nuclei and two negative electrons, and almost no packing effect results from the aggregation of these helium nuclei into more complex atoms. On this view the helium nuclei must be very greatly more stable than the nuclei of the more complex atoms which they form, so that such an atom, made up entirely from helium units, should give helium and not hydrogen by its primary decomposition. This is in accord with the behavior of the radioactive elements when they disintegrate. It is of interest to note that the members of the radioactive series which are now known to give helium on decomposition, belong to the even numbered groups on the periodic table, and therefore to those groups which are shown in Table IV, as helium aggregates alone. That these heavy atoms must contain a considerable number of helium units is shown by the fact that uranium changes into lead by eight steps in which it loses $\alpha$-particles.
7. The hydrogen-helium system gives an explanation of the fact that argon has an atomic weight of 40 , which is higher than that of potassium, which has an atomic number higher by I . A study of Table IV makes the reason apparent, and shows that in comparison with other members of Series 4 in the periodic table, it is potassium and calcium, and not argon, which are exceptional. In comparison with the members of Series 3, and potassium and calcium, it is of course the argon which is exceptional. As the atoms grow heavier there is a tendency to take on helium (or perhaps hydrogen) groups more rapidly than is the rule in the case of the lighter elements.

Later papers by one of the writers will consider the nuclear and nonnuclear electrons, and the relations of the periodic system to the hydro-gen-helium system presented in this paper.

Chicago. Ill.
[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

RECENT WORK ON THE STRUCTURE OF THE ATOM.<br>[THIRD PAPER ON ATOMIC STRUCTURE.]<br>By William D. Harkins and Ernest D. Wilson.<br>Received March 27, 1915.

When Dalton ${ }^{1}$ advanced his atomic theory of the constitution of matter, he thought of the atom as the ultimate material unit. The discovery of the phenomena of radioactivity, however, made it evident that this view was incorrect, and showed that the atom must be complex. The question of its structure has remained unsolved for a long time, and it is only very recently that there has been any experimental work upon which to base a theory. In this paper practically all of the important
${ }^{1}$ "On Chemical Synthesis, from a New System of Chemical Philosophy," Manchester, 1808 , pp. $2 \mathrm{II}-6,2 \mathrm{I} 9-20$.
recent work bearing on this subject will be considered, and, wherever possible, the results due to the different investigators combined. As the results often seem to be contradictory, the difficulty of reaching any definite conclusion is great.

One of the first difficulties which arises in the attempt to develop an "atom model" is the fact that even at the present time we know nothing of the nature of positive electricity. The different characteristics of the negative electron have been known for some time, but the question of a positive electron is still open.

The first atom model was suggested by Lord Kelvin, ${ }^{1}$ and consisted of concentric rings of rotating negative electrons in a sphere of homogeneous positive electricity the size of the atom. This model has come to be known as the Thomson atom, due to the fact that he developed it quite completely, and worked out in detail the number of electrons in the various rings necessary to give stable systems. The advantages of this construction lie in the relative simplicity of the mathematical calculation of the distribution and velocities of the electrons, as compared with the great difficulties involved in a satisfactory solution of such problems in connection with the later atom models. Thomson has shown that such an atom imitates to a large extent the properties of our known chemical atoms and explains why some are electropositive, others electronegative, and the variation of the chemical properties with the atomic weight.

One objection to this model, which also applies to the other models unless a rather questionable assumption is made, is that the atoms so formed would not be stable, for according to the electromagnetic theory, electrons in orbital motion must radiate energy, and hence at some time the atom would break up.

An objection that is even more important is that the positive spheres of Kelvin would have an electromagnetic inertia which would be negligible compared with that of even a single negative electron, leaving practically all of the mass of the atom unaccounted for on this theory.

The first theory of the constitution of the atom with any experimental work as a basis is due to Rutherford. He made use of the phenomenon of the scattering of alpha and beta particles in passing through matter. ${ }^{2}$ The deflection is more marked for the beta than for the alpha particle, due to the smaller momentum of the former. There seems to be no doubt that the particles pass through atoms, and that their deflections are due to the intense electric field within the atom. Calculation shows that the distribution of the positive electricity assumed in the Thomson atom does not admit of sufficiently strong fields to deflect an alpha particle through a large angle, and the scattering of the alpha and beta rays in passing through thin sheets of metal had been attributed to a number of small scatterings. Geiger and Marsden, ${ }^{3}$ working with gold foil
0.00004 cm . thick, found that about i in 20,000 alpha particles was deflected at an average angle of $90^{\circ}$. Also, Geiger ${ }^{4}$ showed by the theory of probabilities that the most probable deflection was $0.87^{\circ}$, and that the chance of a $90^{\circ}$ deflection was vanishingly small. In the theory of the Thomson atom the large deflections were considered as due to the accumulative effect of a number of small ones. The distribution of alpha particles deflected through large angles does not follow the probability curve. Also, after one collision the probability of the same ray suffering another in such a way as to give a larger deflection is very small.

Considering the deflections as due to a single encounter with an atom, Rutherford has obtained an expression for $d m$, the fraction of the total number of alpha particles which are deviated between $p$ and $p+d p$.

$$
d m=\pi / 4 n t b^{2}(\cot \phi / 2 \csc \phi / 2) d p
$$

where $n$ is the number of atoms per unit volume, $t$ the thickness of the metal, $b$ the distance from the center to which an alpha particle would penetrate if shot directly at the atom, and $p$ the perpendicular distance from the center of the atom to the extension of the line of path of the approaching alpha particle. Geiger ${ }^{5}$ has shown this equation to be true between $30^{\circ}$ and $550^{\circ}$.

Thomson considered the scattering as due to the accumulative effect of a number of small scatterings, and obtained the following expressions: The average deflection, $\theta_{i}$, for a sheet of thickness $t$ is $\theta_{i}=3 \pi b / 8 \sqrt{\pi n t}$. The probability $p_{1}$ that the deflection is greater than $\phi$ is $p_{1}=e^{-\phi^{2} / \theta_{t}}$.

Rutherford shows that the probability $p_{2}$ for the same thing based on the theory of a single scattering is

$$
\begin{gathered}
p_{2}=\frac{\pi}{4} b^{2} n t \cot ^{2} \phi \\
\text { If } p_{2}=0.5, p_{1}=0.24 . \quad \text { If } p_{2}=0.1, p_{1}=0.0004 .
\end{gathered}
$$

Thus the probability on Rutherford's assumption is greater than that on Thomson's. Both of these theories are developed on the assumption that the forces between the particles are electrical, and follow the inverse square law. Darwin has shown that this is the only law of force which is consistent with the facts.*

These considerations would seem to indicate that the large deflections actually found must be due to a single encounter with an atom, and in order to obtain the necessary strength of field, the positive charge would have to be concentrated at a small point instead of being evenly distributed throughout the entire volume of the atom, as in the theory of Thom-

[^0]son. The negative electrons vibrate around this positive nucleus, forming a kind of miniature solar system. This is the type of atom first suggested by Nagaoka. ${ }^{6}$ From the measured deflections, Rutherford estimated that the charge on the nucleus was approximately equal to one-half the atomic weight of the element times the electronic charge. The large deflections are due to the alpha particle passing very close to the nucleus.

With beta rays the effects are slightly different, for since the force is attractive they increase speed on approaching the atom. By ordinary electrodynamics this involves a loss of energy by radiation, and an increase in apparent mass. Darwin showed that if the beta particle passed very close to the nucleus it would describe a spiral, and eventually fall in. This might explain the disappearance of swift beta particles in their passage through matter.

The case of the passage of the alpha particles through hydrogen is of particular interest, ${ }^{7}$ for, since the alpha particle is heavier than the hydrogen atom, the recoil due to the close approach of the atom and the particle should be very large. It was shown that, as' a result of a collision, the hydrogen atom should attain a velocity of r .6 times, and hence a range of about four times that of the alpha particle itself. Marsden ${ }^{8}$ actually, found hydrogen atoms with a range of about 90 cm . in hydrogen in which the alpha particles had a range of only 20 cm .

