The Ions of Gases.
By William Sutherland.

Recent accumulations of experimental work on this subject show the need of a more comprehensive theory than has yet been advanced. The following is an attempt to state the fundamentals of a theory wide enough to contain the chief phenomena now known. The simplest theoretical ion in a gas is an atom charged with an electron, just as in electrolytic solutions. But the calculations of J. J. Thomson, Langevin, and others, seem to show that the smallest ions in gases consist of a few molecules, say two or three. P. Phillips in his experiments on Ionic Velocities in Air (Proc. Roy. Soc. lxxviii. 1906, p. 167), with a wide range of temperature finds the number of molecules in a gaseous ion to vary apparently with the temperature. It will be shown immediately that this variation of the size of the small ion in gases is only apparent, that the experimental ion is the simple ion of theory and electrolysis, and that the seeming change of size is due to the same cause as the seeming change of size of molecules with temperature in the viscosity of gases and allied phenomena before the effects of cohesional force were allowed for in the kinetic theory of gases. When the electric force of the simple ion in a gas is introduced into the calculation of the ionic mobilities to be expected at the different temperatures in the experiments of
Phillips, it removes all necessity for ascribing varying complexity to that ion. Wellisch ('Nature,' lxxix. 1908, p. 148) has already shown by reasoning which is not supported by the present investigation, that by considering the electric force of an ion in the same way as cohesional force in the theory of gaseous viscosity, it becomes no longer necessary to hold that the linear dimensions of the smallest ions in gases betoken a complex structure for them. But in the larger ions formed by spraying electrolytic solutions into flames and hot gases we find on a more elaborate scale just such a variable gaseous ion as the simplest has hitherto been supposed to be. As an extreme case of this type we have the large ion discovered by Langevin in the atmosphere. Of this ion we know little more than its small mobility, except the demonstration by Pollock (Austr. Assoc. for the Adv. of Sci. 1909) that this mobility varies considerably with the humidity of the atmosphere. Premising that the mobility of an ion is its velocity in cm. per second under an electric force of a volt per cm. we shall for convenience divide gaseous ions into three classes, those having at about 15°C. mobilities of the order of magnitude 2, 0.02, and 0.002. No doubt these types merge continuously each into the next. They can be specified more accurately according to the following definitions. Let the ion formed of atom and electron be called a nucleolus, such an ion surrounded by molecules forming a solid or liquid mass be called a nucleus, and let a collection of molecules in the form of a vapour round a nucleus or nucleolus be called an envelope; then the three types of gaseous ion are (1) nucleolus alone, (2) nucleolus and envelope, and (3) nucleus and envelope. The third type merges into the visible drop of fog and rain, though it is probably distinguished from these by the fact that the majority of the molecules in the nucleus and envelope are more directed by central electric force from the electron than by the mutual cohesional forces. The present theory will be divided into three sections, each devoted to one of these types of ion with a reference to theories of condensation and a summary.

1. The Ion formed by Atom or Radical with Electron.

Let the ion of charge $e$ move with velocity $u$ in the direction $x$ under uniform fall of potential whose rate is $dE/dx$, then, if the viscous resistance of the gas to its motion with unit velocity is $F$

$$ Fu = edE/dx \quad \ldots \quad \ldots \quad \ldots \quad (1) $$
If cohesional and electric force were neglected, the molecules of gas being treated as forceless spheres of radius $a_3$, mass $m_3$, and number per cm.³ $N_3$, suffix 1 allotting the corresponding quantities to the ion, the expression found for $F_u$ in the kinetic theory of "perfect" gases is

$$F_u = \frac{3}{2} N_3 (a_1 + a_2)^2 \left\{ 2\pi (v_1^2 + v_2^2) / 3 \right\} \frac{m_1 m_3}{m_1 + m_3} u \quad \ldots (2)$$

The immediate problem is to find how we must modify this expression to provide for the greater frequency of collisions caused by electric and cohesional force. The treatment can proceed almost exactly on the lines of my paper on the Viscosity of Gases and Molecular Force (Phil. Mag. [5] xxxvi. 1893, p. 507). Select an ion and a molecule which are initially far enough apart to exert negligible force on one another and are each destined to have their next collision with one another. Let $r_1$ and $r_3$ be their distances from the centre of mass of the two, so that $m_1 r_1 = m_2 r_3$ and let $r_1 + r_3$ their distance apart be denoted by $r$. Let the cohesional force between them be $-d\phi(r)/dr$ and the electric force between the electron of the ion and the molecule be $-d\psi(r)/dr$, then using $z$ for $1/r$ we have for the motion of the molecule relative to the centre of mass the usual equation

$$\frac{d^2 z_3}{dt^2} + z_3 + \frac{1}{m_3 h_3^2 z_3^2} \left( \frac{d\phi(r)}{dr} + \frac{d\psi(r)}{dr} \right) = 0 \quad \ldots (3)$$

