protons or α-particles, which on account of their positive charge suffer a repulsion from the nucleus. This fact was first made use of by Fermi in producing artificial radioactivity in ordinarily stable nuclei. By using a strong source of neutrons, *viz.*, a mixture of beryllium and 800 mg of radium, Fermi and his collaborators could obtain induced radioactivity in almost all the elements up to uranium. Fermi, however, discovered that the efficiency of the neutrons to produce artificial radioactivity was greatly increased if they were made to pass through blocks of paraffin. The neutrons by their encounters with hydrogen-nuclei in their passage through paraffin get very much slowed down, as the masses of the colliding particles are almost equal and it is these slow neutrons that are responsible for the increased efficiency. For such slow neutrons the encounter cross-section is enormously increased—so much so that in the case of gadolinium it is as high as 30,000 times the nuclear cross-section. With such slow neutrons a 'resonance' effect is also obtained, that is to say, within certain velocity limits about hundred times more neutrons are absorbed than on either side of the range.

According to a view expressed by Prof Bohr, a full account of which appeared in *Nature*, this resonance phenomenon of neutron capture is of great importance in the investigation of the constitution of nuclei, and Bohr in collaboration with Kalckar has obtained an expression for the capture cross-section which looks very much like the formula for *anomalous dispersion* in light. Or alternatively, this phenomenon of neutron resonance capture may be said to correspond to Auger process in X-rays.

Next Heitler gave an account of his work on the production of 'Bremsstrahlung' by high-energy electrons moving in the coulomb field of nuclei. He said that the work was undertaken in order to find out how much of the energy loss of cosmic-ray particles was due to this mechanism, *viz.*, radiative collisions. His theory predicts the energy loss to be proportional to the energy content of the original beam and also to the square of the nuclear charge. Former experiments did not conform to the theory, but the new experiments of Anderson agree very well, and now one can safely say that the theory stands the test of experiments with particles of energies up to 10^9 or a thousand million electron volts.

Dr. Oliphant from Cambridge gave an account of the work done at the Cavendish Laboratory. He said that the work done at the Cavendish Laboratory and other places showed that atoms with all mass numbers from 1 to 212 have been found to exist, the only exception being mass number 5, which has not been so far definitely proved to exist, though its occurrence as ${}^{5}_{3}\mathrm{Li}$ has been reported from America. At the Cavendish Laboratory they searched for it as ${}^{5}_{2}\mathrm{He}$ from the bombardment of ${}^{7}_{3}\mathrm{Li}$ by deuterons according to the reaction equation

$${}^{7}_{3}\mathrm{Li}+{}^{2}_{1}\mathrm{D}={}^{5}_{2}\mathrm{He}+{}^{4}_{2}\mathrm{He}$$

but were unsuccessful.

In the Cavendish Laboratory homogeneous neutrons are obtained from the bombardment of deutrons (heavy hydrogen ${}^{2}_{1}\mathrm{D}$) by deutrons. The primary beam of ${}^{2}_{1}\mathrm{D}$, accelerated through any voltage, is made to impinge on sheets of $\mathrm{Al(DO)_3}$.* It is estimated that about 10^6 bombarding particles produce one neutron: the production of neutrons also depends upon the voltage according to the law $N = N_0 e^{aV}$, up to an upper limit of 1×10^6 volts. By this method a source

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*$\mathrm{Al(DO)_3}$ is the heavy hydrogen compound corresponding to the ordinary compound $\mathrm{Al(HO)_3}$.

of neutrons which corresponds to 4·0 g beryllium-radium source is obtained. The reaction equation for neutron production may be written as

$$ {}^{2}_{1}D + {}^{2}_{1}D \longrightarrow {}^{3}_{2}He + {}^{0}_{1}n. $$

But this is not the only reaction possible; we have protons according to

$$ {}^{1}_{2}D + {}^{2}_{1}D \longrightarrow {}^{3}_{1}H + {}^{1}_{1}H. $$

The most interesting thing about the deutron-deutron reaction is that the angular distribution of both the neutrons and the protons is exactly identical. Further, this angular distribution is not isotropic and may be represented roughly as shown on the left. Such a distribution indicates certain restrictions on the spin and angular moments in the reactions given above, but their exact nature is not yet fully known.

Fig. 1

One of the most important problems in nuclear physics is the nature (not yet known) of the forces between the elementary particles. A number of workers spoke upon this subject. Some years ago Heisenberg showed that we could assume the nucleus to be made up of neutrons and protons. Ordinarily the protons repel each other, but within the nucleus repulsion changes into attraction, or, put more precisely, a stronger nuclear attractive force overcomes the ordinary coulombian repulsive force. According to present views, three kinds of forces are involved in the building up of a nucleus, (pp) force between two protons, (nn) force between two neutrons, and (pn) force between a proton and a neutron. It has been shown that these forces are very large within nuclear dimensions but fall off very rapidly with increasing distance. On account of the convenience in mathematical calculations these forces are supposed to vary as e^{-ar^2} with the distance r. The (pn) interaction force is believed to be much larger than the (pp) or (nn) interactions, which in turn are believed to be almost equal. Attempts are being made to find out the magnitude and law of these forces by determining the scattering of one swarm of particles by another. Teller reported experiments on scattering of protons by protons within the range 600—900 kV. The results of the experiments certainly show deviations from what would be expected from purely coulombian repulsive force, and can most probably be explained by assuming an attractive force expressed as a potential hole of $2 \cdot 8 \times 10^{-13}$ cm radius and 10 MV depth. Goldhaber reported experiments on (1) scattering of neutrons by protons, (2) capture of neutrons by protons leading to the formation of the deutron, and (3) decomposition of deutrons by quanta. None of these experiments at the present stage appear to be decisive; Goldhaber's experiment on the scattering of slow and fast neutrons by protons gave cross-sections, the variations of which could not be understood on the assumption that the forces between the particles were of the nature of short range forces, on which assumption it would be necessary to postulate that the deutron may have excited nuclear states.

Max Born gave an account of his new work on the modification of Maxwell's equations. These works have been published in several numbers of the *Proceedings* of the Indian Academy of Sciences of Bangalore and of the Royal Society. He remarked that it was generally agreed that Maxwell's equations in their present form could not explain atomic phenomena, the most glaring case being that of the mass of the electron which becomes infinite if the electron is considered a point-charge. In his new electrodynamics this difficulty does not arise. His equations are also in qualitative agreement with the changed form of Maxwell's equations deduced by Heisenberg, Euler, and Kockel in their work on the scattering of photons by photons.

The same problem of electrodynamics has been approached by Weisskopf from a different standpoint. The vacuum, according to Dirac's theory of negative energy states, is no longer a void, but contains electrons filling all the negative energy states; it ought to have a polarizability, which will be affected by an electromagnetic field. Weisskopf calculates the polarizability of the vacuum in the presence of an electromagnetic field by making use of the 'relativistically invariance' property of the Lagrangian function of the system. Proceeding on these lines, he obtains an expression for the scattering of light by light which is exactly similar to that obtained by Heisenberg and Euler who had to make very lengthy and tedious calculations and made use of not very convincing assumptions to get rid of the infinities that of necessity enter into the calculations.

The greatest amount of interest was excited by Heisenberg's description of his new theory of 'shower' production, and the way he has tried to connect this mysterious phenomenon with the Fermi theory of β-ray disintegration. It was in 1932 that Prof. Bohr in a ecture to the Faraday Society pointed out for the first time that the phenomenon of β-ray disintegration formed a challenge to all existing systems of dynamics, for the simple reason that the β-rays emitted by the nucleus do not possess definite energies like α-rays, but form a continuous energy spectrum with a sharp upper energy limit, the end products being always the same and the life period of the disintegrating atoms quite definite. This phenomenon, as already pointed out, stands in sharp contrast to that of α-rays, where the life of the disintegrating atom depends upon the energy of the emitted α-particle in a way which is described by the Geiger-Nuttal relationship. The mechanical problem of the β-ray disintegration is therefore quite different, and any theory must explain the behaviour of β-particles within the nuclei and the continuous energy spectrum of β-rays.

Now an electron (β-particle) in the free state has a spin equal to $\frac{1}{2}$ and a magnetic moment equal to that of a Bohr magneton, but the magnetic moment of the nucleus is found to be a thousand times smaller than that of a Bohr magneton, thus we see that we cannot assume that a β-particle as such exists in the nucleus. Further, if we assume the presence of a β-particle as such in the nucleus, then its kinetic energy comes out to be much larger than the binding energy of the nucleus so that it could not remain inside a nucleus. Besides these, considerations of spin of the various nuclei and the statistics (Fermi-Dirac or Bose-Einstein) obeyed by them leads to the same conclusion that we cannot postulate the existence of electrons within the nucleus.

The situation became somewhat clear with the discovery of 'neutron' by Chadwick in 1932, for now the neutron and the proton could be taken as the building stones of the nuclei. Heisenberg later on showed that we could suppose a nucleus to consist of Z protons and (A-Z) neutrons. β-ray emission could now be explained by postulating that a neutron within the nucleus gets converted into a proton by giving out a β-particle, this process being analogous to the emission of light quanta by an excited H-atom. But if the process was to be mechanically definite, the electrons must have a definite energy, which, as remarked above, is not found to be the case. So here then the physicists were faced with a dilemma; they had to make a choice between the law of conservation of energy on the one hand and the definite quantum states of the nucleus on the other; it was a choice which would have, either way, meant the undoing of all that had been achieved so far. Here Pauli came to the rescue by postulating that along with the electron another chargeless particle, which was baptised 'neutrino', is also emitted. This particle has a very small mass and shares with the β-particle the energy difference between the disintegrating atom A and the final atom B. The 'neutrino' hypothesis enables us to get over the spin difficulty if we ascribe to it the spin equal to $\frac{1}{2}$. The neutron, proton, and the electron have been shown to possess a spin equal to $\frac{1}{2}$ each. Now when a neutron changes into a proton with the emission of β-particle, we have to explain the conservation of spin. With the postulate of the neutrino β-disintegration process may be described as follows:

$${}_0^1\mathrm{n} = {}_1^1\mathrm{p} + \ -1{}_1^0\mathrm{e} + \nu\,.$$

$$\text{spin} \qquad \tfrac{1}{2} = \tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2}$$

$$\text{charge} \qquad 0 = 1 + (-1) + 0,\ \nu = \text{neutrino.}$$

It may be mentioned here that no experimental trace of this 'neutrino' has yet been found. Neither is there any likelihood of its being experimentally detected, because the neutrino has no charge and practically no mass. In spite of this fact, there appeared to be a general agreement among the physicists assembled at Copenhagen that the neutrino hypothesis of β-decay describes the phenomenon correctly.*

This hypothesis was given a mathematical precision by Fermi, who postulated that the *interaction energy* involved during the conversion of a neutron into proton with the emission of a β-particle and a neutrino may be put equal to a new universal constant g multiplied by a function of the Ψ-functions of the particles taking part in the reaction. In quite a phenomenological way analogous to Dirac's radiation theory of the interaction of atoms and the radiation field, he was able to give a general explanation of the β-decay, but quite recently important modifications in the theory have been introduced by Uhlenbeck and Konopuiski.

A further tinge of reality to the neutrino has been given by Jordan, who gave an account of the theory in which a photon is considered as consisting of a pair of a 'neutrino' and an "anti-neutrino". (The terms 'neutrino' and 'anti-neutrino' correspond to Dirac's electrons

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*Ed. note: The existence of neutrino has since been established experimentally. It is known to exist in two forms; the neutrino, which is emitted with positrons, and the anti-neutrino, which is emitted with negative electrons (e.g. neutron decay). Both forms also appear in the decay of muons.

and holes or positrons.) Jordan showed that one can give a consistent theory where all the reactions of light with atoms can be formally deduced by a pure theory of "neutrino-pairs".