From the data on the scattering of the alpha rays in passing through a gold leaf, it is possible to calculate an upper limit for the radius of the nucleus of the gold atom.
$\mathrm{Ne}=$ charge on the nucleus (positive).
$\mathrm{R}=$ the radius of the sphere of electric action.
$\mathrm{Ne}=$ the value of the negative charge surrounding the nucleus.
$x=$ electric force at a distance $r$ from the center.
$v=$ potential force at a distance $r$ from center.
Then $x=\mathrm{Ne}\left(\frac{\mathrm{I}}{r^{2}}-\frac{r}{\mathrm{R}^{3}}\right)$ and $v=\mathrm{Ne}\left(\frac{\mathrm{I}}{r}-\frac{3}{2 \mathrm{R}}+\frac{r}{2 \mathrm{R}^{3}}\right)$.
$m=$ mass of alpha particle.
$u=$ velocity of alpha particle.
$\mathrm{E}=$ charge on the alpha particle.
Let the alpha particle be shot directly at the atom, being brought to rest at a distance $b$ from the center. Then

$$
1 / 2 m u^{2}=\operatorname{NeE}\left(\mathrm{I} / b-3 / \mathrm{R}+b^{2} / 2 \mathrm{R}^{3}\right)
$$

If N is assumed to be roo, which cannot be very far from the correct value for gold, the distance $b$ for an alpha particle of velocity $2.09 \times \mathrm{ro}^{9}$ cm . per second is found to be $3.4 \times 10^{-12} \mathrm{~cm}$. This gives a maximum value for the radius of the nucleus of the gold atom.

Darwin ${ }^{8}$ has made a similar calculation for the hydrogen atom and obtains the value $1.7 \times 10^{-18} \mathrm{~cm}$. for the diameter. This is smaller
than the diameter of the negative electron, which is ordinarily given as $2.0 \times 10^{-13} \mathrm{~cm}$. The question arises as to whether the mass of this positive nucleus is entirely electromagnetic, like that of the negative electron. The electrical mass of a charged body is $2 e^{2} / 3 a$, where $e$ is the charge, and $a$ the radius. Using this formula the radius of the positive nucleus of hydrogen comes out to be $1 / \mathrm{r} 830$ that of the negative electron. Rutherford ${ }^{9}$ suggests that it is probable that the hydrogen nucleus is the long sought positive electron.

Rutherford has shown that it is impossible to account for the high speed of expulsion of some of the alpha and beta particles if they come from a ring of atomic radius. They must come from a point very close to the center, which suggests that they are shot from the nucleus of the atom.

The present theory of the constitution of the atom is based on the facts given above. Each atom of matter is supposed to be made up of a positively charged nucleus around which rotate the negative electrons. In the heavier atoms there are negative electrons in the nucleus also. The nucleus is the seat of practically all of the mass of the atom, for the negative electrons contribute very little mass. Barkla, ${ }^{10}$ from his work on the passage of X -rays through matter, suggested that the charge on the nucleus is about $1 / 2 \mathrm{~A} e$, where $A$ is the atomic weight of the element. Vau den Broek, ${ }^{11}$ and later Bohr, ${ }^{12}$ suggested that the number of units of charge is Ne where $N$ is the number of the element when the elements are arranged in order of increasing atomic weight, or what is now called the atomic number.

Moseley's ${ }^{13}$ work on the X-ray spectra of the elements is very important also, in helping to give an insight into the constitution of the atom. Working along the line first suggested by Laue, ${ }^{14}$ and Bragg; ${ }^{15}$ Moseley, and Darwin have developed an experimental method for determining the X-ray spectra of the elements by reflection from crystal surfaces. When an element is used as the anticathode in an X-ray tube, it emits a characteristic radiation of a frequency roughly rooo times as great as that of the visible light waves. Each element is characterized by two different radiations which have been called the K radiation and the L radiation. ${ }^{16}$ The K radiation is composed of two lines which Moseley has called the $\alpha$ line and the $\beta$ line. These are the ones used the most by him for purposes of calculation. The $L$ radiation is not nearly as penetrating as the K radiation, and usually consists of about five lines.

Moseley recorded the spectra photographically, instead of using an electroscope for a detector as did Bragg, and he examined he X-ray spectra of the elements from aluminium to gold. He found a very remarkable relationship between the frequencies of the lines of the various elements. In going from one element to the next higher in atomic weight there was a shift of the two lines of the K series toward the violet. That is, there is
a change in the frequency of the spectrum lines with a change of the element. Moreover there is a very simple relationship between these frequencies. Thius considering the $\alpha$ line, the frequency is expressed by the formula

$$
\nu=\mathrm{K}(\mathrm{~N}-\mathrm{I})^{2}
$$

in which K is a constant, and N is a number which increases by one in passing from one element to the next higher in atomic weight. If 13 is chosen for the value of N for aluminium, and a corresponding value of $\mathrm{K}, \mathrm{N}$ turns out to the the atomic number of the elements. Thus N determines the X-ray spectrum of any element. Moseley finds that between aluminium and gold the order of the elements according to N is the same as that of the atomic weights except where the latter would put the element out of place in the periodic table. Moseley finds only three unknown elements between aluminium and gold.

He has shown that neoytterbium and lutecium exist, but that Urbain's celtium is a mixture. According to his system thulium I and thulium II of Welsbach exist, but not thulium III. A homolog of Mn between Mo and $R_{u}$ remains to be found as does another element between Os and W.

Moseley concludes that the number N is the charge on the nucleus of an atom, and that this charge increases one step at a time from one element to the next. According to this view it is perfectly possible to have two elements of very different atomic weight that have the same X -ray spectrum, providing only that they have the same nuclear charge.

Such elements would also be identical chemically, and so far as is known at the present time would have identical spark and arc spectra.

This seems to be borne out by the fact that Aston, ${ }^{17}$ working with J. J. Thomson, found two neons with atomic weights 20 and 22, which are otherwise identical, and have the same spectrum. He was only able to separate them by diffusion methods, which depend on the atomic weight and hence upon the density. Also Russell and Ross, ${ }^{18}$ and Exner and Haschek, ${ }^{19}$ working with a strong ionium solution, could not obtain any spectrum except that of thorium, of which ionium is an isotope.

This theory of the dependence of the chemical and physical properties of the elements on the nuclear charge is supported by recent work on the radioactive elements. The position of all these elements in the periodic table was an unsolved problem until it was shown that two or more elements could occupy the same place in the table. It has been supposed for some time that certain of the radio-elements were inseparable by any known chemical means. Fajans, Soddy, and others make this a general property of these elements, and treat each as the chemical ana$\log$ of one or the other of the known elements. Two elements which occupy the same space in the periodic table and are inseparable by ordinary chemical means have been called "Isotopes" by Soddy.

The rule advanced by Soddy, ${ }^{20}$ Fajans, ${ }^{21}$ and others, that the expulsion of an alpha particle causes the element to shift its position in the periodic table two places to the left, and to decrease in atomic weight by four units is also in accord with the theory if we consider that the alpha particle comes from the nucleus of the atom. Similarly the expulsion of a beta particle, which is a negative electron, would cause the element to shift its position in the table one place to the right, without any change of mass. In this case the positive charge on the nucleus is increased by one unit.

In radioactive changes the expulsion of a beta particle, which evidently is shot out of the nucleus, as is shown by its extremely high velocity, causes the element to move one group to the right in the periodic table, which means an increase of one in the atomic number. From this it seems evident that this gives a proof, at least for the radioactive elements, and probably in the case of all lower atomic weight elements, that an increase of one in the atomic number means an increase of one in the positive charge on the nucleus. It seems probable, therefore, that the number of positive charges on the nucleus is equal to the atomic number.

Table I.


[^1]The work of Rutherford and Andrade ${ }^{22}$ serves to further confirm these views. The wave length of the soft $\gamma$ rays from Ra B was determined, and also the X-ray spectrum of lead, with a view to determine the atomic numbers of these and the other radioactive elements. Ra B and lead were found to have the same atomic number, 82, as they gave the same X-ray spectrum. From Table I it is seen that there are several groups of elements having the same atomic number but with different atomic weights. These are tabulated at the bottom of Table I.