in which $h_3$ is twice the area swept out by $r_3$ as it describes the angle $\theta$. From this for the equation of relative motion we get

$$\frac{d^2 z}{d\theta^2} + z + \frac{m_1 + m_2}{m_1 m_3 h^2 z^2} \left( \frac{d\phi(r)}{dr} + \frac{d\psi(r)}{dr} \right) = 0, \quad \ldots (4)$$

and then the first integral of this gives the equation of energy

$$\frac{1}{2} h^2 \left\{ \left( \frac{dz}{d\theta} \right)^2 + z^2 \right\} = \frac{1}{2} v^2 = \frac{m_1 + m_3}{m_1 m_3} \left\{ \phi(r) + \psi(r) \right\} + \frac{1}{2} V^2 \quad (5)$$

in which $v$ is the relative velocity when ion and molecule are at distance $r$ apart, and $V$ is the relative velocity when $r$ is so great that the relative orbit nearly coincides with its asymptote. Let $b$ be the length of the perpendicular from the ion on the asymptote so that $h = bV$. When the relative orbit is such that there is no collision, we can determine the
minimum value of \( r \) by the condition \( \frac{dz}{d\theta} = 0 \). Denote the reciprocal of this distance by \( w \) which is given by

\[
\frac{1}{2} b^2 w^2 = \frac{m_1 + m_3}{m_1 m_3} \left\{ \phi(r) + \psi(r) \right\} + \frac{1}{2} V^2 \quad \ldots \quad (6)
\]
onumber

or

\[
\frac{m_1 + m_3}{m_1 m_3} \left\{ \phi(r) + \psi(r) \right\} - \frac{b^2 V^2}{2(a_1 + a_3)^2} + \frac{1}{2} V^2 = 0.
\]
onumber

There must be a collision if \( 1/w \) is less than \( a_1 + a_3 \). Hence the greatest value of \( b \) for which a collision is possible is given by

\[
\frac{m_1 + m_3}{m_1 m_3} \left\{ \phi(a_1 + a_3) + \psi(a_1 + a_3) \right\} - \frac{b^2 V^2}{2(a_1 + a_3)^2} + \frac{1}{2} V^2 = 0,
\]

or

\[
b^2 = (a_1 + a_3)^2 \left( 1 + \frac{2(m_1 + m_3) \{ \phi(a_1 + a_3) + \psi(a_1 + a_3) \}}{m_1 m_3 V^2} \right). \quad (7)
\]

Thus it is proved that to adapt (2) to the case where electric and cohesive forces are operative \( (a_1 + a_3)^2 \) is to be replaced by the right hand of (7). Just as the corresponding result in the theory of the viscosity of a gas applies strictly only to gases above their critical temperature and at moderate densities, that is to say, under conditions which allow the relative orbit of a pair of colliding molecules seldom to consist of a curve of finite range, so the result just obtained is strictly applicable only when the relative orbit of ion and molecule is seldom a curve of finite range. For the resistance to an ion we now get from (2) with \( m_1 v_1^2 = m_3 v_3^2 \), \( V^2 = v_1^2 + v_2^2 \).

\[
\bar{F} = \frac{4}{3} N (a_1 + a_3)^2 \left( \frac{2\pi}{3} \cdot \frac{m_1 m_3}{m_1 + m_3} m_3 v_3^2 \right)^{\frac{1}{2}} \left\{ 1 + \frac{\phi(a_1 + a_3) + \psi(a_1 + a_3)}{m_3 v_3^2/2} \right\} u. \quad \ldots \quad (8)
\]

To adapt this for comparison with experimental results we put \( m_3 v_3^2 \) proportional to \( T \) the absolute temperature, and remembering that \( N \) varies as \( 1/T \), we get \( \bar{F} \) proportional to \( T^{-\frac{3}{2}} (1 + C'/T) \) where \( C' \) is proportional to

\[
\phi(a_1 + a_3) + \psi(a_1 + a_3).
\]

If then in (1) we make \( dE/dx \) a volt per cm., we get for the relation between ionic mobility \( u \) and temperature \( T \) the equation

\[
u = \frac{A T^{\frac{3}{2}}}{1 + C'/T} \quad \ldots \quad \ldots \quad \ldots \quad (9)
\]

in which \( A' \) and \( C' \) are parameters having values characteristic of each gas, the dashes being used to distinguish them.
from the corresponding parameters in the similar equation for the viscosity of a gas. We can test the validity of (9) by means of the experiments of Phillips (loc. cit.). In air for the positive ion $A' = 0.222$ and $C' = 509.6$, and for the negative ion $A' = 0.222$ and $C' = 333.3$. These give the following calculated mobilities for comparison with the experimental.