These works, therefore, amount to an acceptance of the situation and simply postulate the mechanical act of production of an electron by the nucleus. In the case of 'shower' production, it is found that a cosmic-ray particle which may be an electron or a positron on meeting a nucleus, suddenly gives rise to a large number of pairs of positrons and electrons $(\beta^+\beta^-)$ whose total energy may sometimes be as large as 10^{12} or million million electron-volts. As this energy is much larger than the mass of the heaviest nucleus known, it becomes evident that the energy of the shower must have come from the original particle. The point is, therefore, how the energy of the original particle is converted by the action of the nucleus into pairs forming the showers ?

Dirac's theory of the electron gives a possibility of pair-production, i.e. the conversion of energy quanta into β^- and β^+ in the presence of a nuclear field, but according to this theory the probability for the n^{th} order process, i.e. the production of n pairs involves the factor $\left(\frac{2\pi e^2}{ch}\right)^n$ which evidently goes on decreasing with increasing n. Note that $\frac{2\pi e^2}{ch}$ is the Sommerfeld fine-structure constant, in other words; it means that the probability of occurrence of higher order processes is extremely small; so that this theory completely fails to give an account of the phenomenon of production of big showers, involving billions of electron-volts.

But on the other hand, if we write the energy function, making use of Fermi interaction field, then the expression involves a factor f which is equal to g/hc. If now a usual perturbation theory be applied, i.e. the expression be developed in ascending powers of the interaction term, powers of the factor f will be involved. This factor is of dimension cm² and so must be divided by t^2. So that now in the expression for energy various higher order terms which give the probability for the corresponding order processes involve powers of factor (f/λ^2). Now as we go to higher-energy particles, λ decreases till we come to a value when f/λ^2 is of the order unity. When this is the case, the probability for the higher order processes is just the same as for low order processes, *viz.*, unity and hence the phenomenon of showers becomes possible.

The phenomenon of the production of electrons and positrons on this theory may be pictured as follows:

	Cross-section for each process
proton ——> neutron (n) + positron (β^+) + neutrino (ν)	$\left(\frac{Ze^2}{hc}\right)^2 f^2/\lambda^2$
——> proton + β^- + β^+ + 2ν	$\left(\frac{Ze^6}{hc}\right)^2 f^4/\lambda^6$
——> proton + $n\beta^- n\beta + 2n\nu$	$\left(\frac{Ze^2}{hc}\right)^2 \frac{f^{4n}}{\lambda^{8n-2}}$.

In the case when (f/λ^2) is of the order unity. we see that the cross-section for all the processes is the same. and hence we can get the 'showers'.

The academic discussions of the conference came to an end with the discourse of Prof. Bohr on 'the theory of measurements of the field strengths and charge density'. Now, according to quantum electrodynamics as put forward by Pauli and Heisenberg. the electric and the magnetic fields form two conjugate variables which means that we cannot measure simultaneously both the electric and magnetic fields exactly in the same way. as we cannot measure both the position and momenta co-ordinates of a particle. Pauli and Heisenberg quantum electrodynamics requires certain exactness with respect to time in the measurements of fields and charge. In a previous paper Bohr with the collaboration of Rosenfeld had shown that such an exactness as demanded by the theory was quite consistent with experimental measurements only if we took test bodies large enough and considered a continuous distribution of charge. But then Landau and Peierls tried to show that on relativistic grounds such measurements could not be possible. Bohr and Rosenfeld showed that we could measure either the electric or the magnetic field strength quite definitely according to the requirements of the Pauli-Heisenberg theory. It was further shown that the argument in favour of the possibility of measurements of the fields or the charge-density remains unaffected even when the creation of pairs is taken into account.*

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*The line of argument has been purposely avoided as it is too complicated to be put down here.

1.3.3 URANIUM FISSION*

THE total number of elements in this universe is known to be ninety-two. It has been an old question, why no elements beyond ninety-two have been found in Nature? Has the number ninety-two any magical significance as was ascribed to the number seven by the mystery-loving ancients, without any reason whatsoever? Fermi, an Italian physicist, reflected about these questions and thought of outwitting Nature by smuggling a neutron into the nucleus of Uranium, thus forming a nucleus of weight 239 and looking for the consequences. It was a perfectly feasible procedure as the neutron, having no charge, has no shyness for the nucleus. Fermi found that several new products were formed all emitting β-rays; these were separated by chemical methods, and were found to possess properties which could, with a certain amount of plausibility, be ascribed to elements 93 (ekarhenium), 94, 95, 96 (ekaplatinum). It was argued that nucleus of weight 239 was short-lived, emitted β-ray and became element ninety-three, which in turn emitted another β-ray, and became 94, which is likewise unstable......and the chain was continued till ninety-six (ekaplatinum) was reached.

$$\begin{array}{rl} {}_{92}\mathrm{Ur}^{238}+\mathrm{n}= & {}_{92}\mathrm{Ur}^{239} \\ & \downarrow \\ & {}_{93}\mathrm{Eka\ Re}^{239} \\ & \downarrow \\ & {}_{94}\mathrm{Eka\ Os}^{239} \\ & \downarrow \\ & {}_{94}\mathrm{Eka\ Ir}^{239} \\ & \downarrow \\ & {}_{95}\mathrm{Eka\ Pt}^{239} \end{array}$$

But the very success of the experiments excited a certain amount of distrust. Other workers notably Hahn of Berlin, a celebrated worker in radioactivity, stepped in and found that the number of new products was much larger, in fact Hahn identified nine distinct β-ray emitting

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*Based on a lecture delivered by the author on March 26, 1941, before the Indian Physical Society—Sci & Cult **6**, 694, 1941.

products. One of these products was investigated by Curie and Savitch for its chemical properties, and though it was found to resemble to some extent the hypothetical element 89 in its properties, the similarity was found to be more pronounced with lighter element lanthanum, No. 57. Following this work Hahn and his co-workers showed that some of the products appeared to have the chemical properties of radium (88). But how could radium be produced at all in this class of reaction? Radium is element No. 88, and it could be produced only if the nucleus 92, or any hypothetical higher element produced on neutron bombardment, emitted alpha-particles and proton simultaneously or successively. This was not considered probable, at least no alpha particle or proton could be detected, even after prolonged work. So Hahn and Strassmann began to doubt whether the radium-like products were at all radium: might not they be lower homologue of radium, *e.g.*, the common element barium, No. 56, which is very similar to radium in all its properties? The thought was given a trial and after a series of experiments requiring chemists' skill of the highest order, it was found that some of the products obtained by bombarding uranium with neutrons were undoubtedly barium nuclei.

This was a startling revelation. The element uranium is Number 92, while barium which is formed from it is Number 56. How can we get barium out of uranium at all? The explanation was almost forced upon the investigators that as a result of the impact of the neutron, the nucleus breaks up into two halves, one having the atomic number 56 and therefore the other probably having the atomic number 36 or 37. It may be emphasized, as will be elucidated presently, that the neutron which starts the process, need not necessarily be a 'high energy' one. Even small energy neutrons are capable of starting the reaction, which is therefore to some extent conditioned by something inherent in the properties of the uranium nucleus itself, or as was subsequently shown, of some of the other heaviest nuclei (*e.g.*, thorium and protactinium). Nuclei lighter than these have not yet shown the effect. We, therefore, conclude that the heaviest nuclei, particularly the uranium nucleus, possess to some extent latent instability in their structure, can divide itself on the slightest provocation, like some biological cells, into two distinct nuclei; the A-product having an atomic number varying from 50 to 60, the other, the B-product having an atomic number which varies from 35 to 42.

A diagrammatic sketch of the process of uranium fission is shown in figure 1. The uranium nucleus is shown, not as a spherical body,

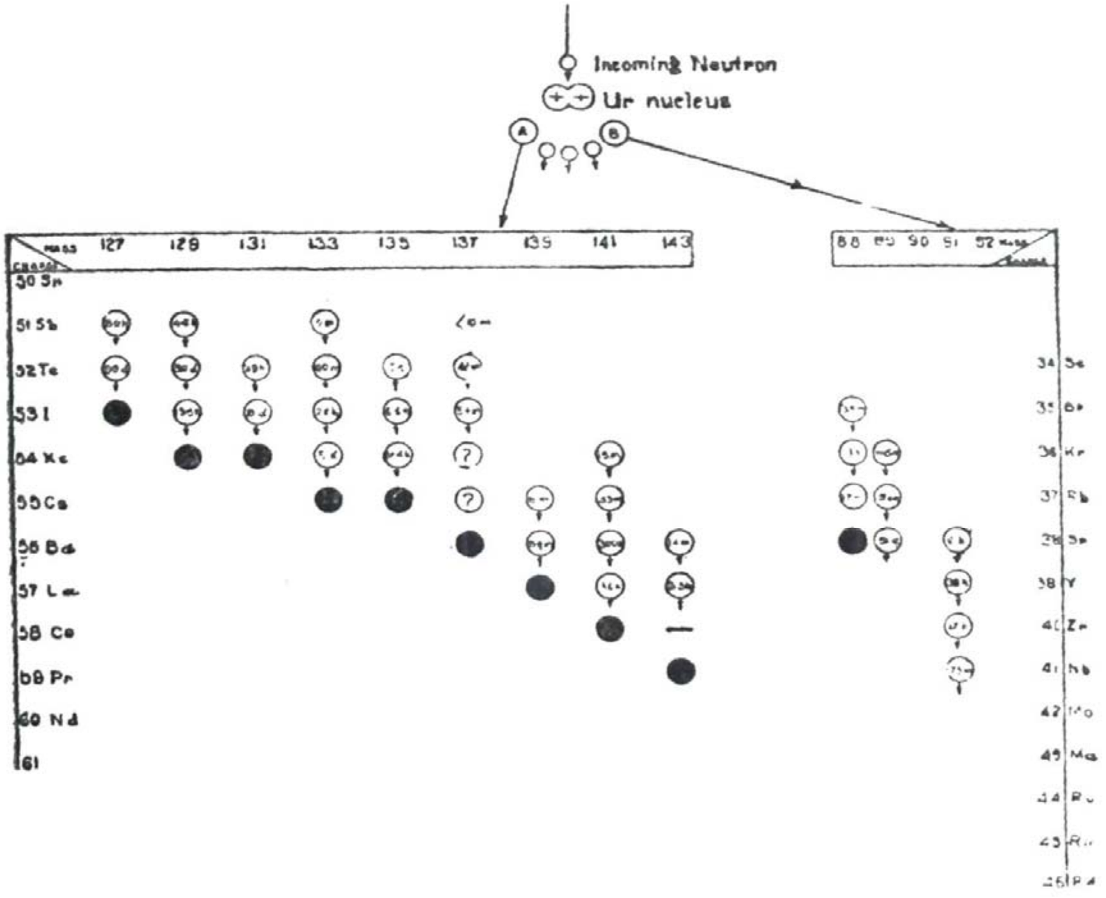

Fig. 1

but as a dumbell-shaped one. The total charge '92' is distributed amongst the two spheres constituting the dumbbell. In fact, Bohr compares the nucleus to a drop of liquid which, when highly charged, gets deformed, is set into violent vibration, and ultimately breaks up into two fragments. In a liquid drop, the struggle is between the surface forces of attraction and the repulsive forces due to the electrical charge. In the nucleus, the struggle is between the forces which keep the nuclear particles together, and the electrical forces of repulsion. The nucleus is *naturally* in a state of agitation owing to the large forces of repulsion and as a neutron approaches it exerts a kind of trigger action which make the two parts fly as under. As predicted by Bohr, it is the rare isotope U^{235} occurring in common uranium of atomic weight 238 in the proportion of 1 : 137, to which most of the fission activity is to be ascribed. It has been also found that at the time of rupture, a few neutrons (variously estimated at 2 to 3 per fission) are also emitted.