It will be noted that the atomic weight of lead, if its source is the uranium series of elements, should be 206. I8, using the latest value of the atomic weight of uranium as 238.r8. The atomic weight of lead has recently been determined by Richards, ${ }^{28}$ who obtained the value 207 . I5 for ordinary lead, not radioactive. In analyzing the lead from a large number of radioactive minerals, mostly uranium, he obtained values varying from 206.4 to the ordinary value, 207 . 15. Soddy, ${ }^{24}$ working with thorium minerals, obtained the value 208 , which would be expected if the end of the thorium series is also lead. More recently Soddy ${ }^{25}$ has started a more extensive investigation, and has obtained about 80 grams of lead from thorium minerals. He finds that the lead has a higher density than the ordinary lead. This is to be expected if the atomic volumes of the isotopes are the same. Richards found no difference between the spectrum of the lead of low atomic weight and the ordinary lead, but Soddy claimed to have found at least one line in the new material which was not given by the old. In some work as yet unpublished, done by Aronberg working with Gale and one of the writers, no difference was found between the spectrum of some lead from Carnotite and the ordinary lead, although the Zeeman effect was also investigated. In this investigation a 2 I foot concave grating was used, and the wave lengths could be measured to 0.001 of an Angstrom.

Lindemann* shows by means of simple thermodynamical reasoning that two elements of different atomic weight must differ either in their chemical or physical properties. Since Soddy has shown that the isotopic forms of lead have the same atomic volumes, and also, of course, the same chemical properties, it follows that the forces between the atoms, and therefor the vapor pressures and the melting points, must vary, and that Soddy's lead from thorite should have a melting point 1.54 degrees higher than ordinary lead. Lindemann concludes that the forces of attraction and repulsion between the atoms have their origin in the nucleus, while, as is generally considered, the chemical properties and the radius of the atom are conditioned by the external electrons. In isotopes the forces of attraction and repulsion are proportional to the atomic weight, that is, probably to the number of positive particles. These forces are, however,

[^2]not usually additive, but are so only in isotopes, so the nuclei of isotopes probably differ in their linear dimensions, but not at all, or very little, in the arrangement of the particles. The question as to the melting point of lead from carnotite is now being investigated by one of the writers of this paper.

The fact that $\alpha$ particles are expelled in so many of the transformations seems to show that the nucleus is composed, in part at least, of helium atoms. The energy of the expulsion of the alpha particles can be accounted for by their passage through the intense electric field around the nucleus. The primary beta particles probably arise from a disturbance of the nucleus, which must be very complex.

The general facts which seem to be proved by all this work described above are, that the nucleus is a fundamental constant of matter, and that the charge on the nucleus determines the character of the element. The atomic weight is not so characteristic as the atomic number or the nuclear charge. The atomic weight is a complex function of the number and configuration of the electrons. Those properties of matter such as gravitation and radioactivity, which are entirely beyond our control by any chemical or physical agents, are functions of the nucleus.

Up to this point, beyond the fact that the atom is a sort of Saturnian system, nothing has been said as to the arrangement of the electrons in the atom, or the distribution of the forces. The first attempt to treat this problem as one of mechanics, and to give a definite picture of the atom, was made by Bohr. ${ }^{26}$ In his calculations, Bohr has used an atom of the Rutherford type, and has combined with the classical mechanics Planck's quantum hypothesis. While Bohr's work has been severely criticized, the very remarkable results he was able to obtain with hydrogen alone make it worthy of careful consideration. Bohr's success lies only in the consideration of atoms with one vibrating electron. The following is a simplified form of his analysis:

Let $m=$ mass of the electron.
$-e=$ charge of the electron.
$\mathrm{M}=$ mass of nucleus.
$\mathrm{E}=$ charge on nucleus.
$a=$ radius of ring of rotation of electrons.
$\omega=$ frequency of revolution of electrons.
Then, $2 \pi \omega=$ angular velocity.
The kinetic energy of an electron can be expressed in two ways:

$$
1 / 2 m(2 \pi \omega a)^{2} \text { or } 1 / 2 e \mathrm{E} / a .
$$

The work necessary to remove an electron from its orbit to a position of rest at $\infty$ is:

$$
e \mathrm{E} / a-1 / 2 m(2 \pi \omega a)^{2}=1 / 2(e \mathrm{E} / a)=\mathrm{W} .
$$

Then

$$
2 a=e \mathrm{E} / \mathrm{W} \quad \text { and } \quad \omega=\frac{\sqrt{2}}{\pi} \frac{\mathrm{~W}^{3 / 2}}{e \mathrm{E} \sqrt{m}}
$$

According to Newtonian mechanics, the energy $W$ should go on increasing as energy is given out by radiation, until the orbit gets smaller and smaller and the electron falls into the nucleus; that is, " $a$ " would decrease and $\omega$ increase. Here Bohr introduces the quantum hypothesis. He assumes that the angular momentum of the electron is constant, and equal to $\tau h / 2 \pi$, where $\tau$ is an integer, and $h$ is Planck's constant; that is, the angular momentum of the electron in its orbit is

$$
2 \pi m \omega a^{2}=\mathrm{W} / \pi \omega=\tau h / 2 \pi
$$

This prevents continuous variations of $\mathrm{W}, a$, and $\omega$.
Then,

$$
\mathrm{W}=\frac{2 \pi^{2} m e^{2} \mathrm{E}^{2}}{\tau^{2} h^{2}} \quad \quad 2 a=\frac{\tau^{2} h^{2}}{2 \pi^{2} m e \mathrm{E}}
$$

Much of the criticism of Bohr's work is directed at this point in his analysis. The idea of an electron undergoing accelerated motion without radiating energy is difficult to accept. There is also difficulty in obtaining any satisfactory physical picture of the process by which light is emitted when the electron changes from one steady state of vibration to the next, as described below.

In a neutral hydrogen atom $\tau$ is equal to I . If this value is substituted in the second equation, the value for the diameter of the hydrogen atom is obtained as I. I $\times 10^{-8} \mathrm{~cm}$., which is of the right order of magnitude.

The electron radiates energy only when it changes from one steady state of vibration to another, and then one quantum of energy is released; that is, for a sudden shrinkage from orbit of $\tau_{2}$ to $\tau_{1}$, there must be a loss of energy $\mathrm{W}=h \nu$ where $\nu$ is the frequency of the radiation.

$$
\begin{gathered}
h \nu=\delta \mathrm{W}=\mathrm{W}_{\tau_{2}}=\mathrm{W}_{\tau_{1}}=\frac{2 \pi^{2} m e^{2} \mathrm{E}^{2}}{h^{2}}\left(\frac{\mathrm{I}}{\tau_{2}{ }^{2}}-\frac{\mathrm{I}}{\tau_{1}{ }^{2}}\right) \\
\nu=\frac{2 \pi^{2} m e^{2} \mathrm{E}^{2}}{h^{3}}\left(\frac{\mathrm{I}}{\tau_{2}{ }^{2}}-\frac{\mathrm{I}}{\tau_{1}{ }^{2}}\right) .
\end{gathered}
$$

In the case of hydrogen, $\mathrm{E}=e$. We can then calculate the value of the constant $2 \pi^{2} m e^{2} \mathrm{E}^{2} / h^{3}$ which is equal to $3.26 \times 10^{15}$. The wellknown Balmer formula for the series of lines in the hyrogen spectrum is $\nu=\mathrm{K}\left(\mathrm{I} / \tau_{2}{ }^{2}-\mathrm{I} / \tau_{1}{ }^{2}\right)$ in which K as determined by experiment is 3.29 times $10^{15}$. This practical identity of Bohr's calculated value of the Rydberg constant and the experimental value is probably the greatest triumph of Bohr's work.

If the value $I$ is assigned to $\tau_{2}$, and a series of values, $I, 2,3$, etc.,
given to $r_{1}$, the frequencies of a series of lines in the ultraviolet are determined. This series was not known at the time of Bohr's first work, but has since been found by Lyman of Harvard. (Not published.) The physical picture obtained of the production of this series of spectrum lines is as follows:

$N$ represents the nucleus of the atom. The rings $\mathrm{I}, 2$, and 3 correspond to the orbits of the electron in the various steady states of motion. When an electron falls from one steady state to the next one of smaller radius of vibration, one quantum of energy is liberated. In the above spectral series, all the lines are formed by electrons falling from the second ring and beyond, all the way to the first ring. The first line in the series is due to an electron falling from the second to the first ring; the second line to an electron falling from the third to the first ring, and so on.