**Table I.**

<table>
<thead>
<tr>
<th>T</th>
<th>411</th>
<th>399</th>
<th>383</th>
<th>373</th>
<th>348</th>
<th>333</th>
<th>285</th>
<th>209</th>
<th>94</th>
</tr>
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<tr>
<td>Pos.</td>
<td>$u_{exp.}$</td>
<td>2.00</td>
<td>1.95</td>
<td>1.85</td>
<td>1.81</td>
<td>1.67</td>
<td>1.60</td>
<td>1.39</td>
<td>0.945</td>
</tr>
<tr>
<td></td>
<td>$u_{cal.}$</td>
<td>2.01</td>
<td>1.95</td>
<td>1.86</td>
<td>1.81</td>
<td>1.68</td>
<td>1.60</td>
<td>1.34</td>
<td>0.934</td>
</tr>
<tr>
<td>Neg.</td>
<td>$u_{exp.}$</td>
<td>2.495</td>
<td>2.40</td>
<td>2.30</td>
<td>2.21</td>
<td>2.125</td>
<td>2.00</td>
<td>1.755</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>$u_{cal.}$</td>
<td>2.487</td>
<td>2.42</td>
<td>2.33</td>
<td>2.27</td>
<td>2.12</td>
<td>2.03</td>
<td>1.73</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Down to $T = 209^\circ$ the mobilities of both ions are given with satisfactory accuracy by the theoretical formula (9), but at $94^\circ$ the formula fails, as theoretical considerations led us to expect that it would, because 94 is about 30 below the critical temperature of air. It is notable that at this lowest temperature the experimental mobility is the same for both ions. This shows that at this temperature some rather profound change has occurred in the conditions of movement of the two ions. From the values of $A'$ and $C'$ it appears that at high temperatures the mobilities of the two ions will tend to become equal again. It appears also that the difference in the mobilities is caused by the difference in the values of $C'$ which are proportional to the potential energy of ion and molecule in contact. If we compare these values, namely 509.6 and 333.3, with 113 the value of $C$ the similar parameter in the viscosity of air, which is proportional to the potential energy of two molecules of air in contact, we see that in both cases the potential energy of ion and molecule is larger than that of molecule and molecule. This is what we should expect from our knowledge that the potential energy of molecule and molecule is like that of two electric doublets of charges $e$ and moment $es$ in which $s$ is less than the diameter of a molecule. It seems then we must trace the remarkable difference in the mobilities of the two ions to differences of their potential energies when in contact with a molecule of air. Unfortunately we do not know experimentally what the ions are. In pure gases we may infer that the ions are atoms charged with a positive or a negative electron, but we do not yet know whether in the
presence of impurity there may be a tendency for one or both sorts of electron to associate specially with the impurity. But in spite of these remaining uncertainties the interpretation of the experiments by (9) proves that the small ion in air does not attach to itself satellite molecules whose number varies with temperature. The electric force of the ion accounts for the facts just as cohesional force accounts for the corresponding facts in the viscosity of gases. I may mention that for the negative ion in air the result at 94° can be expressed as well as all the others by changing (9) to

$$u = \frac{A'T'}{1 + C'/(T - T_a)}$$

where

$$T_a = 70°, A' = 0.1764, C' = 150.5.$$  

In the further investigation of (8), until experiment informs us definitely as to the atoms or radicals which form the ions, we shall be forced to make assumptions. For the diatomic element gases we can write \( m_2 = 2m_1 \) if the ions are formed of their atoms, and we may also put \( a_3 = 2a_z \), although we must be on the watch lest the atom when made an ion may undergo change of volume. Possibly the change caused by the positive electron is different from that caused by the negative. In such a compound gas as CO₂ we shall assume an average ion of mass \( m_3/2 \) and of volume \( 2\pi a_3^2/3 \), and shall consider the average of the nearly equal mobilities of the positive and negative ions. Then (8) becomes

$$e \frac{dE}{dx} = 3.59N_3a_3^2m_3v_3[1 + 2\{\phi(a_1 + a_3) + \psi(a_1 + a_3)\}/m_3v_3^2]u. \quad (10)$$

For air at 0° C. the left side of this equation has the value \( 10^{-12} \) because \( e = 3 \times 10^{-10} \) and \( dE/dx = \text{volt/cm.} = 1/300 \). To evaluate the right side we put \( N_3m_3 = 0.001293 \), and \( N_3m_3v_3^2 = 3pV \) in the usual notation of the gas laws, with \( V = 1 \), and \( p = 1,014,000 \) dynes/cm.², and \( 2a_3 = 2.38 \times 10^{-8} \) (Phil. Mag. Feb. 1909, p. 321), while

\[
[1 + 2\{\phi(a_1 + a_3) + \psi(a_1 + a_3)\}/m_3v_3^2]u = u(1 + C'/T)
\]

\[
= A'T' = 0.222 \times 273\frac{1}{3} = 3.67
\]