Fission Fragments and Chain of β-ray Products

The two initial fractions A and B have charges varying from 50 to 56, and 42 to 36 respectively. The total mass 235 is lessened by the number of neutrons emitted: hence the mass of the remainder, say, 230, is distributed between the two fragments. We have as yet no precise knowledge of the exact masses and charges of the fission-products at the moment when the fission takes place but let us denote them by M_1 and Z_1, M_2 and Z_2. From examination of fission products, it has been found that M_1 may vary from 127 to 143, and M_2 from 88 to 100 (this limit is indefinite). But a nucleus of this type is unknown in Nature. It has too small a charge for the given mass to be stable. For example, as far as we can see at the present times, one of the direct A-products has a charge of 51, and mass of 133. Now in Nature, we have the following isotopes of Number 51, antimony.

$_{51}$Sb	121	123
	56	44

(The numbers on the upper line denote the weight, and those on the lower line the percentage of occurrence of the corresponding mass in a sample of the atom.)

The A-product, $_{51}$Sb^{133}, is too heavy to be stable. It emits an electron (β-particle) and becomes $_{51}$Te^{133}: this also does not occur amongst the known stable isotopes of Te, which are:

$_{52}$Te	120	122	123	124	125	126	128	130
	·1	2·9	1·6	4·5	6	19	54	33

The $_{52}$ Te^{133}, therefore, emits a β-ray, and becomes I^{133} . . . and the chain of β-emitting products goes on till we land at the stable isotope $_{55}$Cs^{133}. Altogether four successive β-emissions have taken place in this chain. The instability due to the excess of mass in the fragments is compensated by increase in charge due to successive emission of β-rays.

So far, as many as nine sets of A-products having masses from 127 to 143 have been discovered, as shown in Fig. 1, and the successive chain of decay products have been traced satisfactorily. Curiously enough, they all appear to have odd mass numbers. Probably there are also even-mass numbered products amongst the A-fragments, but these appear to be stable and therefore appear so far to have escaped detection. The B-products have not been so far much investigated; the chains which have been definitely traced are shown in Fig. 1, but Japanese and American workers have reported Pd, Ag, and others to be present among B-products.

Energetics of Uranium Fission

The energetics of uranium fission have proved to be quite as interesting as the process itself, and opens up an alluring field of speculation on energy production.

It was surmised from some theoretical considerations that the fission products should separate from each other with energies amounting to as much as 180 million electron volts on the average. The conclusion follows from certain empirical formulae enunciated by Bethe and Weisäcker which lays down the conditions of the stability of nuclei having the mass number M and the charge number Z. According to this speculation, the uranium nucleus is found to be somewhat heavier than the products of fission taken together. The excess mass should therefore, according to Einstein's principle of equivalence of mass and energy, appear as the kinetic energy of separation of the fission products. The paths of the fission fragments have been photographed in a specially designed Wilson Chamber and from the range and ionisation, it is possible to calculate the energy of each fragment. It is found that on the average, the energy with which the particles fly apart amounts to 180 MeV. thus confirming the theoretical prediction. This is an abnormally high figure and the discovery opens up a new vision of energy-production, which is extremely exciting.

Let us therefore compare the possibilities of this process with the usual thermal methods used in industry. All these methods employ in one form or other the burning or to use scientific language, the combustion of coal. The energetics are:

$$C+O_2=CO_2+98 \text{ kcal.}$$

i.e. 12 gm of coal, on complete combustion gives us 98 kcal, i.e. the heat energy available is 8 kcal per gm of coal consumed.

In the present reaction, we have

$$U+n=A+B+180 \text{ MeV.}$$

When we convert the relation to energy-production per gm of uranium fissioned we obtain:

238 gms of Ur gives us

$$\frac{180 \times 10 \times 4{\cdot}8 \times 10^{-10} \times 6 \times 10^{23}}{300 \times 4{\cdot}2 \times 10^{7}} = 4{\cdot}1 \times 10^{9} \text{ kcal.}$$

This gives us an energy-production of nearly $1{\cdot}7 \times 10^7$ Kcal per gm of uranium consumed, i.e. *by fissioning completely one gm of uranium, we obtain as much energy as is obtained by burning about 2 tons of coal* (2×10^6 *gm*).

At the present time, every civilized country has to husband her power-resources and organise production and supply of energy for the whole country. According to modern standards, a civilized man should have at his disposal 1800 units of energy per year: barely 4 per cent of the amount is available from human labour. The rest must be produced from coal, water power, or petrol. Thus England produced and consumed in 1939 nearly 25,000 million units of electrical energy and this was obtained by burning 40 million tons of coal (efficiency of conversion of heat to mechanical work is taken to be 30 per cent.). In addition to this, 60 to 80 million tons of coal were directly used in steam engines of all descriptions for producing energy. Let us ponder over the huge organisation and construction work required for generation and distribution of this huge amount of energy. First of all, nearly 100 million tons of coal have to be mined each year in Great Britain for power generation. This requires a capital investment of hundreds of millions of sterling, and employment of millions of labourers for working the mines. The coal has to be burned in 60 superstations located in different parts of the United Kingdom, and distributed by thousands of miles of wire to substations in the principal cities; from these substations, they are distributed by licensed undertakers to the individual consumers in the city. The total capital involved in electrical undertakings is nearly 400 to 500 million pounds, and the number of men employed in various capacities amount to nearly a million.

Now let us find out the amount of uranium whose fission will give us an equal amount of electrical energy. If we take a cube of uranium oxide (4·2 tons) the form in which uranium usually occurs, each side being one metre, then provided the whole amount of uranium contained in it can be made to undergo fission, the amount of heat produced will amount to nearly $5{\cdot}8 \times 10^{13}$ kcal. If we succeed in converting 40 per cent of this heat to useful work we shall get nearly 25,000 million units of electrical energy, i.e. a cube of Ur_3O_8 one meter on each side (weight 4·2 tons) will give us as much energy as 40 million tons of coal.

The calculation raises a lot of speculations but the main question is whether the scheme can ever be a practical one. The first difficulty is the assumed cent per cent fission of uranium. Under the present experimental conditions, the efficiency of fission is extremely slight. It is estimated that hardly one in 10^{24} neutrons hurled at uranium succeed in causing fission in Ur^{238}, and probably one in 10^{21} neutrons in Ur^{235}. Most of the neutrons, therefore, pass out innocently and are lost to us, without causing any damage to the uranium mineral. But cannot a process be discovered analogous to chain reactions in chemistry ? Let us contrast this process with the case of combustion of coal. Here by raising a small amount to the proper temperature, we ignite the coal, then combustion of the remaining part goes on automatically, provided the supply of oxygen is assured. The heat liberated in the initial combustion, is sufficient to raise the next lying parts to a sufficient temperature, ensuring the reaction to proceed on with sufficient velocity. Can we have a somewhat similar process in uranium fission ? Suppose we have a cube of uranium oxide, and in the centre, we put a constant source of neutrons (say a Ra-Be source). Under the present conditions of working most of the neutrons will pass out without causing any damage. They must, therefore, be slowed down. This can be easily done by mixing up paraffin intimately with uranium or taking uranium hydride or deuteride: but slow neutrons appear to be able to react only on Ur^{235} which occurs in ordinary Ur in the proportion of 1 in 137. However, with the discovery of the new method of separation of isotopes by the process of thermo-diffusion, complete isolation of Ur^{235} appears to be within the range of practical possibility. In fact, a Swedish engineer was reported to be actively engaged in carrying out this separation. But even when we experiment with a paraffined block of Ur^{235}, or a hydride or deuteride of U^{235}, with a neutron gun inside it, not more than a small number of neutrons can actually be effective in producing 'Fission'. But in each process of fission 2 to 3 fresh neutrons are produced, and these may cause further fission. We have, therefore, the possibility of having a chain reaction, but the practicability of the idea can be only gauged when experiments have been actually carried out. Experiments of this kind are being carried out in Germany, but no knowledge of progress on these lines is available.

The above process, if it can ever be perfected, can give us an enormous amount of heat. This must not be allowed to occur with explosive violence but should be sufficiently slowed down. After these problems are solved and we get a steady supply of heat, we can utilize it to feed our machinery for the conversion of heat to electrical energy.[1] So if the efficiency of fission process can be improved, coal mining would be rendered obsolete, but the present system of power engineering would, as far as we can see, remain unaltered.

It is also quite possible that a process may be discovered which would render the reactions to proceed with explosive violence. At the present time, nearly several tons of explosives are required to sink a Super-Dreadnought. About 10 million kilocalories, or 10^5 units of energy (Kw) have to be generated within one hundredth of a second. For getting this energy, we have to detonate a ton of trinitrotoluene, or cordite within a fraction of a second. But this amount of energy is available from the complete fission of only a gm of uranium. But it is still a far cry whether the whole amount can be liberated within a fraction of a second. Still the idea that a tablet of Ur^{235}, not more than a homoeopathic globule in size, may blow off a mighty Super-Dreadnought—a feat which can at the present time be performed only by a torpedo carrying several tons of explosives in its head—cannot but be an exciting one.[2]

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[1] Controlled chain reaction was first achieved by Enrico Fermi at Chicago on December 2, 1942. Ed.

[2] The first atomic-fission bomb was exploded on July 15,1945 at a test site at Alamogordo Air Base, New Mexico. It was an implosion type bomb using plutonium. Ed.

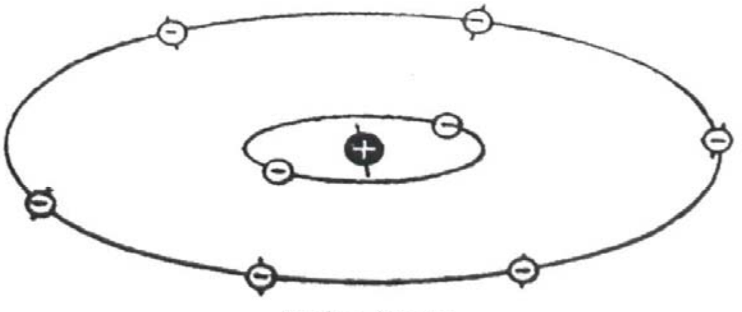
1.3.4 THE STORY OF THE ATOMIC BOMB*

In relating the story of the 'Atomic Bomb' one has to narrate almost the whole story of the progress of physics within the last fifty years.

We may make a convenient start with a mathematical theorem of revolutionary nature given by Einstein in 1905. The theorem stated the equivalence of mass with energy. It followed from the Principle of Relativity and was regarded with scepticism for some time, till the cumulative experience of laboratory work compelled its acceptance.

In mathematical language, the relation is written as $E=mc^2$ where c is the velocity of light, E is energy, m is mass. Let us explain this for the lay reader. We all know that mass which is measured in grammes and energy may be expressed in ergs, calories or kilocalories, which are all related. According to Einstein's formula, one gm of matter is equivalent to 9×10^{20} erg, for the velocity of light has the tremendously large value of 3×10^{10} cm/sec. This energy is equal to 2×10^{13} calories, or $2{\cdot}1\times10^{10}$ kilocalories and is obtained by burning 2,500 tons of coal. Just fancy somebody claiming that a small cube of coal each side measuring $\frac{1}{2}$ of an inch contains as much energy as can be obtained by burning 5 train loads of coal. The deduction looked quite fantastic, but the logic of Einstein's mathematics was inexorable and scientists looked for phenomena where the relation has its application.

The first of these came from the precise measurement of the weight of atoms. At this time it gradually emerged that the atom consisted of two essentially different parts: the nucleus which consisted of a core containing most of the mass and carrying a positive charge. This is surrounded by electrons arranged in orbits (*vide* fig.). For our theme, the electrons are of no use, and we fix our attention on the nucleus only.