If $\tau_{2}=2$, and a series of values be assigned to $\tau_{1}$, the ordinary Balmer series for hydrogen results. For $\tau_{2}=3$, there results an infra-red series predicted by Ritz, and later discovered by Paschen. This model does not account for the Pickering series of lines which is ordinarily attributed to hydrogen, but Bohr shows that this series is accounted for by the helium atom.

Very recently another confirmation of Bohr's theory has been given by Evans ${ }^{27}$ in his work on the spectra of hydrogen and helium. Bohr's formula, when modified so as to take account of the mass of the nucleus, is

$$
\nu=\frac{2 \pi^{2} e^{2} \mathrm{E}^{2} \mathrm{M} m}{h^{3}(m+\mathrm{M})}\left(\frac{\mathrm{I}}{\tau_{2}{ }^{2}}-\frac{\mathrm{I}}{\tau_{1}^{2}}\right)
$$

This makes a slight change in the value of the constant in passing from hydrogen to helium, and the ordinary Balmer series for hydrogen, which according to Bohr's original work could come from either of the two
elements, is found to be slightly different for the one than for the other. Thus it became very important to investigate carefully the spectra of these two elements, and see if this series could be detected in helium, and whether the slight differences just spoken of existed. Evans was able to observe the first few members of this series, and the measured values of the lines are very close to the theoretical.

Bohr ${ }^{28}$ has also shown that if the principle of relativity is introduced, his formula takes the following form, which accounts for some of the extremely small errors found by Evans.

$$
\nu=\frac{2 \pi^{2} e^{2} \mathrm{E}^{2} m \mathrm{M}}{h^{3}(m+\overline{\mathrm{M}})}\left(\frac{\mathrm{I}}{\tau_{2}^{2}}-\frac{\mathrm{I}}{\tau_{1}^{2}}\right)\left[\mathrm{I}+\frac{\pi^{2} e^{2} \mathrm{E}^{2}}{c^{2} h^{2}}\left(\frac{\mathrm{I}}{\tau_{2}^{2}}-\frac{\mathrm{I}}{\tau_{1}^{2}}\right)\right] .
$$

Helium is considered to have a charge on its nucleus of $2 e$, or $\mathrm{E}=2 e$. The atom with one positive charge has one vibrating electron. The following formula results for helium:

$$
\nu=\mathrm{K}\left(\frac{\mathrm{I}}{\left(\tau_{2} / 2\right)^{2}}-\frac{\mathrm{I}}{\left(\tau_{1} / 2\right)^{2}}\right)
$$

The physical interpretation is the same as for hydrogen. For various values of $\tau_{2}$, the following series result:
$\tau_{2}=\mathrm{I}$-Extreme ultraviolet; not known.
$\tau_{2}=2$-Extreme ultraviolet; not known.
$\tau_{2}=3$-Two series, as $\tau_{1}$ is odd or even. (The lines of the two series alternate.) These series were observed by Fowler in mixtures if hydrogen and helium, but had been attributed to hydrogen.
$\tau_{2}=4$-The lines of two series, alternating as $\tau_{1}$ is odd or even. The first of these is the ordinary Balmer series, which evidently can come from either hydrogen or helium. The second is a series which was observed by Pickering in the star $\zeta$-Puppis, and was attributed to hydrogen.
In the work of Evans which was mentioned, there is a further confirmation of Bohr's theory. By carefully adjusting conditions he was able to obtain the Pickering series of lines from absolutely pure helium, which should be the source of them, according to Bohr.

Balmer's series has never been observed in the laboratory beyond $\tau_{2}=12$, while in stellar spectra it extends to $\tau_{2}=33$. Therefore in vacuum tubes no hydrogen atoms exist of greater diameter than corresponds to $\tau_{2}=12$, or $2 a=1.6 \times \mathrm{ro}^{-8} \mathrm{~cm}$. For $\tau_{2}=33,2 a=\mathrm{I} .2 \times$ $\mathrm{r}^{-5} \mathrm{~cm}$. Therefore, according to Bohr's theory, there are in the stars hydrogen atoms 1000 times the diameter of those on the earth.

Jeans ${ }^{31}$ points out that in the above work the value of M is supposed to be very great in comparison with $m$. If this is not true, the value of Rydberg's constant is given by

$$
\mathbf{K}=\frac{2 \pi^{2} e^{2} \mathrm{E}^{2}}{h^{3}} \frac{m \mathrm{M}}{(m+\mathrm{M})}
$$

If $M$ refers to the value for hydrogen, 2 M is the value for helium. Then $\mathrm{K}_{\mathrm{H}}: \mathrm{K}_{\mathrm{H} e}=\frac{4}{\mathrm{M}+1 / 2 m}: \frac{\mathrm{I}}{m+\mathrm{M}}$. From the best observed value of the ratio $\mathrm{K}_{\mathrm{H}} / \mathrm{K}_{\mathrm{He}}, \mathrm{M} / m$ is given as $\mathrm{I} 836 \pm \mathrm{I} 2$, which is in close agreement with the experimental value.

The above calculation would seem to be inconsistent with the idea of the atom as developed by Rutherford, for he states that practically all of the mass of the atom lies in the nucleus. In that case, the value of M for helium would not be twice but four times the value for hydrogen, and the helium nucleus would consist of four positive and two negative electrons.

Bohr extends his calculations to the lithium atom, and in considering only one vibrating electron obtains good results. In all of his work, however, when more than one electron is considered, his results are not correct. One of the serious objections to Bohr's theory is that he has been unable to explain the ordinary spectrum of hydrogen. Nicholson ${ }^{22}$ has extended Bohr's calculations to every possible mode of vibration in attempting to secure a formula or formulas, giving the lines of the ordinary hydrogen spectrum, but has found that they can be accounted for by no possible vibration.

Perhaps the most fundamental objection to Bohr's work lies in the fact that he has combined two basically different kinds of mathematics in working out this theory. It might be possible under such conditions to obtain results which are absolutely incorrect, for the two are contradictory.

Nicholson claims to have proven both by the classical mechanics and by Bohr's mechanics that coplanar, concentric rings of vibrating electrons are unstable. That is, if there are to be two or more rings of electrons in an atom, they cannot lie in the same plane, which would make Bohr's theory untenable. This presents difficulties in still another way. If we consider valence as due to certain electrons which are ordinarily considered as being near the outside of the atom, these electrons would either have to be in an outer ring, by themselves, or else have some peculiar properties different from the other electrons in the ring. J. J. Thomsen not only believes in the existence of more than one ring of electrons, but is some work yet unpublished, states that he has actually counted the number of rings in certain atoms. This claim of Nicholson's would seem to be wrong, but it may be very true, as he says, that a large number of the vibrations in such a system are unsteady, and would result in the expulsion of an electron.

Bohr has not had better success in accounting for a large part of the
spectrum of helium than he had in the case of hydrogen. Helium has six Balmer series which are not explained. Bohr considered only the first electron in his calculations on this element, and Nicholson thought that possibly the rest of the spectrum might be due to the other electron. He therefore made the necessary calculations, but could obtain no other series. Two of the series of lines calculated for helium lie in the ultraviolet, and are not knowm. Lyman of Harvard, as a result of his investigations, states that helium has no Schumann region spectrum.

It is well to remember that Bohr attempts no physical picture or cause of the change of an electron from one steady state of vibration to the next. In his theory of spectra, the energy which goes into the spectrum is atomic energy. This would be a serious objection if it were not for the fact that it is very easy to think of it in a slightly different way. The energy which it is necessary to apply to hydrogen to give these spectral lines may be used to remove an electron from one of the inner rings of vibration to one farther out from the nucleus. This is equivalent to increasing the atomic energy, and the increase, which came from an outside source, is given out as monochromatic radiation when the electron falls toward the nucleus.