for both the positive and the negative small ion in air at 0° C. With these values the right side of (10) is \( 1.18 \times 10^{-13} \), whereas the left side is \( 10^{-12} \). Here we meet, even in a more pronounced form, the discrepancy which has led previous writers to suppose the small ion to be a cluster of molecules, for which \( 2a_3 \) would be large enough to make the
right side equal to the left. It shows that Wellisch's theory does not give the right reason for the difficulty. The frictional resistance expressed by the right side of (10) must be made 8.6 times as great to make the dynamical theory of the small ions in air correct. The additional resistance is introduced if we take account of the two new types of viscosity (Phil. Mag. [6] xiv. p. 1) shown to be fundamental for the motion of ions in liquids. We shall find these to be as important in the dynamical theory of ions in gases. The first of these viscosities, whose coefficient is $\zeta$, has its origin in the mutual potential energy of the opposite electron charges of the two kinds of ion. The second has its origin in the mutual potential energy of an ionic charge, and the polarization which it induces in the neighbouring molecules of the surrounding medium. Its coefficient was denoted by $\theta$. As the causes producing ionization and maintaining it in a liquid solution are different from those acting in a gas, it will be necessary to make a special calculation for $\zeta$ and $\theta$ in a gas, though similar to that furnished for liquid solutions.

In the paper just mentioned it is shown that if $q$ positive and $q$ negative ions of charge $e$ are uniformly distributed through a cm.$^2$, of a medium of dielectric capacity $K$, they possess a rigidity

$$N = \frac{2\pi}{3K} e^2 q^{4/3}.$$

If they are strained by electric force so that each positive electron is displaced in one direction and each negative in the opposite, a corresponding stress is developed. Now the presence of molecules may cause this strain to relax by forcing the ions back to uniform distribution; they will convert the rigidity $N$ into a viscosity $NT$, where $T$ is the time required to reduce the stress to $1/e$ of its initial amount, $e$ being the base of natural logarithms. When the ions are those of an electrolytic solution, the relaxing action of the molecules of solvent is due to their ionizing force, that force which pulls the ions of the solute apart and keeps them uniformly distributed. In the paper just cited this ionizing force is taken to be proportional to $q^{2/3}$ as it overcomes the direct electric attraction between neighbour opposite ions. But in a gas we do not regard the molecules as direct ionizers. What then are the actions in a gas tending to keep ions uniformly distributed? The chief one is the following. According to the principle of the electric origin of molecular attraction each molecule behaves like an electrically polarized
or electrized sphere, similar to a uniformly magnetized sphere, and its electric axis tends to set itself very readily along the lines of electric force. In the absence of external electric force the axes of neighbours so adjust their mutual directions as to produce cohesion. But when the powerful central electric force of an electron acts upon neighbour molecules, it forces their electric axes all to pass nearly through itself. Those molecules next to the nearest neighbours have their axes caused to converge towards the electron, but not so accurately, and so on. Thus the cohesive forces of the molecules are deranged, and the surrounding molecules are attracted towards the electron. We shall consider the law of this attraction soon, but just now we must recognise that near the electron the gas will be compressed by this attraction to a greater density than the average. The tendency of this denser gas to diffuse outwards from the central electron is just equilibrated by the inward electric attraction. Let \( r \) be the distance between two neighbour electrons, then we may take the average value of the force of diffusion per cm.\(^2\) of section to vary as \( 1/r \). Hence, when two neighbour electrons have \( r \) between them changed to \( r + dr \) by electric force, the unequilibrated force of diffusion called into action will be proportional to \( dr/r^2 \). But \( dr/r \) is the strain to which the associated stress \( F' \) is proportional, so the force restoring uniformity is proportional to \( F'/r \); but in Maxwell's theory of transition from rigidity to viscosity this is proportional to \( F'/r \), therefore in a gas \( T \) is proportional to \( r \). It must also be proportional to the resistance offered by the gas to the motion of the whole ion with unit velocity, which we have denoted by \( F \). Thus we have \( T \propto F q^{-1/3} \) and therefore \( \xi \), the viscosity \( NT \) derived from \( N \), varies as \( F q e^\theta /K \). For a gas we may put \( K = 1 \).

We have now to obtain an expression for \( \theta \). The electric polarization consists in the directing of the axes of electrization of the molecules towards the nearest ion. Let \( R \) be the distance from an ion to the six nearest molecules. Though this is less than the average distance between two molecules because of condensation due to attractive forces round the ion, it is proportional to that distance. The mutual potential energy of an ion and a neighbour molecule is \( \phi(R) + \psi(R) \). The rigidity \( N \) of the system ion and molecules is equal to the potential energy per unit volume and is therefore proportional to \( (\phi(R) + \psi(R))/R^6 \).