Bohr Atom

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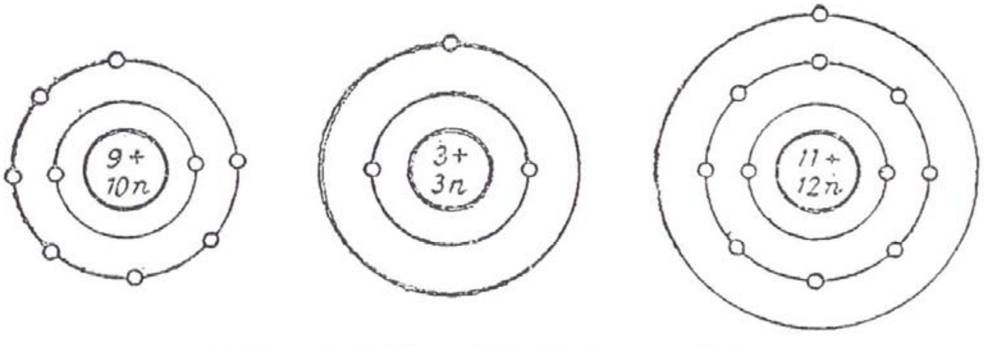
*with B. D. Nag Chaudhuri—Sci & Cult **11**, 111, 1945

Let us illustrate our point by taking the case of the helium nucleus. The mass and charge of the nuclei are too small to be conveniently measured in the usual units, so for our purpose the proton mass and the proton charge will be used as units. The helium nucleus has got the mass 4 and charge 2. It is now proved that the nucleus itself is composed of more fundamental units. These fundamental units are now known to be the proton which is the nucleus of hydrogen and is easily obtained, and the neutron, which is just a little heavier than the proton. The latter is uncharged and is more difficult to obtain.[1] The helium nucleus is composed of 2 protons and 2 neutrons. One should expect that the mass of the helium nucleus should be equal to the sum of the masses of its constituents, but accurate measurements show that it is somewhat less in weight: in exact measure by ·027 mass-units. Where has this mass disappeared? It was suggested that when 2 protons and 2 neutrons combine to form the helium nucleus, a large amount of energy is set free just as when carbon burns in oxygen and carbon dioxide gas is formed, a certain amount of energy is set free. But there is a tremendous difference in degree. One gram of carbon gives us 8 kilocalories on complete combustion to CO_2 but when 2 gm of proton and 2 gm of neutron combine to form 4 gm of helium nucleus, the amount of energy evolved is enormous and can be easily calculated from an application of Einstein's principle. It is 640 million kilocalories or 160 million kilocalories per gm. Mass for mass, the energy evolved is nearly 20 million times larger than that obtained by the burning of coal which is the basis of most of our power technique. This feature of large



Model of Nuclei formed by Neutrons and Protons
[*Left:* Fluorine^{19}, *Centre:* Lithium^{6}, *Right:* Sodium^{23}]

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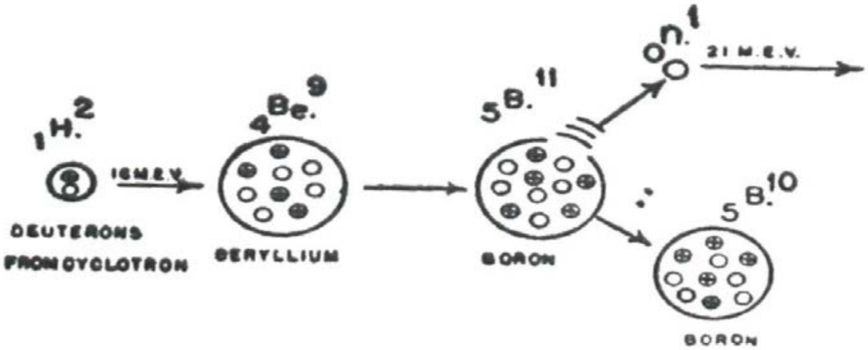
[1] The Neutron was discovered only in 1932. A convenient source is a Beryllium plate over which some radium has been placed.

energy formation is shown by almost all the nuclei of atoms, which have all less mass than these constituent neutrons and protons.

Artificial Nuclear Reactions

Though we are talking of the formation of atomic nuclei from its elementary constituents, the proton and the neutron, nobody was able to effect an artificial nuclear reaction until 1919. It was supposed in a rather vague way that the elementary particles come together in the interior of stars and thus contribute to the maintenance of the fire of stars for billions of years. The first artificial nuclear reaction was performed in the laboratory by Lord Rutherford in 1919 when he bombarded nitrogen by a beam of alpha-particles and obtained an isotope of oxygen (17) and a proton. Lord Rutherford verified in this reaction that the energy relations are satisfied by making use of Einstein's principle of equivalence of mass and energy.



Diagrammatic sketch of Nuclear Reaction
$_4Be^9 + {}_1H^2 \rightarrow {}_5B^{11} + n^1_0$

Nuclear reactions are not very easy to perform because if we want to bring two nuclei together, they must be given very high energies. Also, since the size of the nucleus is about 10^5 times smaller than that of the atom, most of the particles fail to hit the nuclei. Within the last fifteen years machines for producing large numbers of high energy particles have been invented and used to produce hundreds of nuclear reactions and new types of nuclei. But none of these reactions are suitable for tapping the nuclear energy for practical purposes.

Uranium Fission

The particular series of works which yielded a possible method for the tapping of nuclear energy was started by Fermi, the most celebrated Italian physicist of modern times. In 1938, Fermi was awarded the Nobel Prize for his discoveries, went to Stockholm to receive it, but instead of returning to Italy, ran away to the USA where he was given an asylum in the Columbia University, New York. Before Fermi, only beams of proton and alpha-particles (helium nucleus) had been used for nuclear bombardment, but Fermi showed that the 'neutron' was a far better agent for this purpose, and he was able to perform hundreds of nuclear reactions with it, for which the Nobel award was made to him. Then his thoughts ran in a new direction. He tried to use the new technique for the manufacture of entirely new elements.

The total number of elements so far known is 92, uranium being number 92nd. It has always been a puzzle why elements beyond number 92 are not found in nature. Has the number 92 any magical significance as was ascribed to the number seven by the mystery loving ancients? Fermi thought of submitting this query to an experimental test by smuggling a neutron into the nucleus of uranium. He found several new products, which could be separated by chemical methods from parent uranium. He thought these elements were elements 93 to 96—*transuranic* elements. These elements are not known in nature but from Mendeleev's periodic classification, we can make plausible prediction about their chemical properties. Fermi thought that the nucleus 239 formed by the entry of a neutron into the U-nucleus was shortlived, emitted an electron, had its charge increased by one and became 93. This process goes on till we obtain element 96 which was supposed to have properties similar to platinum and to which the name ekaplatinum had been given by Mendeleev.

But these deductions excited a certain amount of distrust. There was no doubt that a large number of new products was formed, but were they really transuranic elements? In fact there were too many of them. At this stage the investigation was taken up by Hahn and Meitner in the Kaiser Wilhelm Institute in Berlin-Dahlem and I. Curie and Savitch in the Radium Institute in Paris. They found that the number of new products was much larger. In fact, Hahn and Meitner counted no less than 9. Curie and Savitch found a new product which they said was similar to the radioactive element actinum No. 89 but was much closer to the known element No. 57 called lanthalum. Had Curie[1] and Savitch followed this matter further they would have discovered the phenomenon, but somehow they stopped here. In the

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[1] Two contemporary physicists of reputation ascribe the discovery of uranium fission to I. Curie. This is a mistake. They just missed it.

meantime Hahn[2] at Berlin had been hard at work with his pupil Strassemann and proved definitely that one of the products which was supposed to be an isotope of radium was not radium at all, but barium which is element No. 56. This confusion is to be ascribed to the fact that radium and barium are almost identical in their chemical properties and none but a very experienced chemist of the type of Dr Hahn could have succeeded in identifying definitely the very minute amount of barium produced in the experiment and recognising it clearly as distinct from radium. This discovery gave them the clue to the mystery and led to very startling results. The element uranium is No. 92 and the element barium which is formed from it after it has been bombarded with neutron is number 56. How can it be possible for barium to be produced out of uranium at all? The explanation was almost forced on the investigators that as a result of the impact of the neutron, the nucleus breaks up into two halves, one having the atomic number 56 and the other having the atomic number 36 or 37. Further work by Hahn and Strassemann and others showed that U can break up into two fragments in many other ways. The fission results are illustrated in the figure reproduced from an article in SCIENCE AND CULTURE published four years earlier (see fig. 1 in page no. 364).

Mechanism of Uranium Fission

It was very soon found that this fission of uranium nucleus is not due to the force of impact of the neutron, for even neutrons slowed down by paraffin to an energy of a few volts show this effect. Further, no other element excepting uranium and its next heaviest neighbours protoactinium (No. 91) and thorium (No. 90) show this effect. There is, therefore, some latent instability in the nucleus of uranium itself; the introduction of a neutron acts as a trigger like the lighting of a

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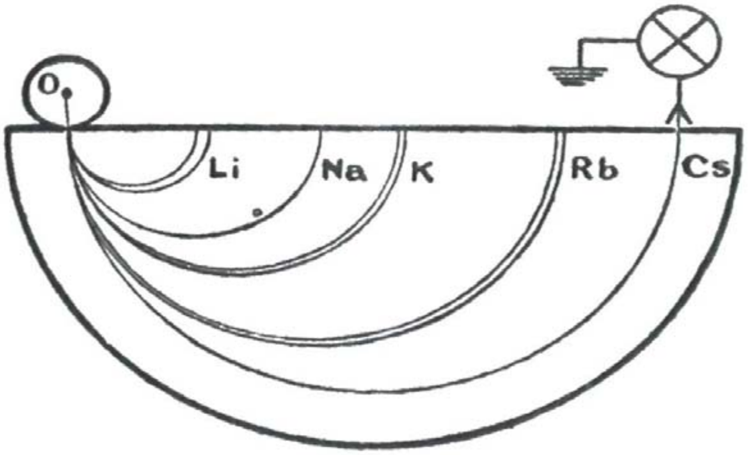
[2] Otto Hahn, the discoverer of uranium fission, which ultimately led to the Atomic Bomb, was born on 8 March, 1879. He started life as a young organic chemist in an industrial concern, but gradually transformed himself into a radioactive chemist. He had worked with the English chemists, Ramsay, Soddy and Rutherford and when elected to the Membership of the Prussian Academy of Sciences, he spoke of his good luck in being able to work with such great names in the chemistry of radioactive substances. But Planck, President of the Academy, replied, "*In science we very often find work without luck, but never luck without work.*" The great work on uranium fission which Hahn brought to light from a series of obscure and puzzling observations could only be done by one with the training of a great analytical chemist, and was the result of a solid amount of work. From 1912, he was Director of the radioactive section of the Kaiser Wilhelm Institute at Berlin-Dahlem, and was the discoverer of Mesothorium and Radiothorium.

match box in a powder magazine. This point of view is further corroborated by a comparison of the mass of U to those of the fragments in which it is likely to break. The U-nucleus is somewhat heavier and is thus endothermic like certain explosives. Bohr compares the nucleus of uranium to a drop of liquid which, when a high charge is given to it, is somewhat deformed from its spherical shape, but is kept together by surface forces and can be ultimately broken up if the deformation is large. When the neutron enters the U-nucleus the vibrations set up in the body of the nucleus are so violent that it breaks up into two, may be in more fragments. Bohr further discovered one very important point. Uranium as found in Nature consists of two isotopes, U^{235} and U^{235}. This last is also known as actino-uranium and occurs in very small quantity, only one part in 140. Bohr showed that it is really this rarer variety of uranium, U^{235}, which is the active agent. In fact mass for mass its activity is nearly 1000 times more than that of its bigger brother U^{238}.