Of the work on the structure of the atom none is more interesting than that of Nicholson, a number of his predictions from a theoretical standpoint having been confirmed in a most spectacular way. His work is also of extreme interest to chemists, since it deals with elements which have not as yet, been discovered on the earth. For a considerable time it has been known that there are at least two important elements which are recognized by their spectrum, but which have not as yet been discovered on earth. A number of spectral lines of unknown origin were known to be given by the corona of the sun, and these were attributed to an element coronium, while the lines of unknown origin emitted by the nebulae were supposed to be due to an element which was given the name nebulium. The chief line of its spectrum is the line $\lambda 5007$. Nicholson was able, by the assumption that certain lines belong to the spectrum of nebulium, to calculate the wave lengths of all of the other lines but two, for which he was altogether unable to account. Just at the time when Nicholson made his calculation, Wolf of Heidelberg was engaged in the study of these same lines in the spectra of the nebulae, and he found that certain lines, which had formerly been attributed to nebulium, acted differently from the others. He found, for example, that in the ring nebula in Lyra, discovered by Darquier in 1779, certain of these lines were emitted by the interior, and others by its outer part. The remarkable part of this discovery was that the two lines which were thus shown to have different origin from the true lines of nebulium, were just the two lines which Nicholson was unable to connect theoretically with the spectrum
of nebulium. Another of Nicholson's predictions, which was confirmed in a remarkable manner, was that of the existence of a new nebulium line of wave length 4352.9. On photographing the spectrum, Wright, of the Lick observatory, found this line, and on looking over his older photographs, he found the line on a plate taken several years before the prediction of its existence was made, but the line was so weak that it had escaped observation.

In an extremely long series of papers Nicholson ${ }^{30}$ has arrived at a very comprehensive theory of spectra, and has applied it to such problems as cosmic evolution. It gives a picture of operations in vast nebulae, many light years in extent, in connection with atomic and subatomic structure; changes occupying milleniums of time are discussed in connection with those occurring in a fraction of a second. Its very comprehensiveness causes some skepticism, but the remarkable results he has obtained would seem, in part at least, to justify the theory.

Nicholson also uses an atom of the Rutherford type, in which the electrons are vibrating in orbits around the positive nucleus. All of Nicholson's work is, however, based on calculations made by the classical mechanics. The quantum hypothesis is not introduced to obtain any of the results, but in the course of his work, Nicholson shows how the results seem to be related to this hypothesis.

One of the interesting points of this theory is that the energy which goes into the spectrum is secured from the outside, and is not, as originally in the theory of Bohr, atomic energy. This would seem to be much more probable.

The electrons are considered as moving in a steady state, in a ring around the nucleus. Outside forces acting on these cause them to take up a vibration perpendicular to the plane of the ring. There are several modes of vibration, depending on the number of electrons in the ring. The strongest vibration would have a frequency equal to the frequency of the electrons in the ring. This is expressed by $q=\omega$, or $q / \omega=\mathrm{I}$. In vibrations of class zero the entire ring vibrates as a whole, always keeping parallel to its original position. The second class of vibration consists in the ring vibrating in halves. That is, there are two nodes and two crests in the wave which travels around the ring. It is evident that there are as many classes of vibrations as there are electrons in the atom. The vibrations of the higher classes would not be expected to be strong, and Schott has shown that the vibrations of a class higher than three would not ordinarily be strong enough to see. The mathematical analysis is largely the same as that developed by J. J. Thomson in his work on his atomic model, and will not be given completely here. Only the results which are used directly will be reproduced.
$e=$ charge on an electron.
$a=$ radius of the ring.
$\nu=$ no. charges in nucleus.
$m=$ mass of an electron.
$q / \omega=$ frequency of revolution.
The equation for the period of vibration which Nicholson obtains is

$$
m q^{2}=e^{2} / 8 a^{3}\left(8 \nu+\mathrm{P}_{k}+\mathrm{P}_{o}\right)
$$

where

$$
\mathrm{P}_{k}=\Sigma^{n-1}\left(\cos 2 \mathrm{~K} s \pi / n \csc ^{3} s \pi / n\right)
$$

and

$$
\mathrm{P}_{0}=\mathrm{\Sigma}^{n-1^{\circ}}\left(\mathrm{I} \cdot \csc ^{3} s \pi / n\right) .
$$

There may be as many values of the period as there are of $\mathrm{P}_{k}$, which is as many as the number of electrons. $k$ is called the class of the vibration.

The first atom which Nicholson considered was one in, which the number of positive charges in the nucleus is four. That is, $\nu=4$. This atom he has called nebulium. First consider the neutral atom, in which there are four negative electrons. The period equation may be written as

$$
m a^{3} q^{2}=e^{2}\left[\nu+\left(\mathrm{P}_{k}-\mathrm{P}_{0}\right) / 8\right], k=0, \mathrm{I}, 2, \text { etc. }
$$

If $\omega=$ the angular velocity of the ring, the force of an electron towards the center is $m a \omega^{2}$. The radial attraction of the positive nucleus is $\nu e^{2} / a^{2}$. The combined action of the other electrons gives a radial repulsion of $e^{2} \mathrm{~S}_{n} / 4 a^{2}$ where $\mathrm{S}_{\boldsymbol{n}}=\Sigma^{n-1} \csc s \pi / n$. Therefore,

$$
m a \omega^{2}=e^{2} / a^{2}\left(\nu-\mathrm{S}_{n} / 4\right) \quad \text { or } \quad e^{2} / m a^{3}=\omega^{2}\left(\nu-\mathrm{S}_{n} / 4\right)
$$

is the equation for the steady state of the neutral atom. The period equations of this system then become

$$
\begin{aligned}
q^{2} / \omega^{2} & =\frac{16}{15-2 \sqrt{2}}, k=0 \\
& =\mathrm{I}, k=\mathrm{r}=3 \\
q^{2} / \omega^{2} & =\frac{8}{8+\sqrt{2}}, k=2
\end{aligned}
$$

or

$$
q / \omega=(\mathrm{I} .146533, \quad \mathrm{I}, \quad 0.849778)
$$

Correcting for a stationary observer, and introducing negative values of $k$,

$$
\begin{gathered}
q / \omega=(\mathrm{I} . \mathrm{I} 46533, \mathrm{I} \cdot \mathrm{I} 50222, \quad 2, \quad 2.849778, \\
k=\mathrm{o} \quad k=-2 \quad k=\mathrm{I} \quad k=2, \quad k=3
\end{gathered}
$$

In wave lengths ( $\mathrm{C}=$ velocity of light) and considering a vibration in the plane where $q=\omega$, which we would expect to be strong,

$$
\lambda=2 \pi C / \omega(\mathrm{I}, 0.872 \mathrm{I} 94,0.86939)
$$

The first value is for $q=\omega$, the second for $k=0$, the third for $k=-2$.

The chief nebular line is $\lambda=5006$.9. If this is chosen as the fundamental line, then $(5006.9)(0.872194)=4367.0$ should be the next line of this set. A strong line is known at 4363.4 . Also (5006.9)(o.86939) $=$ $435^{2.9}$ should be the next. At the time of this work, no line was known at 4352.9 but it was afterward found by Wright ${ }^{31}$ of the Lick Observatory, and measured as 4352 .3. Nicholson made similar calculations for this atom with $2,3,5$, and 6 electrons. The results are given below:

| $n=6\left\{\begin{array}{l} \lambda=2 \pi \mathrm{C} / \omega \times \\ \lambda= \\ \text { Observed.... } \end{array}\right.$ |  |  | $\begin{gathered} k=1 . \\ 1 \\ 4959 \cdot a \\ 4959 \end{gathered}$ | $\begin{gathered} k=2 . \\ 0.81934 \\ 4063.2 \\ 4059.0 \end{gathered}$ | $k=-2 .$ | $\begin{gathered} k=3 . \\ (0.6666) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n=5\left\{\begin{array}{l} \lambda=2 \pi \mathrm{C} / \omega \times \\ \lambda= \\ \text { Observed } \ldots . \end{array}\right.$ | $\begin{gathered} \text { I } \\ 4743.0 \\ 4740.0 \end{gathered}$ | 0.80991 $3838.9 a$ 3835.8 |  |  | $\begin{aligned} & 0.81573 \\ & 3869 . a \\ & 3869 . \end{aligned}$ |  |
| $n=3\left\{\begin{array}{l}\lambda=2 \pi \mathrm{C} / \omega \times \\ \lambda= \\ \text { Observed. } \ldots .\end{array}\right.$ | $4026.8 a$ 4026.8 | $\begin{aligned} & 0.9250 \\ & 3724.8 \\ & 3729.0 \end{aligned}$ |  |  |  |  |
| $n=2\left\{\begin{array}{l} \lambda=2 \pi \mathrm{C} / \pi \times \\ \lambda= \\ \text { Observed.... } \end{array}\right.$ | $3967.6 a$ 3967.6 | $\begin{aligned} & 0.96826 \\ & 384 \mathrm{I} .5 \\ & 3835.8 \end{aligned}$ |  |  |  |  |

" $a$ " placed after a wave length shows that this one was assumed for that particular series.