We have now to find the time of relaxation \( T \). The force between ion and molecule is

\[
d\{\phi(R) + \psi(R)\}/dR.
\]
Per unit area it is proportional to
\[ R^{-2}d\{\phi(R) + \psi(R)/dR, \]
and the change of this for change \( dR \) is
\[ dRd[R^{-2}d\{\phi(R) + \psi(R)/dR]/dR. \]
But the associated stress \( F' \) is proportional to \( dR/R \), so in this case the force restoring uniformity when the system of ion and molecules is strained is proportional to
\[ F'Rd[R^{-2}d\{\phi(R) + \psi(R)/dR]/dR \]
and also to \( F'/T \), so that \( T^{-1} \) is proportional to
\[ Rd[R^{-2}d\{\phi(R) + \psi(R)/dR]/dR. \]
Now we know that for two electrons the potential varies as \( 1/R \), for an electron and an electric doublet as \( 1/R^2 \), and for two doublets as \( 1/R^3 \). In the actual case at distance \( R \) the form of \( \phi(R) + \psi(R) \) is almost that of \( 1/R^2 \), as will appear in Table II; hence in the product \( NT \) we get a result proportional to \( R^2/R^2 \), that is, a constant. Thus in a gas this factor of \( \theta \) is independent of the density, just as the ordinary viscosity of a gas is. In the previous reasoning we have considered only the molecules which are immediate neighbours of an ion. Similar reasoning applies to the next more remote lot of neighbours and so on. It is important to notice that the argument by which this factor of \( \theta \) was proved independent of density makes it also independent of the nature of the gas; it is a universal constant. To the above reasoning we must add the statement that \( T \) is proportional to \( F \), so that \( NT \) and therefore \( \theta \) is proportional to \( F \), which varies from one gas to another. In applying these new viscosities \( \zeta \) and \( \theta \) in the study of the motion of ions through gases we treat \( \theta \) as acting just like \( F \), while as regards \( \zeta \) we consider it to act over area \( q^{-2/3} \) with a relative motion \( u_1 - u_2 \) between two neighbour ions at distance \( q^{-1/3} \) apart, \( u_1 \) being the velocity of the positive ion and \( u_2 \) of the negative, so that the resistance experienced by an electron is
\[ \zeta(u_1 - u_2)q^{-2/3}/q^{-1/3}. \]
For the motion of the ions in a field of intensity \( dE/dx \) we have the equations
\[ e \frac{dE}{dx} = \zeta(u_1 - u_2)q^{-1/3} + (\theta + F)u_1 \]
\[ -e \frac{dE}{dx} = -\zeta(u_1 - u_2)q^{-1/3} + (\theta + F)u_2 \]
(11)
The easiest case is that in which \( q \) is so small as to make \( \sqrt[2]{q^{-1/3}} \) negligible. These equations then take the same form as (1) with \( F \) replaced by \( \theta + F \). We found that in the case of air the right-hand side of (10) must be made 8.6 times as large as it is to give the facts of experiment. Thus for air then we have \( \theta = 7.6F \), and in forming the theory of \( \theta \) we found that this same relation must hold for all gases. Thus then we have found that the small ion in gases does not consist of a cluster of molecules, but that its electric charge causes it to experience a viscosity of electric origin and also to behave as if it had an enlarged radius. Introducing the factor 8.6 into the right-hand side of (10) we get as the general equation for the mobility of a small ion the equation

\[
e \frac{dE}{dx} = 30.9Nqas^2mv^2_s[1 + 2\{\phi(a_1 + a_2) + \psi(a_1 + a_2)\}/m_3v^2_s]u \]

or

\[
1 = \frac{uT^{-1/2}(1 + C'/T)}{A'}.
\]

In establishing this we have confirmed the theory of electrically induced viscosity by finding that it is the chief factor in determining the mobility of ions in gases. We have also found that the potential energy of ion and molecule in contact in gases plays the same part as the mutual potential energy of molecules in contact in the theory of the ordinary viscosity of gases. Investigations of \( C \) in the theory of gaseous viscosity and of \( C' \) in (12) enable us to study the potential energy of molecules under ideally simple conditions. To find \( C' \) directly for any substance experiments like those of Phillips on air will be necessary. But from the known values of \( u \) for different substances we can make a preliminary indirect determination of \( C' \) and therefore of \( \phi(a_1 + a_2) + \psi(a_1 + a_2) \).

From (12) we have, when \( dE/dx = \) volt/cm., and the temperature and pressure are fixed,

\[
uml^{1/2}a^2(1 + C'/T) = \text{constant}. \quad (13)
\]

This is the origin of a roughly approximate law announced by Lenard that \( um^{1/2}a^2 \) is constant for several gases. For both positive and negative ion in air at 15° C. we have seen that

\[
u(1 + C'/T) = \frac{AT^{1/2}}{a} = 0.222 \times 288^{1/2}, \quad a = 1.19 \times 10^{-8}.
\]