Energetics of fission—It can be shown from mass relations that when the two fragments of uranium fly away from each other, they do so with tremendous energy. In fact the energy carried by these particles has been experimentally measured and found to reach the high value of 200 million electron volts. Converted into familiar energy units, it means that when 235 gm of uranium is broken up in this fashion the energy produced is $4{\cdot}9\times 10^9$ kilocalories, that is to say, when one gm of uranium is completely fissioned it will give us $1{\cdot}9\times 10^7$ kilocalories. The process really gives thousand times less energy than that from total conversion of mass, but still it is million times more energy yielding, mass for mass, than a chemical reaction. This energy is obtained by burning 2 tons or 2 million grammes of coal. This shows that the fission process, if it could be actually realized in practice, would usher a new age in the science of energetics, in power technology and in explosives.

What stands in the way of these ideas being put to practice? The real difficulty is that the efficiency factor is extremely low. If we shoot a billion neutrons into a mass of uranium, hardly one will hit the nucleus. So what we gain in the individual process is lost in the inefficiency of the process. Can we improve the efficiency?

The first step, it is obvious, is to get a good supply of U^{235}, for if we can use this exclusively we could increase the efficiency factor by about 200 times. But this is not an easy task. U^{235} has the same chemical properties as U^{238} and cannot be separated from its isotope by chemical methods. We must use physical methods of which several exist now. In the preparation of the atomic bomb a large quantity of U^{235} must have been produced as a first step, although it is not clear which method has been used. Isotope separation is really a heart-breaking job. Aston started separating the isotopes of neon in 1906, and worked for 10 years without any result. One of the methods that has been successfully used is the mass-spectrograph. The particles are given a certain charge and are deflected in the magnetic field. Particles of different mass will then separate and collect at different places.



Separation of masses by means of Mass-Spectroscope

[The two isotopes of lithium of weights 6 and 7 are separated in the magnetic field as indicated by the two semicircular lines close together marked Li. The semicircle of smaller diameter represents the path of lithium 6, the larger circle the isotope 7.]

Just before the outbreak of the war, another German physicist Clusius, developed a very powerful method of separation of isotopes which can be used for gases and substances which can be used in the form of solutions. It is known as the thermal diffusion method. By this method, considerable quantities of Cl^{35} have been separated from Cl^{37} in a few hours, a task which the earlier workers could not accomplish in 10 years. The method requires long columns of glass, plenty of refrigerating material, etc. Large quantities of U^{235} must have been produced by one or both of these methods.

Copious Supply of Neutrons

The next step is the production of sufficient quantity of neutrons for starting U-fission. In the laboratories the neutron is produced either by the cyclotron or high voltage apparatus or by the contact of radium with beryllium or other light elements.

Such methods cannot evidently be used in the atomic bomb. One cannot attach a high voltage apparatus or a cyclotron to a bomb and radium would be too expensive even for the dollar-land. In the bomb, use is probably made of the deuteron-deuteron reaction. Let us see what it is.

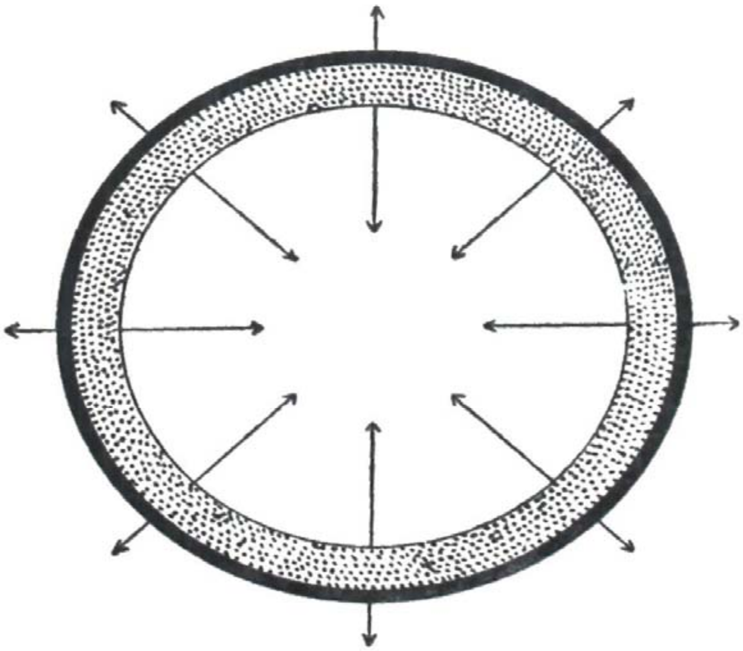
'Deuteron' or heavy hydrogen is the isotope of hydrogen; while ordinary hydrogen has the weight one, the deuteron has the weight two; its nucleus is twice as heavy as the proton. It occurs in the proportion of 1 : 8000 in all sources of hydrogen and its supply is apparently unlimited. Even 15 years ago its existence was unsuspected, when Urey, an American physicist, was led to formulate its existence from some obscure data in the density determinations of hydrogen and could actually separate it in quantity from water subjected to repeated electrolysis. This is the method used at the present time for obtaining heavy water, which consists of water with heavy hydrogen in place of hydrogen. Once heavy water is obtained, we can obtain any amount of deuteron by electrolysis.

The nucleus of heavy hydrogen or the *deuterium* is a compound of the proton and neutron; in fact it is the simplest compound known of the two fundamental nuclear particles. The deuteron nucleus is very useful for nuclear reactions. It passes almost as easily into nuclei as neutrons and has been used to produce a number of novel reactions. The deuteron has also the property of producing neutrons when it impinges at a moderately high speed on other deuterons. As was first shown by Lord Rutherford, the nuclear reaction can be represented as

$$\mathrm{D}+\mathrm{D}=\mathrm{He}^3+\mathrm{n}.$$

Further this reaction starts at a comparatively low acceleration of the deuterons. In fact an acceleration of about 20,000 volts is sufficient to produce this reaction. This is equivalent to a velocity of 1000 kilometres per second. This is a small velocity for nuclear reactions, although moderately high compared to velocities that may be obtained in a discharge tube with a high voltage transformer.

It will be interesting to examine the possibilities for obtaining the high velocity deuterons for producing neutrons in the small weight and volume that make up the atom bomb. A chemical explosion generates a large temperature and pressure. The velocities of the flying gas particles due to the pressure as well as the temperature are never more than 90 or 100 kilometres per second under the most favourable conditions. The deuterium of course will be introduced in the explosive by replacing chemically hydrogen in the explosive charge by deuterium. Using a hollow charge explosion the relative velocity of the gas particles moving towards the centre from opposite directions will be twice as much as illustrated in the figure. If the velocity of the flying gas particles flying towards the centre could be increased about 5 times to around 500 km/sec., the deuterium particles in the flying gas could collide with each other to produce a burst of neutrons on the detonation of the explosive. This of course is a plausible guess, as the exact technique for producing such velocities by explosive means is not known. The second possibility of generating deuterons at high velocity by a high voltage discharge is entirely feasible and is the cheapest method of producing neutrons in the laboratory. The difficulty of including inside the bomb a high voltage transformer or induction coil, a source of electric power, a properly designed discharge tube and starting devices for these into the small space and weight of a bomb seem to argue against the possibility of such devices being used in the bomb. However, since the exact mechanism of producing the neutrons in the bomb is not known, the remote possibility of using such devices should not be entirely ignored.



Principle of the hollow charge explosion

Let us now examine how a burst of neutrons produced initially by any of the methods outlined above could release the latent energy of fission of a greater part of the uranium^{235} in a bomb. The number of atoms of uranium that may be fissioned by a certain number of neutrons depends on what is termed the cross-section of fission, i.e. the chance of producing a fission by a single neutron incident on uranium. The number of fissions n per second equals the product of this cross-section, the number of neutrons incident per second and the number of uranium atoms in the volume on which the neutrons are incident. Mathematically this is expressed as $n=Nn'\sigma$ where n is the number of fissions per second, σ is the cross-section, n' the number of neutrons incident per second and N is the number of uranium atoms in the volume. σ for the slow neutrons on U^{255} is nearly 100 times greater than the fast neutrons and is somewhat greater than 10^{-22} cm^2. If we take a gramme of U^{235}, the number of fissions, assu- ming a million neutrons in a second are incident on the uranium, equals

$$2\times 10^{-22}\times 2{\cdot}4\times 10^{21}\times 10^{6}=480{,}000.$$

During each fission, in the process of the two parts of the atomic nuclei separating, about 4 neutrons are given up by the nucleus. This implies that $1{\cdot}9\times 10^{6}$ neutrons are generated by the million neutrons inducing fission. These neutrons in turn can produce fission in the remaining uranium. It may be noticed that with a million neutrons per second to start with, we can produce almost twice the number of neutrons per second as we originally used in the first step. These in turn will cause further fission on uranium^{235} and break up a further number of uranium nuclei. Each time twice the number of neutrons as the previous fission proceeds will be generated so that it will be a chain process and will only stop when the number of uranium atoms has decreased to such an extent that the number of neutrons generated is smaller than the number of neutrons causing fission.

In our present example this will happen after more than 90% of the uranium has been fissioned, so that the energy of about $\frac{9}{10}$ths gramme of uranium may be obtained in such a reaction starting with one gramme of uranium. If we started out with a bomb containing 100 grammes of uranium^{235} and weighing 500 pounds, the energy released will be roughly 100 times as much which, from our previous data, is about $1{\cdot}9\times 10^{9}$ kilocalories. Seven hundred gms. of U^{235} in the bomb would give us the same energy as was produced in the great explosion which took place at Oppau in Germany in 1921, where nine million pounds of ammonium nitrate stacked in the open exploded, killing 1000 and wounding 1500, and the zone of serious damage extended to a four mile radius. The recent explosion in the Bombay Harbour, where 2000 tons of TNT exploded, was on the same scale. Just fancy what would have happened to Bombay if the shipload of TNT, instead of exploding 1 mile from the harbour, exploded in the centre of the city. That would give one the terrible ordeals to which the people of Hiroshima and Nagasaki were subjected.

The energy of the explosion may be assumed to be dissipated uniformly through the 500 pounds of the bomb materials, enabling us to calculate the temperature reached in the bursting of the bomb; we obtain it by dividing the total energy of uranium fission in calories by the mass of the bomb in grammes and making a rough guess as to the average specific heat of the material of the bomb. The temperature comes out between ten million and a hundred million degrees Centigrade. This calculation does not take into account the losses of heat due to radiation, ionisation and mechanical effects that will surely take up a part of the energy of fission. The temperature is well in the order that exists within the interior of stars and one may well imagine what the effect of this temperature will be for miles around. This makes it possible for the first time to produce and find out on the Earth the effects of such high temperatures. It may help us to understand in the future the mechanisms that go on in the interior of the stars.

We might well consider at this stage the cost of making such bombs. The main item of course is the separation of uranium^{235}. A rough calculation on the basis of the mass-spectrographic method of separation is possible. Nier and Dunning in 1940 separated $1{\cdot}3\times 10^{-9}$ grammes of uranium^{235} by mass-spectrographic method in 10 hours and used approximately ·5 kWh energy (·5 units) in the process. The efficiency must have been considerably improved since those days. Assuming an overall improvement of 3 times due to technical developments and improved efficiency, it will still require 10^8 kilowatt-hours of energy to separate one gramme of U^{235}. Even at 1 cent a unit this will amount to a million dollars per gramme of uranium^{235}.

To this we must add the cost of obtaining and separating the element uranium which is quite rare and that of manufacturing proper alloys and materials to produce the preliminary explosion which will yield the neutrons.

According to these calculations, the whole amount of electrical energy now produced in India in the year is barely sufficient to produce 100 gms of U^{235}, and even the USA cannot manufacture material for more than 50 such bombs per year. But it is quite possible that more efficient and economical apparatus for separation have since been developed, *e.g.*, by the thermal diffusion of uranium tetrabromide. It is obvious that the production of this terrible weapon of destruction under the present state of our knowledge is beyond the capacity of individuals or even of small States. Only large States like the USA, England, or Soviet Russia have the capacity to undertake their manufacture.