The first method of attack used by Nicholson is briefly this, as is seen from the previous work. Making use of the theoretical analysis, he obtains the ratios of the wave lengths of what might be called a series, but not their absolute values. If a value for one of them is assumed, the rest are given. The agreement in some cases is far from good, and later it was found necessary to consider certain of the lines as due to a different source than given here. It is not clear as to why in the series for $n=5$ for instance, the line for $k=-2$ should appear, and not the one for $k=2$, or for the vibrations which should be still stronger, $k=\mathrm{I}$.

It will be seen that there is an error of about $4 \mathrm{~A}^{\circ}$ in a large number of these calculated wave lengths. Nicholson shows that, except in the case of the vibration of Class $O$, this can be accounted for by the fact that the velocity of the electron is not small compared with that of light, or at least is not small enough so that it can be neglected without error. He calculates that the error due to this cannot be greater than about one part in a thousand, which amounts to about $4 \mathrm{~A}^{\circ}$ with the wave lengths considered.
Bromwich pointed out to Nicholson that in the case of the vibration of Class O , the mass of the electron and the nucleus did not cancel out, but that a correction term of the form

$$
(\mathrm{I}+n m / \mathrm{M})
$$

should be introduced into the period equation. If $H$ is the value of $M$ for a hydrogen atom, then

$$
m / H=0.00054 \text { approximately }
$$

This makes it possible to calculate the atomic weight of nebulium, which gives the value I. 3 .

Using this method of ratios, Nicholson has calculated the wave lengths of lines for systems of $\nu=2,3,5$, and 6 . For $\nu=2$ and 3, the lines were found by Wolfe in the nebulae. $\nu=5$ was found in the solar corona, where Nicholson accounted for 2 I out of 27 lines found.

For the systems $2 e, 4 e, 5 e$, and $6 e$, calculations have been made for the atomic weight by the method described above. From the values obtained, it can be shown that the atomic weights of these simple ring systems are proportional to the squares of the number of charges on their nuclei. For the entire series, the results are as follows:

| Element. | Pr.H |  |  | Nu | Pf | Arc |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Atomic no. | Ie | $2 e$ | 3 e | $4{ }^{2}$ | 5 | $6 e$ |
| Atomic wt. | 0.082 | 0.327 | 0.736 | I. 3 I | 2.1 | 2.9 |
| Ratio. | $\mathrm{I}^{2}$ | $2{ }^{2}$ | $3^{2}$ | $4^{2}$ | $5^{2}$ | $6^{2}$ |

Here is a relation involving $\mathrm{N}^{2}$ as in Moseley's work.
Up to this point, Nicholson used his method of ratios, and thus calculated the wave lengths of the most of the unknown lines in the nebulae and the solar corona, and succeeded in securing approximate values for the atomic weights. No connection has as yet been shown to exist between the systems of different nuclear charge. This relation is brought out later. Also, no relation has been shown between the principal frequency of vibration of the systems of the same nuclear charge, with varying numbers of electrons. This relation is shown by the consideration of the energy of the systems involved.

As Nicholson points out, it is impossible to know the absolute energy of the atom, ${ }^{1}$ but changes of energy may be used. By a very simple analysis Nicholson arrives at the following equation of energy of the atom, in which the term D is equal to the energy in a standard configuration:

$$
1 / 2 m n v^{2}=n e^{2} / a\left(\nu-1 / 4 \mathrm{~S}_{n}\right)+\mathrm{D}
$$

By the condition of steady motion,

$$
m a^{3} \omega^{2}=e^{2}\left(\nu-1 / 4 \mathrm{~S}_{n}\right)=m a v^{2}
$$

Now, $\omega=2 \pi \mathrm{C} / \lambda^{\prime}$, where $\lambda^{\prime}$ is the principal wave length. This gives

$$
m n a^{2} \omega^{2} \cdot \frac{2 \pi}{\omega}=\frac{m n}{\mathrm{C}}\left\{\frac{e^{2}}{m}\left(\nu-1 / 4 \mathrm{~S}_{n}\right) 2 \pi \mathrm{C}\right\}^{2 / 2} \lambda^{1 / 3}
$$

[^3]Therefore it is seen that the ratio of energy to frequency is proportional to $n\left(\nu \cdots 1 / 4 \mathrm{~S}_{n}\right)^{2 / 2} \lambda^{1 / 3}$, and for convenience this will be called the atomic energy, E . Then $\mathrm{E}=n\left(\nu-1 / 4 \mathrm{~S}_{n}\right)^{2 / 3} \lambda^{1 / 3}$.

Now the calculation of E for the various atoms of protofluorine where $\nu=5$, gives the following result:

|  | $n=5$. | $n=4$. | $n=3$. | $n=2$. |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{E} \ldots \ldots \ldots \ldots \ldots$ | 187.04 | 164.6 | 134.7 | 97.4 |

If 7.482 is chosen as the unit of energy, the number of units for the different systems is as follows:


It is now possible to calculate the wave length of the line of principal frequency for the system $n=2$. For this system it is seen that there are 6.5 units of E per electron, therefore

$$
E=2(6.5 \times 7.482)=2\left(5-1 / 4 S_{2}\right) \lambda^{1 / 8} \quad\left(S_{2}=1.000\right) .
$$

From this $\lambda=5073$. A weak line is known at this point.
If the energy of one of these systems is decreased by radiation by certain discrete amounts, we would expect a series of lines of some sort to be the result. That is, a series of spectrum lines might emanate from atoms whose internal angular momenta have run down by discrete amounts from a standard, In the case of protofluorine with two electrons, the loss of energy would be expected to be large enough so that the series could be observed. The wave lengths of the lines of this series may be expressed by the formula

$$
\lambda=(97.107 / 2-\mathrm{I} .223 r)^{3} /(4.75)^{2} .
$$

That is, the energy E is being decreased by an amount 2.2446 each time. The term $r$ takes successively the values $\mathrm{I}, \mathbf{2}, 3$, etc. The series is as follows:

| $r$ | 0 | I | 2 | 3 | 4 | 5 | 6 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Calculated. | 5073 | 4725 | 4400 | 4086.5 | 3788 | 3506 | 3238 |
| Observed. | 5073 | 4725 | 4400 | 4087.4 |  | 3505 |  |

All these are weak lines. It may be pointed out that this method of calculating a series is very similar to Bohr's method where he decreases the internal energy of the atom by discrete amounts to give the members of the series. Bohr has given some sort of an idea as to how this takes place, while Nicholson merely states that the energy is lost by radiation. Such vibrations as give rise to this type of series are vibrations in the plane of the ring, as in Bohr's model. It will be noted later that Nicholson makes considerable use of this method, even discarding his original identifications of some of the nebulium and protofluorine lines, and putting them into series of this type.