It is rather more convenient at present to use \( B^2 \) instead of \( a^2 \), \( B \) being the limiting volume of a gramme-molecule, and to use the ordinary molecular mass \( M \) instead of \( m \), namely 28.86 for air. The relation between \( B \) and \( a \) is

\[
B = 4 \times 10^{19} \times 22430(2a)^3.
\]
Thus we transform (13) to
\[ uM^{1/2}B^{2/3}(1 + C'/288) = 106.9 \ldots \ldots \ldots (14) \]
which is the desired equation for finding \( C' \) from a single measurement of \( u \) for a substance and its known values of \( M \) and \( B \). The values of \( u \) have been collected by J. J. Thomson in his book on 'The Conduction of Electricity through Gases,' and by Wellisch with new determinations of his own for a number of vapours, in a paper read before the Austr. Assoc. Adv. Sc. Jan. 1909. There is a difficulty in comparing the values of \( B \) when these are arrived at by different methods for different substances. This can be seen by comparing the results of two methods for one substance, for example, \( \text{Cl}_2 \). For this gas its viscosity gives \( 2a = 3.13 \times 10^{-8} \), and so \( B = 27.4 \), whereas in the inorganic chlorides as well as in the organic \( B \) for \( \text{Cl}_2 \) is 38 (Phil. Mag. [5] xxxix. p. 1). It cannot be assumed that the value of \( B \) for \( \text{Cl} \) in \( \text{Cl}_2 \) is necessarily the same as that for \( \text{Cl} \) in compounds, but I think the chief part of the discrepancy between 27.4 and 38 is to be traced to the assumption that molecules of a gas can still be treated as spheres while they are in collision. The kinetic theory of gases gives us \( 2a \) as the distance between the centres of two molecules while they are in collision, which may be less than the mean diameter of either. For this reason I shall present the data for discussion in two ways, first using only the values of \( B \) derivable from the kinetic theory of gases, and second only those derived from the apparent limiting volumes of liquids and solids.

**Table II.**

<table>
<thead>
<tr>
<th></th>
<th>( H_2 )</th>
<th>( \text{He} )</th>
<th>( \text{N}_2 )</th>
<th>( \text{O}_2 )</th>
<th>( \text{Cl}_2 )</th>
<th>( \text{CO} )</th>
<th>( \text{CO}_2 )</th>
<th>( \text{N}_2\text{O} )</th>
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<td>160</td>
<td>246</td>
<td>225</td>
<td>313</td>
<td>228</td>
<td>241</td>
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<td>( 100B )</td>
<td>528</td>
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<td>28</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>( 100C'/288 )</td>
<td>241</td>
<td>293</td>
<td>125</td>
<td>133</td>
<td>39.5</td>
<td>290</td>
<td>278</td>
<td>175</td>
</tr>
<tr>
<td>( 100C'(2a)^2/288 )</td>
<td>731</td>
<td>698</td>
<td>702</td>
<td>708</td>
<td>359</td>
<td>1404</td>
<td>1501</td>
<td>1251</td>
</tr>
</tbody>
</table>

The values given for \( 10u \) are \( 5(u_1 + u_2) \), that for \( \text{He} \) being obtained by Franck and Pohl (Ann. d. Ph. Beibl. xxxi. 1907, p. 1133), namely \( u_1 = 5.09 \) and \( u_2 = 6.31 \). To this monatomic gas the formula (14) for diatomic and compound
gases has been applied without change. The values calculated for 100C'288 belong to an imaginary mean ion. For the positive and negative ions separately they can be found by using \( u_1 \) and \( u_2 \), instead of their mean \( u \). In the last line 100C'/(2a)²/288 has been given. For four out of five element gases it is nearly 710, the exceptional value for Cl₂ being 359. For the three compound gases the values are not far from 1385, which is nearly \( 2 \times 710 \). At 15°C both CO₂ and N₂O are a few degrees below their critical temperature, so that their actual condition does not comply with the stipulations made in obtaining the theoretical equations. Probably the error introduced is not great. But in the case of the more easily liquefied gases with higher critical temperature like NH₃, SO₂, and HCl, and of the vappours of liquids the orbit of the relative motion of ion and molecule after collision will be too often a curve of finite range to allow the theory founded upon infinite range to hold. Nevertheless, for the sake of information I shall apply (14) to the data for easily liquefied gases and vappours. For these the values of B can be obtained from “Further Studies on Molecular Force” (Phil. Mag. [5] xxxix, p. 1).