Strangely enough both the basic discoveries of the uranium fission and the thermal diffusion method of separation of U^{235}, which brought the dreams of utilization of atomic energy within the range of practica bility, were made in Germany, and in the early part of 1939. The Germans were also the earliest to take up seriously the problems of practical utilization of these discoveries. Apparently this was the secret weapon which Hitler was threatening to use against his enemies when his end came. But why were not the Germans able to perfect the 'Bomb' before their collapse?

It may not be realized by the public that between the first suggestion regarding the utilization of atomic energy and the actual use of the atomic bomb, there must have intervened concerted team work by hundreds of nuclear physicists and chemists, including some of the most eminent living men on these subjects, and also geologists, engineers and technicians. They must have used huge plants to generate electrical energy required for the separation of U^{235}, set up factories for manufacture of heavy hydrogen and using it in place of hydrogen in the chemical explosives, and carried out researches on the manufacture of special alloys and their manufacture. The money spent was, we are told, four billion dollars, which is two years' revenue of the Government of India and the Provincial Governments. It is not an unlikely figure, considering the magnitude of the effort made.

But apparently even in spite of such effects, the bomb could not be made a practical proposition before the collapse of Germany! It was probably after the collapse that the knowledge of scientists on both sides had to be utilized in a common pool before success could be achieved. But this is a mere guess, and if the story be ever told, it will prove terribly fascinating!

The failure of the Germans, in spite of their initial start, may be in part due to the expulsion of some of their best scientists on racial grounds, and their failure to enlist the services of scientists of occupied countries.

A few words regarding the basic element uranium of which these bombs are made may not be entirely out of place. Uranium is the heaviest of elements, and its radioactive properties have been well-known since the discovery of radioactivity in the closing years of the last century. It appears to play quite a prominent part in the heat economy of the Earth, which is assumed to have been cooling through at least 2000 million years after its separation from the Sun. The rate of cooling is rather too slow and indicates that the heat lost by radiation is largely compensated by a source of heat within the Earth. With the discovery of radioactivity, the source has been identified with the radioactive matter in the Earth. On this basis, Holmes and Paneth estimate that there are about 8×10^8 tons of uranium in the Earth. If there were more, they conclude, the Earth would have burst some day. On this basis, the surface crust of the Earth up to a mile in depth should contain about 3×10^4 tons of this material. Extensive surface assays of the radioactive content of the Earth's crust indicate a much larger figure for the radioactive content of the surface crusts. Some assays indicate as much as ten times the figure. Assuming a more modest figure of 10^5 tons, the total U^{235} present on the Earth's surface is about 780 tons and the radium content in equilibrium with U^{238} is about 15,000 grammes. The interesting point that emerges is that the crustal rocks contain a great deal of more uranium than the interior magma and that perhaps no very extensive sources of uranium minerals remain to be discovered. The most extensive deposits known occur in the region of the Great Bear Lake in Canada, with deposits in Katanga region of Belgian Congo and Joachimstal in Czechoslovakia following in the order mentioned. Russians claim discoveries of rich deposits in the Urals and in the Khibin peninsula (Murmansk). Smaller deposits occur almost all over the world. Norway, Cornwall in England, the USA, China and India have all reported the occurrence of these minerals. The extent of the deposits in India have not been well investigated. Thorium occurs in larger proportion in India and though this can be fissioned, the efficiency is too low, and this cannot take the place of uranium as is claimed by some enthusiastic Travancorians. All uranium deposits are potential sources of U^{235} and undoubtedly greater interest will now be displayed in their occurrence, extent and other possibilities specially since the limited nature of these resources will make it imperative for nations to try to own as much of it as possible.

The effect of the atomic bomb burst over a city will be to produce instantaneously a mass of ionised vapour with a pressure of 10^9 atmospheres and at a temperature of nearly 100 million degrees. It is as if a chunk from the interior of stars is just thrown on the earth. The effect of the blast will be to reduce all buildings within a short distance to atoms, and then burn everything within a few kilometers. Whatever living beings, men, animals or plants, who happen to escape probably at the outer periphery of the central zone, will have a further terrible ordeal to face.

For one of the after effects of large scale fission of uranium is the generation of large amount of temporary radioactivity; for the immediate fission-products are all radioactive. Most of it, of course, will decay quickly but there are fission-products whose activity decays more slowly and it is possible that even days after an explosion of 100 grammes of U^{235}, which in itself is sufficient to destroy completely a city of a million inhabitants, there will be a large amount of radioactivity still contaminating the area where the explosion took place. This radioactivity is likely to have very harmful effects on all living matter, men, animals and plants, exposed to it. The usual effects at much lower intensity of radioactivity is known. In most cases the subject is doomed to a slow death depending on the amount of exposure, as well as deep seated change in the blood of men and animals. It is possible that many people may be so affected. The long range effect of these strong radiations on those plants and animals that survive is unpredictable but biologists think that some of the harmful effects may become apparent years later or even in the second or third generations. These are really devastating consequences on which it is well to ponder. Recent newspaper reports confirm that the effects of radioactivity have played havoc with the population in the two cities bombed with these atom bombs.

It is indeed a very great pity that science has lent itself to the evolution of destructive weapons that threaten mankind with a horrible doom (?). Is it not time for scientists to take stock of the situation and to think about effective control of the tremendous forces that he has learnt to use?

But is the 'Uranium Bomb' the limit of "*Schrechlichkeit*"? No, for in this, we convert only a small amount of mass, barely 1 in 1000, to energy. More efficient processes are not ruled out. In fact, some physicists are of opinion (though others do not agree with that view) that the mysterious cosmic rays are due to the total conversion of matter into energy, taking place somewhere in space, probably in some *supernova* outburst. The possibility of carrying out experiments on the total conversion of mass into energy in the laboratory in the near future should not be lightly dismissed particularly in view of the rapidity with which the 'Atomic Bomb' has been evolved. But let us hope the world will be spared from any further atomic bomb, or superatomic bomb "*Schrechlichkeit*".

[Amongst the comments on the atom bomb, the extracts from the letter published in "The Times" by the famous scientist, Sir Henry Dale, the President of the Royal Society, who is on the new Anderson Committee, may be quoted: "While scientists loyally kept the secret of the atom bomb while war was in progress, they, once the war with Japan is finished, will all wish to be done with the secret for ever. We have tolerated much and would tolerate anything to ensure victory for freedom, but when victory has been won we shall want the freedom."

Dr. Norman Campbell asked whether "it was really necessary to conceal so carefully the fact that nuclear fission on which the atomic bomb depends was discovered in Germany."

American papers just received say that the explosive power of the atomic bomb that was thrown over Hiroshima was equivalent to 20,000 tons of T.N.T. The preliminary experiment carried out on a steel tower in Arizona showed that the explosion was so violent that the city of Albuquerque, 120 miles away, was illuminated as in broad daylight. The experiments were carried out in three cities, Oak Ridge, 10 miles west of Knox Ville, Pascoin, Washington State, and Los Alamos near Santa Fe, New Mexico.—Ed. *Sc & Cul*]

1.3.5. THE LOGIC OF THE ATOMIC BOMB*

It is said that Louis XIV, the grand monarch who ruled France during the seventeenth century caused the words "Logice Regum", i.e. Logic of Kings, to be inscribed on his guns. It is well known to students of history that flushed with power, Louis tried to apply this logic to the countries surrounding France, viz., the Netherlands, Germany, Spain and Italy. For a time, the logic of guns worked all right, and in favour of France. But when the rulers of these countries combined and began to retaliate on Louis with the same logic, a bitter struggle ensued, but ultimately the grand monarch's projects collapsed, and he had to suffer defeat, humiliation and extreme bitterness of disappointment during the closing years of his life.

History has now repeated itself. Hitler who tried to repeat the exploits of the grand monarch by the use of bombing aeroplanes, tanks and guns as the King's or should we say the Dictator's Logic has been defeated and destroyed by the use of his own logic, and has dragged down in his fall, the great country of Germany to a depth of degradation unknown in her history. But Hitler had hopes that Germany's scientists would be able to devise a weapon far more terrible in its effects than anything hitherto known and he would enable to apply this new logic, i.e. the logic of Atomic Bombs, on his adversaries in a last hour attempt to avoid encirclement and destruction. But his scientists probably failed him by a few months, and it was reserved for his adversaries probably to some extent aided by captured German scientists, to bring this weapon to perfection, and apply this logic on Japan, and compel that proud country which has never known subjection to her knees.

A story of the discoveries in physics which led to the invention of the Atomic Bomb has been given in the August number of *SCIENCE AND CULTURE*, and Great Britain's part in the work is recounted in a publication by H.M.'s Government which is reproduced with a running commentary in our next article. The part played by the chief actor, viz. the USA and of Canada is not yet known with precision, but can be guessed. The potentiality of the great discovery of Uranium Fission by Otto Hahn in 1939 had been almost immediately grasped by the leading scientists of all nations, but probably if things were left to run their usual course, the actual invention of the atomic bomb would have taken decades, and it was quite possible it might never

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*Sci & Cult **11**, 212, 1945, (editorial, unsigned) have come at all. But as our next article shows the exigencies of the war compelled the leaders of allied nations to mobilize their best scientists and technicians in an all-out effort and place at their disposal unlimited funds for carrying out the necessary experiments on a scale undreamt of before. And thus was evolved the great weapon which cut short the war by at least two years.*

But there is another side of this fascinating story of the power of co-operative scientific effort, which is far less pleasing. It is the question of the probable use of the logic of the Atomic Bomb in future conflicts in the course of human history !

As our London contemporary *Nature* (August 11, 1945) puts it:

"Great Britain, the United States of America and Canada hold in their hands a weapon with which they can dominate the world."

Our contemporary either fails to note, or refrains from saying so from a sense of delicacy that these countries dominate three-fourths of the land surface of the globe leaving only one-fourth to Soviet Russia.

The present position is that the USA being already in the possession of the secret technical knowledge of the atomic bomb, and having all industrial plants ready is in a position to produce a fairly good number of far more powerful atomic bombs within a short time, and has shown herself extremely reluctant to share this secret with any other power. This has given rise to an outburst, which appears to us largely hypocritical, or moral indignation on the part of some powers which are not possessed of the secret, though they have not in the past shown any scruples in using Louis XIV's logic on their own subject races.

It is doubtful whether any other power is just now in a position to emulate the USA in the production of the atom bomb. But this position of inferiority cannot continue for a long time, and provided a State is allowed to retain its sovereignty, it can undertake making of 'Atomic Bombs', and can probably produce them in sufficient number within a short time, as Professor Oliphant, the Australian physicist

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*Compare with this the story of the invention of the internal combustion engine. It may not be known to the general public that it was the Dutch physicist Huygens who made the first suggestion of making an internal combustion engine in 1660 by a series of well timed explosions of gunpowder, but it took two hundred years before the first crude internal combustion engine could be produced for the market. The discovery of Uranium Fission took only four years to bear fruit in the form of the most terrible engine of war! Thanks to State aid and co-operative work of a team of scientists, technicians and industrialists, centuries have been compressed into as many years.

who has taken part in the evolution of the atomic bomb pointed out in a press statement: "There is not much of secret in the Atomic Bomb. The fundamental physical processes are well known to scientists of all countries, and even those countries who do not possess it now can have it within a short time say a few months or at most two years if they harness their scientists for team work as the USA had done, and are prepared to spare the necessary power and equipment." Professor Oliphant thinks that Atom Bombs of 50 times more destructive power than those hurled on Hiroshima can be prepared and a few of these can destroy all the great cities of a country.