If $Q$ equals the number of quanta of energy per electron, choosing as a unit the value $h / \underline{5}$, where $h$ is Planck's unit, a still more useful equation is obtained,

$$
Q=\mathrm{E} / n=\frac{\lambda^{1 / 3}\left(\nu-1 / 4 \mathrm{~S}_{n}\right)^{2 / 3}}{0.06235} .
$$

For the atom of protofluorine where $\nu=5$, the various values of $Q$ are as follows:

| $n \ldots \ldots \ldots \ldots \ldots \ldots$ | 5 | 4 | 3 | 2 |
| :--- | ---: | :---: | :---: | :---: |
| $Q \ldots \ldots \ldots \ldots$ | 600 | 658.5 | 718 | 778.5 |

These values of $Q$ can easily be shown to be in the ratio of io: II : 12 : 13 : 14 .
In the case of Pf just dealt with, the value of $Q$ may be expressed by a function of the following type:

$$
\mathrm{Q}=\mathrm{A}+\mathrm{B} n+\mathrm{C} n^{2}
$$

where $\mathrm{A}, \mathrm{B}$, and C are constants. If such a formula is to be applied to other atoms than Pf, these terms may not be constants, but functions of the nucleus. Since the function $\mathrm{E} / n$ has been shown to be harmonic, it may be supposed that the function $\mathrm{E} / \nu$ would be of the same general type, that is:

$$
\mathrm{E} / \nu=\alpha+\beta \nu+\gamma \nu^{2},
$$

where $\nu=n$, a neutral atom. Therefore the function $\mathrm{E} / n$ for any atom is of the form

$$
\mathrm{E} / n=\mathrm{A}+\mathrm{B} \nu+\mathrm{C} \nu^{2}-n(\mathrm{D}+\mathrm{E} \nu)+\mathrm{G} n_{2}
$$

Since E in all cases is very closely a multiple of Planck's unit, the constants A to G will be close to whole numbers. The divergencies might be due to the rotation of the nucleus of the atom as a whole, at the expense of the angular momentum of the system, which otherwise might be exactly a multiple of $h / 2 \pi$. Nicholson calculates the values of these constants from the case of Pf, and then uses this method for the recalculation of the lines of the sytem $4 e$, nebulium. He finds that it is necessary to change the source of a number of the lines from that given them by his first method. More of them are now thought of as coming from vibrations which fall into the type of series where the cube roots of the wave lengths differ by constant amounts, as in the series calculated for the system $\nu=5, n=2$. The value of $Q$ for such series can be found from a formula of the type used in the series just referred to:

$$
Q=\left(Q_{n} / \mathrm{I} 8 r\right),
$$

where $r$ is variable, taking successively the values $\mathrm{I}, 2,3$, etc.
The law relating the number of quanta of positive and negative systems is:

$$
(\mathrm{E} / n)_{\nu-m}+(\mathrm{E} / n)_{\nu+m}=2(\mathrm{E} / n)
$$

A series might arise from negatively charged systems, from the energy disturbances due to the repulsion of negative electrons by the system. Such series might be expected to be quite strong. A neutral system would be unaffected by electrons, only becoming ionized by virtue of its own unstable vibrations.

Some very important relationships may be brought out by the consideration of the relations between the energy of the various neutral systems of different nuclear charge. If the principal wave length of the system is known, it is possible to calculate the value of $\mathrm{E} / n$ from the formula

$$
\mathrm{E} / n=\frac{\lambda^{1 / 8}\left(\nu-1 / 4 \mathrm{~S}_{n}\right)^{2 / 3}}{(0.06235)^{2}}
$$

The values of $\mathrm{E} / n$ for the systems $\nu=5,4$, and 2 are $600,576.08$, and 374.04, respectively. These are three terms of the following harmonic sequence:

| D................ 5 |  | 4 |  | 3 |  | 2 |  | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| E/n............. 600 |  | 576.08 |  | 500.76 |  | 374.04 |  | 195.92 |
| Difference. | 23.92 |  | 75.32 |  | 126.72 |  | 178.12 |  |
| Second difference. . |  | 54.40 |  | 54.40 |  | 54.40 |  |  |

As stated before, it might be expected that these values of $\mathrm{E} / \nu$, which are obviously the same as $\mathrm{E} / n$, could be expressed by the formula

$$
\mathrm{E} / v=\alpha+\beta \nu+\gamma \nu^{2} .
$$

The following three equations can be solved for the constants:

$$
\begin{align*}
& 600.00=\alpha+5 \beta+25 \gamma  \tag{I}\\
& 576.08=\alpha+4 \beta+16 \gamma  \tag{2}\\
& 500.76=\alpha+3 \beta+9 \gamma \tag{3}
\end{align*}
$$

and $\alpha=-32, \beta=254.4, \gamma=-25.6$. Therefore

$$
Q=\mathrm{E} / \nu=254.4 \nu-25.6 \nu^{2}-32
$$

If the values of $\mathrm{E} / \nu$ for the systems $6 e, 7 e, 8 e, 9 e$ and roe are calculated the following results are obtained:

| $\nu \ldots \ldots \ldots \ldots$ | 6 | 7 | 8 | 9 | 10 |
| :--- | :---: | :---: | :---: | :---: | :---: |
| E/v................... 572.52 | 493.64 | 363.36 | 181.68 | -51.40 |  |

The fact that for $\nu=$ ro the energy is negative points to the fact that there are only 9 simple ring systems possible. If the first one is left out of consideration, and hydrogen is not put in the periodic table, the number of simple ring systems is the same as the number of groups in the first two rows of the periodic table. It will be shown later that the simple ring system $x e$ is very closely related to hydrogen so that leaving them both out of consideration at this point has some justification, particularly as the place of hydrogen in the table is very uncertain.

Knowing the value of $\mathrm{E} / \nu$ for the various systems, it is possible to find their principal frequencies from the following formula:

$$
\lambda=\left(\frac{\mathrm{E} 0.06235}{\nu}\right)^{3} \frac{\mathrm{I}}{\left(\nu-\mathrm{I} / 4 \mathrm{~S}_{n}\right)^{2}}
$$

| $\nu \ldots \ldots \ldots \ldots \ldots$ | 6 | 7 | 8 | 9 |
| :---: | :---: | :---: | :---: | :---: |
| $\lambda . \ldots \ldots \ldots \ldots . \ldots$ | 2613.57 | 1323.12 | 431.02 | 45.15 |

All these are outside of the range of observation, but it will be shown later that the first of these exists in the nebulae, and it has been given the name arconium. It will also be shown that the system $1 e$ exists, and it has been given the name protohydrogen. Its principal wave length is calculated as 1823.55 , which is exactly one-half the limit of the Balmer formula for hydrogen.

The system $2 e$ is present in the nebulae, and in Nova Persei. The atom with nucleus $3 e$ is also present in the nebulae, but its lines are not as strong as those of $2 e$. The system $4 e$ is nebulium and gives rise to the strongest nebular lines. Protofluorine, $5 e$, has not been found in the nebulae, but is one of the main constituents of the solar corona. As just stated, $6 e$, arconium, and the system $7 e$ are found in the nebulae.

The remarkable agreement of these theories of Nicholson's with the facts would seem to indicate that there is here an extremely broad foundation for a system on which the building up of the chemical elements may rest. The relations between the energy of these systems seems to indicate that the.principle of the constancy of angular momentum may be the physical basis of Planck's theory and also the basis of all the possible arrangements of electrical charges into the form of ordinary matter.

One of the most important and interesting pieces of work which Nicholson has done is in connection with the spectra of the Wolf-Rayet stars. These stars are considered by the astronomers as the earliest type known. They are regarded as being some sort of evolution product of the nebulae. The only ordinary elements which are present are hydrogen and possibly helium, although the last is not well represented unless, as Bohr suggests,* the Pickering series is due to this element. Nicholson shows that a number of Balmer series exist in these stars, and identifies them in a remarkable manner with the constants of the simple ring system called nebulium.