### TABLE III.

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>SO₂</th>
<th>HCl</th>
<th>C₂H₅Cl</th>
<th>C₂H₁₂</th>
<th>CH₃CO₂</th>
<th>CH₃(C₂H₅)₂O</th>
<th>CH₃CO₂C₂H₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>21</td>
<td>35</td>
<td>27</td>
<td>57</td>
<td>33.5</td>
<td>62</td>
<td>82</td>
<td>80</td>
</tr>
<tr>
<td>100α</td>
<td>73</td>
<td>41</td>
<td>127</td>
<td>31</td>
<td>34</td>
<td>31</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>M</td>
<td>17</td>
<td>64</td>
<td>36.5</td>
<td>64.5</td>
<td>72</td>
<td>74</td>
<td>74</td>
<td>88</td>
</tr>
<tr>
<td>100C’/288</td>
<td>366</td>
<td>204</td>
<td>53</td>
<td>190</td>
<td>80</td>
<td>156</td>
<td>127</td>
<td>119</td>
</tr>
<tr>
<td>10B²/3C’/288</td>
<td>274</td>
<td>218</td>
<td>48</td>
<td>281</td>
<td>165</td>
<td>244</td>
<td>240</td>
<td>221</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CH₄Br</th>
<th>CH₂I</th>
<th>CCl₄</th>
<th>C₂H₅I</th>
<th>Aldehyde</th>
<th>Alcohol</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>47</td>
<td>57</td>
<td>84.5</td>
<td>74</td>
<td>39.5</td>
<td>48</td>
<td>58.5</td>
</tr>
<tr>
<td>100α</td>
<td>28</td>
<td>21</td>
<td>30</td>
<td>16</td>
<td>29</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>M</td>
<td>95</td>
<td>142</td>
<td>154</td>
<td>156</td>
<td>44</td>
<td>46</td>
<td>58</td>
</tr>
<tr>
<td>100C’/288</td>
<td>201</td>
<td>188</td>
<td>47</td>
<td>203</td>
<td>376</td>
<td>311</td>
<td>229</td>
</tr>
<tr>
<td>10B²/3C’/288</td>
<td>262</td>
<td>278</td>
<td>30</td>
<td>358</td>
<td>436</td>
<td>411</td>
<td>337</td>
</tr>
</tbody>
</table>

In this table we notice that when much the greater part of the mass of a molecule consists of chlorine as in HCl and CCl₄, the potential energy measured by 100C’/288 is con-
spicuously small, as in the case of Cl₂, and so also is $10B^{2/3}C'/288$ conspicuously small. But in C₅H₁₂Cl this effect does not appear. In aldehyde, alcohol, and acetone, which are known to be associative liquids, the potential energy and its product by $B^{2/3}$ are both large. The other substances of the table give values of $10B^{2/3}C'/288$ near to 240, except C₅H₁₂, which has the value 165. This 240 is nearly double 138·5 found for compound gases in the last table. We learn then, that on the whole $B^{2/3}C'$ increases with the liquefiability of a substance. For the substances of Table III., the values of $100C'/288$ are only apparent values of the potential energy, since our theory would apply to them strictly only at temperatures above the critical. Probably the values of $100C'/288$ in Table III. are roughly proportional to the desired potential energies. As stated above, the Table has been drawn up to give only preliminary information. Returning to the more definite facts of Table II., we see that constancy of $B^{2/3}C'$ would imply that the potential energy of ion and molecule in contact varies inversely as the square of the distance between their centres. Now one of the main results found in my studies on molecular attraction is this, that molecules attract one another as though each were a uniformly electrized sphere of total electric moment $E$. If an ion of charge $e$ and volume half that of the molecule were in contact with the molecule in the position of minimum potential energy, that energy would be proportional to $-Ee/B^{2/3}$. This shows the probable origin of the constancy of $B^{2/3}C'$. But I have shown that in most cases $E$ is proportional to $B$. So it appears that, if the ion were able to turn the whole field of electrization of the molecule so that its axis passes through the ion in the position of minimum potential energy, $C'$ would be proportional to $B/B^{2/3}$, that is to $B^{1/3}$, instead of to $1/B^{2/3}$, as we have found above to be the case for H₂, He, N₂, and O₂. It appears then that instead of $E$ which is proportional to $B$ we have to do with another electric moment $E'$ which is the same for these four element gases. An ion does not turn the whole electric field of a molecule so that its axis passes through the ion, but on the average it turns that electric field so that its component along the line joining the centre of ion to centre of molecule is that arising from an electric moment $E'$ which is the same for four out of five element gases in Table II. The absolute magnitude of this moment can be found by means of the following data for H₂ at 15° C., using $4 \times 10^{19}$ for the number of molecules.
in a cm.\(^3\) at 0°C, and 1 atm. \(Nmv^2 = 3pv288/273\) with
\[
p = 1,014,000, \quad V = 1, \quad N = 4 \times 10^{19},
\]
\[
2\{\phi(a_1 + a_2) + \psi(a_1 + a_3)\}/mv^2 = C'/288 = 2.41,
\]
\[
\therefore \quad \phi(a_1 + a_3) + \psi(a_1 + a_3) = 916 \times 10^{-16}.
\]

If \(E'\) were due to two opposite electrons of charge \(e\) at distance \(x\) apart, we should have
\[
\phi(a_1 + a_3) + \psi(a_1 + a_3) = e^2x/4a^2,
\]
whence
\[
x = 0.0352 \times 10^{-8}.
\]

I hope to show in a future communication that the fundamental mode of motion determining the structure of all spectra is that of two opposite electrons vibrating within each atom about positions at a mean distance apart of the order \(0.05 \times 10^{-8}\). It seems very probable then that this electric moment \(E'\), which we have been investigating here, is the moment of this pair of electrons which at the same fixed distance apart in all atoms determine all radiation and the structure of all spectra. The further investigation of \(C'\) must be a matter of special experiment, just as in the case of \(C\) in the viscosity of gases.