The effect of a third world war in which the atomic bomb may be fully and freely used, on human civilization, nay on the very existence of *homo sapiens* on this planet, will be so frightful that blood congeals in our vein to think of such a catastrophe ! Those who were responsible for the making of the Atomic Bomb, and using it on the unfortunate residents of Hiroshima and Nagasaki have therefore taken upon themselves a terrible responsibility. But are these men alive to a sense of their responsibility ?

We have in vain looked for this in the pronouncements of the political leaders of the victorious nations. Their statements and actions show that they wish to keep the secret to themselves, and squeeze the rest of the world, consisting of doubtful friends, vanquished enemies and downtrodden colonials to the "*Fait Accompli*" or "*Status Quo*" by the threat of the Atomic Bomb. The result has been a most unhealthy race for the new weapon, and recently even France has entered the race ! What will be the sequel of this race for atomic power !

The statements which the Allied statesmen are making in justification of the use of the Atomic Bomb recalls Dr Nobel's hope expressed on the discovery of the dynamite that this and other explosives would make war so terrible that in future all wars would cease. Perhaps the God of Destruction was laughing in his sleeves when Nobel made this statement and probably he is no less amused this time over the justification of the use of Atomic Bomb by the war lords, and their satellites on the pseudo-humanitarian plea that the threat of atom bombs would make any further war impossible. [1]The hollowness of such profession is apparent to far-seeing philosophers

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[1] Curiously enough, Chenghiz Khan Jihankusha (world-conqueror) when he ordered wholesale massacre of the inhabitants of the ancient city of Balkh put forward the same humanitarian plea, viz. wholesale massacre of citizens of one city will frighten the rest of the country to quick submission, and thus shorten the war, and avoid unnecessary bloodshed.

like Bertrand Russell who in a recent press statement on the Atomic Bomb pointed out that if mankind were ever to have peace, there should be only a One-Power World.[2] The implications of such policy is, however, too terrible to think of, but who knows if thoughts and events, as they are progressing, may not be marching towards that direction ? But is a One-Power World desirable either from the point of view of the conquerors or the conquered ?

World's history has seen something like a One-Power World during the days of the Roman Imperialism (44 B.C. to A.D. 470). True, there were other great and powerful countries like China, India and Iran which Imperial Rome was unable to conquer, but all these countries except Iran, were little self-contained worlds in themselves. Within the area round about the Mediterranean sea, the Roman Eagle flew unchallenged for four hundred years over an assembly of ancient and cultured nations like Greeks, Egyptians, Carthagians, Phoenicians, and Mesopotamians whose contribution to civilization had been as great as Rome's and a medley of cultureless Northern Barbarians from whom are descended the modern West European Nations. But under Roman domination, though these countries were relieved of the duty of defending themselves and law and order were fully maintained, the springs of culture of these ancient nations dried up almost completely leaving a conglomeration of hungry and poverty striken *amorphous* people, to whom the very existence was a burden. This was the result of loss of political sovereignty. The march of civilization was retarded for nearly 1,500 years. It was recreated and resumed by the descendants of northern barbarians. What was the effect on Rome itself ? The influx of cheap wealth from colonial exploitation and accession of irresponsible power spoilt entirely the ancient virtues which made Rome great and shaped her very vitality. First, as a result of the corruption the big Roman families who had built up the greatness of Rome died out and disappeared, then came rule by foreign-born Romans, and ultimately the original Roman Nation disappeared and was replaced by the Romanised Northern Barbarians. The history of these declining years of Roman Imperialism is not one of progress and happiness, but of stagnation, decay, famine and pestilence.

If in the near future, we have a One-Power World, as appears to be

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[2] Mind that One-Power World is not the same thing as the plea of One World, put forward by Wendell Wilkie, which means a World united by common economic ties, but One-Power World means a world dominated by One Power alone.

the tendency from the intended use of the logic of the Atomic Bomb, its effect on the rulers would be no less ruinous than on the ruled.

The 'Suppressed Nationalities' of the world whose ranks have now been swollen by the vanquished nations can hardly expect any relief, as long as power remains in the hands of the professional power politicians, as our old Kautilya says, "who, amongst those possessing power is not intoxicated, and does not think he is absolutely right ?"

But there is another side of the logic of the atomic bomb to which the attention of politicians may be drawn. The story of the production of the atomic bomb illustrates, as nothing else does, the tremendous powers which science has placed in the hands of man, for good and for evil. It also shows that if a team of well-chosen scientists be selected for studying a problem in an objective way, and be directed to find out the remedy, and if sufficient funds and power be placed in their hands to execute their plans, they can be trusted to solve problems of reconstruction which baffle the professional politician and centuries of neglect can be compressed into decades. The 'Colonial people' which include most of Asia and Africa, suffer from extreme poverty, disease and malnutrition, may be it is due to the stupidity and backward ideas of the people themselves, or to the want of initiative, or the policy of exploitation on the part of the rulers. There is no point in spinning out a controversy over these points, for it is crystal clear that if the great lesson of science and technology be applied, as Russia has demonstrated towards the development of the resources of these exploited countries, they can reach the same level of standard of life as in the countries of Europe, say, Sweden. But this clear issue is being clouded by fogs of controversy in the name of nonessential political points, or is being side-tracked by bogus post-war plans of reconstruction hatched in the secretariats by persons who have little competence and sympathy for such work. But if the rulers of the world really wish to uplift the conditions of the common man throughout the world, let them replace the officials in their colonial secretariat by a band of scientists, technicians, and economists for objective planning as Russia got together in her National Planning Commission for the great work of reconstruction after the first World War.

1.3.6. BRITAIN'S PART IN THE EVOLUTION OF THE ATOMIC BOMB*

THE Government of Great Britain have just issued a pamphlet entitled "Statements Relating to the Atomic Bomb" (H.M. Stationery Office, York House, Kingsway, London, W.C.2, Price 4d net) containing statements by the Prime Minister Mr. Attlee and Mr. Churchill and a report of the Directorate of Tube Alloys, Department of Scientific and Industrial Research. This is the first and the most important official disclosure of the part played by Great Britain in the evolution of the Atomic Bomb, which, we trust, will be pursued by our readers with absorbing interest. Below we reproduce, with our commentaries in the footnotes, the text of those reports, with the omission of part of the historical survey of scientific developments leading to the perfection of the Atomic Bomb, which already appeared in our journal and elsewhere in considerable detail.

Statement by Mr Churchill Issued on Monday, August 6th, 1945

By the year 1939[1] it had become widely recognized among scientists of many nations that the release of energy by atomic fission was a possibility. The problems which remained to be solved before this possibility could be turned into practical achievement were, however, manifold and immense, and few scientists would at that time have ventured to predict that an atomic bomb could be ready for use by 1945. Nevertheless, the potentialities of the project were so great that His Majesty's Government thought it right that research should be carried on in spite of the many competing claims on our scientific manpower. At this stage the research was carried out mainly in our Universities, principally, Oxford, Cambridge, London (Imperial College), Liverpool and Birmingham. At the time of the formation of the Coalition Government, responsibility for co-ordinating the work and pressing it forward lay in the Ministry of Aircraft Produc-

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*Sci & Cult **11**, 214, 1945. (unsigned)

[1] The prospects of harnessing the energy of the atomic nucleus was first rendered possible by the discovery of Uranium Fission in the early part of 1939 by Prof. Otto Hahn, assisted by his pupil H. Strassmann, in the Kaiser Wilhelm Institute, Berlin-Dahlem, as narrated in our article on the Atomic Bomb in the August number of *Science and Culture*. It was another German physicist, Flugge who first discussed the possibility of utilising this process in an article in Naturwissenschaft "Can the Energy of Uranium Fission be utilized for Practical Purposes?" An account of the discovery was given in *Science and Culture*, June, 1941.

tion, advised by a committee of leading scientists presided over by Sir George Thomson.[2]

At the same time, under the general arrangements then in force for the pooling of scientific information there was a full interchange of ideas between the scientists carrying out this work in the United Kingdom and those in the United States.

Such progress was made that by the summer of 1941 Sir George Thomson's Committee was able to report that, in their view, there was a reasonable chance that an atomic bomb could be produced before the end of the war. At the end of August 1941, Lord Cherwell,[3] whose duty it was to keep me informed on all these and other technical developments, reported the substantial progress which was being made. The general responsibility for the scientific research carried on under the various technical committees lay with the then Lord President of the Council, Sir John Anderson. In these circumstances (having in mind also the effect of ordinary high-explosive which we had recently experienced), I referred the matter on August 30, 1941, to the Chiefs of Staff Committee in the following minute:

> "General Ismay for Chiefs of Staff Committee.
>
> Although personally I am quite content with the existing explosives, I feel we must not stand in the path of improvement, and I therefore think that action should be taken in the sense proposed by Lord Cherwell, and that the Cabinet Minister responsible should be Sir John Anderson.
>
> I shall be glad to know what the Chiefs of Staff Committee think."

The Chiefs of Staff recommended immediate action with the maximum priority.

"Directorate of Tube Alloys"

It was then decided to set up within the Department of Scientific and Industrial Research a special division to direct the work, and Imperial Chemical Industries Limited agreed to release Mr W. A. Akers to take charge of this Directorate, which we called, for purposes of secrecy, the "Directorate of Tube Alloys". After Sir John

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[2] Sir George P. Thomson, F.R.S., Professor of Physics in the Imperial College of Science and Technology. He is famous for his experiment on Electron Diffraction, for which a Nobel Prize was awarded to him. Son of the famous physicist Sir J. J. Thomson.

[3] Lord Cherwell, formerly Professor F. A. Lindemann of the Oxford University. As Paymaster General he was a Member of the War Cabinet.

Anderson had ceased to be Lord President and became Chancellor of the Exchequer, I asked him to continue to supervise this work, for which he has special qualifications. To advise him, there was set up under his chairmanship a Consultative Council composed of the President of the Royal Society, the Chairman of the Scientific Advisory Committee of the Cabinet, the Secretary of the Department of Scientific and Industrial Research and Lord Cherwell. The Minister of Aircraft Production, at that time Lord Brabazon, also served on this Committee. Under the Chairmanship of Mr Akers there was also a Technical Committee on which sat the scientists who were directing the different sections of the work, and some others. This Committee[4] was originally composed of Sir James Chadwick, Professor Peierls, and Drs Halban, Simon and Slade. Later it was joined by Sir Charles Darwin and Professors Cockcroft, Oliphant and Feather. Full use was also made of University and industrial laboratories.

On October 11, 1941, President Roosevelt sent me a letter suggesting that any extended efforts on this important matter might usefully be co-ordinated or even jointly conducted. Accordingly all British and American efforts were joined and a number of British scientists concerned proceeded to the United States. Apart from these contacts, complete secrecy guarded all these activities and no single person was informed whose work was not indispensable to progress.

By the summer of 1942 this expanded programme of research had confirmed with surer and broader foundations the promising forecasts which had been made a year earlier, and the time had come when a decision must be made whether or not to proceed with the construction of large-scale production plants. Meanwhile it had become apparent from the preliminary experiments that these plants would have to be on something like the vast scale described in the American statements which have been published today.

Great Britain at this period was fully extended in war production and we could not afford such grave interference with the current munitions programmes on which our warlike operations depended. Moreover, Great Britain was within easy range of German bombers, and the risk of raiders from the sea or air could not be ignored. The United States, however, where parallel or similar progress had been made, was free from these dangers. The decision was therefore taken to build the full-scale production plants in America.

Sir James Chadwick, F.R.S., Nobel Laureate, Professor of Physics, University of Liverpool, and discoverer of the "Neutron".

In the United States the erection of the immense plants was placed under the responsibility of Mr Stimson, United States Secretary of War, and the American Army Administration, whose wonderful work and marvellous secrecy[5] cannot be sufficiently admired. The main practical effort and virtually the whole of its prodigious cost now fell upon the United States authorities, who were assisted by a number of British scientists. The relationship of the British and American contributions was regulated by discussion between the late President Roosevelt and myself, and a Combined Policy Committee was set up.