If the lines of these stars are examined they are found to contain a number of lines in the ratio of $5 / 4$. Thus:

$$
\begin{array}{ll}
5285 / 4228=\text { I.2500 } & 5693 / 4555=\text { I. } 2499 \\
5813 / 4652=1.2495 & 5593 / 4473=\text { I.2503 }
\end{array}
$$

If the Balmer formula is considered for one special case the following relationship is found:

$$
\lambda=\lambda_{0} m^{2} / m^{2}-\mathrm{I}
$$

For $m=2$ and 4 the following results:

$$
\lambda_{2}=4 / 3 \lambda_{0} \quad \lambda_{4}=16 / 15 \lambda_{0} \quad \lambda_{2} / \lambda_{4}=5 / 4
$$

[^4]This suggests that Balmer series exist in the Wolf-Rayet stars, and a simple calculation gives the following:

$$
\lambda=(4104,3963.5) m^{2} / m^{2}-I
$$

A further examination of the lines leads to the following four series:

$$
\lambda=(4 \mathrm{IO4}, \text { or } 3963.5)\left(\frac{m^{2}}{m^{2}-\mathrm{I}} \text { or } \frac{m^{2}}{m^{2}-0.3286}\right)
$$

It was found in the previous work that the three main vibrations of the neutral nebulium atom had frequencies in the following ratio:

$$
q^{2} / \omega^{2}=\text { I, 1.3I45, o. } 8496
$$

Now $0.3286=1.3145 / 4$. This shows that these series are in some way related to the nebulium atom. It seems probable that another series or rather two series might exist in which the term 0.3286 was replaced by one-fourth of the other ratio for the third line of the neutral atom.

$$
0.8496 / 4=0.2124
$$

The formula would then be

$$
\lambda=(4104,3963.5) \mathrm{m}^{2} / \mathrm{m}^{2}-0.2124
$$

Lines calculated for $m=2$, and 3 give lines which are known in these stars, thus confirming the theory.

In general then, the formula for the Balmer series in the Wolf-Rayet stars may be written as

$$
\lambda=(4104,3963.5)\left(\frac{m^{2}}{m^{2}-q^{2} / 4 \omega^{2}}\right) .
$$

A search for another limiting frequency gives the value 5254. We now have nine Balmer series which may be written as

$$
\lambda=(4254,4104,3953.5)\left(\frac{m^{2}}{m^{2}-q^{2} / 4 \omega^{2}} \text { or } \frac{m^{2}}{m^{2}-\mathrm{I}}\right) .
$$

A consideration of the limiting wave lengths gives still another way of expressing these formulae. If they are written in wave numbers their differences are seen to be constant.

$$
10^{8} / \lambda_{0}=25227,24366 \cdot 5,23506
$$

with the constant difference 860.5 . Therefore $\lambda_{0}{ }^{-1}=A+B n$ where $n$ takes integral values. Substituting values for this and rearranging it, the following formula for the Balmar series in the Wolf-Rayet stars is obtained:

$$
\lambda=\frac{2 \lambda_{0}}{\mathrm{I}+n d}\left(\frac{m^{2}}{m^{2}-q^{2} / 4 \omega^{2}} \text { or } \frac{m^{2}}{m^{2}-\mathrm{I}}\right)
$$

in which $\lambda_{0}=5007$, the principal wave length of the neutral atom of nebulium, $n$ takes successive integral values, and $d=0.08609$ and is not arbitrary, but is calculated from data involved in the consideration of the neutral nebulium atom.

The above equation is one of the most remarkable and important points of Nicholson's work, for in it he succeeds in bringing together the simple ring systems which are not known on the earth, and our ordinary elements.

It is evident that a change in the term $n$ means a change of some sort in the atom. It is also evident that it must be of a character that the force between the component parts does not change. It seems inevitable that the change must consist in a change in the nucleus, which does not alter its charge. It is significant that the simple ring systems seem to be incapable of giving rise to Balmer series, and the only logical conclusions is that they depend on the intimate structure of the nucleus. The elements which give rise to Balmer series may then be looked upon as the evolution products of the simple ring system on which the value of $\lambda_{0}$ depends. This is considering $\lambda_{\circ}$ as belonging to any simple ring system and not to nebulium alone.

Nicholson shows that the simple ring system $1 e$ can have only one vibration frequency, $q=\omega$. This has already been calculated as $\lambda=$ 1823.35, which is exactly one-half of the limiting wave length of the Balmer series for hydrogen. From the formula

$$
\lambda=\frac{2 \lambda_{0}}{1+n d}\left(\frac{m^{2}}{m^{2}-4}\right)
$$

it is seen that, to derive the hydrogen Balmer formula, $n$ must be equal to 0 . That is, hydrogen would appear to be the first evolution product of the system $\mathrm{I} e$, protohydrogen.

It should be noted that Nicholson has in a rather round-about way succeeded in evaluating the Rydberg constant even more closely than did Bohr. He has not, however, attempted to give any physical picture of the mechanism of the production of the Balmer series.

While up to the present time the evolution products of the other systems are not known in general, it is likely that they may be some of our terrestrial elements. The lines due to a number of the evolution products of nebulium are shown in the Wolf-Rayet stars.

No work has yet been published connecting helium with the simple ring systems, although from the fact that it appears in the nebulae and the stars about the same time as does hydrogen, it seemed likely that it is one of the early evolution products of one of the systems. In some work as yet unpublished Nicholson has succeeded in showing that helium is the evolution product of the system $2 e$.

From the progressive changes of the spectra of the stars, and other evidence which points to their age, it seems likely that all of our common elements are more complex forms of matter than the simple ring systems and hydrogen, and are built up from them. In such spectra the elements make their appearance in the order of their atomic weights.

According to Nicholson's idea, then, our ordinary terrestrial elements are evolution products of the simple ring systems found in the nebulae and the stars. That is, they have nuclei which are complex, containing both positive and negative electrons. This is in good accord with other facts but it does not agree with Rutherford's idea that the nucleus of the hydrogen atom may be the positive electron. If the astronomical evidence is admitted, it may be safely assumed that in the novae and nebulae, where the temperature is supposed by Nicholson to be very high, the complex atoms are unstable, breaking up into simple ones, or if the process is looked at from the other point of view, as these hot bodies cool the simple ring systems condense, becoming more complex and giving rise to the elements known on the earth.

The only very important papers on atomic structure. which have not been considered are those of Stark. His work has been omitted on account of lack of space, and because he has not as yet been able to obtain from his results any very definite picture of the structure of the atom. Another reason is that this work is already available in book form ${ }^{31}$ which is not true of the material presented in this paper. Stark's greatest discovery is that of the electrical Zeeman effect, or the Stark effect, which is the decomposition of the spectral lines by means of a static electrical charge. Up to the present time this effect, which has been made to give a much greater separation of the components of the lines than has been obtained by the Zeeman effect, has been obtained only in the spectra from canal or positive rays. However this is probably due to the fact that this is the only method which has been found for securing the high field strengths which are essential. In Stark's work he has used a potential fall of from ten to seventy-four thousand volts per centimeter.

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## [Contribution from the Chemical Laboratory of Throop College of Technology.]

## OSMOTIC PRESSURE AND CONCENTRATION IN SOLUTIONS OF ELECTROLYTES, AND THE CALCULATION OF THE DEGREE OF IONIZATION,

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I. Introduction.

Ostwald's dilution law, which is obtained by the application of the law of mass action to solutions of electrolytes, involves the concentration of the ions and that of the undissociated molecules. The large divergence from this law which strong electrolytes exhibit may hence be due to the behavior of the ions, to that of the undissociated molecules, or to that of both. This so-called anomalous behavior may be simply expressed by saying that for one or for both of these molecular species van't Hoff's law,


[^0]:    * Note.-A recent paper by Hicks takes into account the magnetic forces also, and shows that their effect may be of the same order of magnitude as that of the electrostatic forces only. Any theory which is complete must take account of both. Calculations based on only one would seem to be of doubtful reliability. See Hicks, Phil. Mag., Jan., 1915.

[^1]:    ${ }^{1}$ According to recent work by Miss Meitner there seems to be considerable doubt as to the existence of $\mathrm{RaC}_{2}$.
    ${ }^{2}$ This table gives only the isotopes of the radium series.

[^2]:    * Nature, March 4, 1915.

[^3]:    ${ }^{1}$ Equations have been developed from the standpoint of both the electromagnetic theory and the theory of relativity, which give the total energy of an atom in'terms of its mass, but it is of course, not certain that these equations are valid.

[^4]:    * This suggestion is confirmed by the work of Evans.