The Canadian Government,[6] whose contribution was most valuable, provided both indispensable raw material for the project as a whole and also necessary facilities for the work of one section of the project which has been carried out in Canada by the three Governments in partnership.

The smoothness with which the arrangements for co-operation which were made in 1943 have been carried into effect is a happy augury for our future relations and reflects great credit on all concerned—on the members of the Combined Policy Committee which we set up; on the enthusiasm with which our scientists and technicians gave of their best—particularly Sir James Chadwick who gave up his work at Liverpool to serve as technical adviser to the United Kingdom members of the Policy Committee and spared no effort; and not

R. Peierls, German refugee, famous worker on Theoretical Physics. Now Professor at Birmingham.

H. Halban, French Physicist, and a pupil of Profs. F. and I. Joliot-Curie. After the fall of France, he managed to escape to the U.K. with a large amount of heavy hydrogen which was very useful for the experiments on Atomic Bomb.

H. Simon, F.R.S., German refugee Physicist, a pupil of W. Nernst, and a great authority on Low Temperature Physics. Now Professor at Oxford.

H. Slade, Physical chemist.

Sir Charles Darwin, F.R.S., and famous theoretical Physicist, now Director of the National Physical Laboratory.

J. D. Cockcroft, F.R.S., Professor in Nuclear Physics, Cavendish Laboratory, Cambridge, famous for his pioneering work on the transformation of Li^7 by proton beams.

Oliphant, F.R.S., Professor of Physics in the University of Birmingham: Australian by birth, and a famous worker on Nuclear Physics.

N. Feather, F.R.S., just elected to Professorship of Physics, Edinburgh University.

[5] 'Nuclear Physics' went underground in the U.S.A. during the war. Authors and journalists were forbidden to mention anything connected with 'Nuclear Physics', and a famous American physicist was warned for mentioning the word 'Cyclotron' in his lecture.

[6] Canada provides almost the whole of the Uranium-ore required for the making of the Atom Bomb.

least, on the generous spirit with which the whole United States organization welcomed our men and made it possible for them to make their contribution.

By God's mercy British and American science outpaced all German efforts. These were on a considerable scale, but far behind. The possession of these powers by the Germans at any time might have altered the result of the war, and profound anxiety was felt by those who were informed.[7] Every effort was made by our intelligence service and by the Royal Air Force to locate in Germany anything resembling the plants which were being created in the United States. In the winter of 1942-1943 most gallant attacks were made in Norway on two occasions by small parties of volunteers from the British Commandos and Norwegian forces, at very heavy loss of life, upon stores of what is called "heavy water", an element in one of the possible processes.[8] The second of these two attacks was completely successful.

The whole burden of execution, including the setting-up of the plants and many technical processes connected therewith in the practical sphere, constitutes one of the greatest triumphs of American —or indeed human—genius of which there is record. Moreover, the decision to make these enormous expenditures upon a project which, however hopefully established by American and British research, remained nevertheless a heartshaking risk, stands to the everlasting honour of President Roosevelt and his advisers.

It is now for Japan to realize in the glare of the first atomic bomb which has smitten her, what the consequences will be of an indefinite continuance of this terrible means of maintaining a rule of law in the world.

This revelation of the secrets of nature, long mercifully withheld from man, should arouse the most solemn reflections in the mind and conscience of every human being capable of comprehension. We must indeed pray that these awful agencies will be made to conduce to peace among the nations, and that instead of wreaking measureless havoc upon the entire globe, they may become a perennial fountain of world prosperity.

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[7] We have yet to hear the German story. The Germans gave out that they used some Atom Bombs during the Runsted drive in December, 1944. If they had done so, they had not received the perfection attained by the Anglo-Americans. It was evident that Hitler built great hopes on the Atom Bomb.

[8] Heavy hydrogen was probably required for making the ordinary explosive "bombs" for the production of neutrons. Norway, with its cheap electric power, has been the largest manufacturer of heavy hydrogen.

Statement Issued by the Directorate of Tube Alloys (Department of Scientific and Industrial Research), on Sunday, August 12, 1945.

SCIENTIFIC PRINCIPLE

Discovery of Fission

Professor O. Hahn and Dr. Strassmann in Berlin became interested in this problem at the end of 1938 and, from the particular point of view of their chemical nature, carefully re-examined the new elements. In January, 1939, they published a most important paper in which they reported positive chemical evidence to show that one, at least, of the new isotopes which were believed to be of higher atomic number and mass than uranium was, in fact, an isotope of the element barium which has an atomic number and mass not very different from half that of uranium.

Immediately afterwards Dr. O. Frisch[9] and Professor Lise Meitner[10] pointed out that this discovery could only mean that, when uranium was bombarded by neutrons, a nuclear reaction took place of a kind utterly different from any so far studied and that the uranium nucleus split into two parts of roughly equal mass. This phenomenon, for which they proposed the name "nuclear fission", could be explained in terms of the theory of nuclear reactions which had been developed by Professor Bohr in the preceding years. They also pointed out that the fragments of the uranium nucleus would fly apart with great energy and this prediction was given a direct proof by experiments carried out by Dr. Frisch in Copenhagen. Confirmation of the reality of the fission process with uranium, and of the great energy released which accompanied it, was obtained by Professor Joliot in Paris independently (and at nearly the same time) and by other physicists throughout the world as soon as the original work was known to them.

Very shortly afterwards, in the spring of 1939, Professor Joliot and his collaborators Drs. Halban and Kowarski gave an experimental proof of the additional fact, which was expected on theoretical grounds, that when the fission of uranium takes place a number of free neutrons is also produced. Their first experiments showed this number to be about 3. Experiments of the same types were carried

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[9] Otto Frisch, a German refugee.

[10] Prof. Lise Meitner, woman-physicist and lifelong co-worker of Otto Hahn. She was turned out of Germany in the Jewish purge.

out by Drs. Anderson, Fermi[11], Hanstein, Szilard[12] and Zinn in the U.S.A., and independent confirmation was obtained of the fact that more than one free neutron is produced for each fission of a uranium nucleus.

It was immediately recognized that this discovery was of the very greatest significance and that, for the first time, there was an experimental basis for the hope that the useful realization of the enormous store of atomic energy in matter could be achieved. Not only did the fission reaction provide the large amount of energy that was calculated from the difference in mass of the reactants and products, but the liberation of more than one new neutron each time that a uranium nucleus underwent fission made possible the continuation of the reaction by the development of a chain process once the initial step had been taken. Such a chain process would enable the reaction, in a suitable mass of uranium, to take place at an ever-increasing rate and would involve so many atoms that there would be a sensible, and indeed possibly an overwhelming, liberation of energy. The whole process could, furthermore, be started by the application of only a minute fraction of the energy that would be liberated and the difficulty, hitherto encountered in nuclear reactions, of obtaining an overall gain in energy would be eliminated.

It was therefore only natural that there should be an outburst of activity in most of the physics laboratories of the world with a spate of publications in the scientific press. This continued until the outbreak of war, when an increasing sense of the great potential value of this work imposed restrictions.

Certain important facts emerged from the work that was published during this period and theoretical conclusions and expectations were announced but it is hardly possible to give any strictly chronological account of them. The work was done in so many laboratories and the results, sometimes in a very preliminary form, were communicated to so many journals and published at such varying intervals after communication that details of priority cannot be clearly settled. But reference should be made to the visit which Professor Bohr paid to

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[11] E. Fermi, Nobel Laureate, most famous Italian physicist of present times who was the first to use neutrons for producing "Transuranic Element'. It is said that when he discovered element No. 93, now provisionally called Neptunium, he proposed to Mussolini that it should be called Mussolinium in his honour. But Mussolini did not argee, as the element was "Unstable". Fermi was awarded Nobel Prize in 1939, and ran away to USA., when he went to Stockholm to receive the award.

[12] H. Szilard, German regugee physicist.

the USA from January till May, 1939. He was able to report directly to American physicists the experiments carried out by Hahn, Frisch and Meitner and their suggested interpretation of the results. In addition, while in the USA, Bohr developed and published, in collaboration with Professor J. A. Wheeler of Princeton University, New Jersey, a theory of the fission process.

One important prediction which was made from this theory related to the different behaviour of the various isotopes of uranium. This element consists, for much the greater part (99.3 per cent). of atoms of mass number 238 but there is also an isotope (0.7 per cent) of mass 235 and a very small proportion (0.008 per cent) of an isotope of mass 234. The first two, which are conveniently designated by the symbols U-238 and U-235 respectively, are the most important in connection with the uranium fission project. Bohr predicted. in February, 1939, that the common isotope. U-238, would be expected to undergo fission only when the bombarding neutrons had a high energy but that the rarer U- 235 isotope[13] would behave differently in that it would not only show this reaction with high energy neutrons but in addition would be particularly liable to undergo fission when the energy, and therefore the velocity. of the bombarding neutrons was very low. This prediction was, in fact. confirmed in March. 1940, by experiments carried out by Nier of Minnesota and Booth. Dunning and Grosse of Columbia University, New York. They used a sample of uranium in which the content of U-235 had been increased above the normal value by means of Nier's mass-spectrograph.

It is relevant, at this point, to refer to a different phenomenon shown by the U-238 isotope when bombarded by neutrons of one rather narrowly defined energy value which is intermediate between the very high energy required to cause fission of this isotope and the very low energy which is most effective in causing fission of U-235. Neutrons which have this so-called "resonance" energy are very strongly absorbed by the U-238 nucleus but fission does not follow. Instead the new nucleus, which now has a mass number 239, emits two electrons in successive steps and is thereby converted first to an isotope of an element with atomic number 93 (for which the name "neptunium" has been suggested) and then to one of an element with atomic number 94. This latter has, provisionally. been named "pluto-

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[13] Next to the discovery of the fission phenomena, the discovery of the importance of U-235 which is due to Bohr, is the most important work in the development of the Atom Bomb.

nium" and the isotope formed from U-238 after resonance capture of a neutron may be represented by the symbol Pu-239. Neptunium and plutonium are true "trans-uranium" elements, of the type suggested by Fermi, and are not found in nature. Of the two, Pu-239 is of particular interest in connection with the general problem of fission and the release of atomic energy because it could be expected, from the Bohr-Wheeler theory, to show the same sort of properties as U-235 and to be capable of undergoing fission with the greatest ease when bombarded by neutrons of very low energy.

Reference must also be made to the fact that the three nuclear species U-235, U-238 and Pu-235 are not the only ones that can undergo fission. The two elements next below uranium in the atomic series were also shown to have this same property. Thorium, with atomic number 90 and consisting of one isotope only of atomic mass 232, behaves in the same way as U-238 and fission can only be brought about when the bombarding neutrons have very high energy. The very rare radio-active element protactinium, with atomic number 91 and atomic mass 231, behaves, as regards fission, in a manner intermediate between U-235 and U-238. These facts, again, are all explicable in terms of the Bohr-Wheeler theory which enumerates certain general rules covering the behaviour to be expected with regard to fission of any heavy nucleus known or unknown.

Chain reaction and the Atomic Bomb

The foregoing survey of the development of atomic and nuclear physics, though necessarily brief and incomplete, has traced the growth of the idea that there are enormous reserves of energy in all matter; that these are of a nature quite different from those involved in chemical processes, such as the burning of coal or oil or the detonation of TNT or other explosives, and that the nuclear reactions by which they are released are more comparable to those occurring in the sun or stars or in the natural radio-active elements found on the earth.

While this idea has been formed and steadily strengthened since the discovery of the phenomenon of radio-activity at the end of the last century it is only since the discovery, reported at the beginning of 1939, of the special phenomenon of fission that a way has been clearly seen by which this atomic or nuclear energy in matter could be released, controlled and put to use by man.

In recent years the enormous effort expended on the solution of this