The coefficients of diffusion \(D\) of ions in gases are proportional to their mobilities, being a measure of their mobilities under the driving force of a certain space-rate of change of partial pressure, instead of the electric force of a volt/cm. Their values have been investigated chiefly by Townsend, and have been found to be some such fraction as a fifth or a tenth of those for comparable uncharged molecules. This difference has been generally ascribed to the formation of molecular clusters round each ion. From the foregoing it is plain that the difference is due to the operation of the electrically induced viscosity \(\theta\) on the ions. In making a useful comparison of the two types of diffusion coefficient we must remember that we are assuming the ion in a pure gas to be of half the mass and half the volume of the molecule. Townsend has determined \(D\) for the positive ions in \(CO_2\) as 0.023, and for the negative 0.026, mean 0.0245. For comparison with this we must choose the value of the diffusion coefficient for a gas which has about half the molecular mass 44 of \(CO_2\) and half its molecular volume. The nearest we can get to this is to take the case of \(CO\) whose molecular mass is 28 diffusing into \(CO_2\) with a coefficient 0.131, or that of \(O_2\) with coefficient 0.136. In these cases the molecular volume of \(CO\) and \(O_2\) is nearly
equal to that of CO₂, a difference which could be approximately allowed for by a short calculation, but it is hardly worth making, as the point under consideration is well enough presented by comparing the mean of 0.131 and 0.136 with 0.0245. Thus we find the resistance to the diffusion of the ion 5.4 times as great as the corresponding resistance to that of the molecule. This result is in general agreement with the demonstration given that the new viscosity θ increases the resistance of ordinary gaseous viscosity to 8.6 times its amount. The hypothesis of molecular clusters is unnecessary to explain the slow diffusion of ions in gases.

We must also discuss another quantity closely related to u, namely α, the coefficient of recombination of ions in gases according to the very simple formula introduced by J. J. Thomson:

\[ \frac{dN_1}{dt} = -\alpha N_1^2. \]  

(15)

There are certain fundamental objections to the excessive simplicity of this formula which makes the recombination take place according to the chemical law of mass action, notwithstanding the large range of the electric forces of attraction and repulsion amongst ions. Langevin has given (Ann. de Ch. et de Ph. [7] xxviii. 1903, pp. 289 & 433) the now generally accepted proof that this simplicity is justified. The essence of his argument is this: that the electric force at the surface of a sphere surrounding an ion being \( e/r^2 \), and the number of opposite ions that can be drawn across the surface of the sphere being proportional to \( 4\pi r^2 N_1 u_1 \), the number entering the sphere in unit time is proportional to \( 4\pi eN_1 u_1 \), and is thus independent of the radius of the sphere and of the range of the electric forces of the ions. If we take account of the mobilities of both sorts of ions we get Langevin's formula

\[ \alpha = 4\pi e(u_1 + u_2), \]  

(16)

where \( e \) is that fraction of the ions drawn into a sphere which combine to form neutral molecules. Langevin has investigated values of \( e \) experimentally, and Richardson (Phil. Mag. [6] x. 1905, p. 242) has applied considerations of probability to the calculation of \( e \). But it seems to me that, though Langevin's theory gives as a first approximation the justification of J. J. Thomson's equation (15), a second approximation is necessary to bring the theory of ions in gases into agreement with experimental facts and the kinetic theory of gases. Experimental proof of the insufficiency of (15) has been given by Barus (Ann. der Phys. xxiv. 1907, p. 225), using J. J. Thomson's condensation method of counting N₁.
The results of Barus will be discussed soon in connexion with the following attempt to carry the theoretical equations of Thomson and Langevin to a higher degree of approximation. If the ions were always distributed symmetrically, each would be in statical equilibrium as regards the electric forces, and the beginnings of recombination would never arise. Recombination depends chiefly upon the rate at which unsymmetrical positions are formed during the motion of the ions. Let us start, then, with a convenient specification of the symmetrical positions. Suppose the space divided into equal cubes of edge $R$ with an ion placed at each corner which is common to 8 cubes, the ions occurring alternately negative and positive along the straight lines formed by the edges of the cubes according to the specimen plan of fig. 1. Like ions are arranged along diagonals. If any ion is displaced from a diagonal, it will be attracted most strongly towards the nearest diagonal. Let us then replace the electrons by lines of electricity of density $e/2^{1/2}R$ along diagonals running downwards from left to right. Then in fig. 2 let us make a section of these parallel lines by a plane at right angles to them, the intersections of the lines and plane being marked # for the positive lines and $\beta$ for the negative. # ranges in diagonal lines, and so does $\beta$. These diagonals are at distance $R/3^{1/2}$ apart, while the distance between # and its neighbour $\#$ is $R(3/2)^{1/2}$. Spread the lines of density $e/2^{1/2}R$ so that they become planes of surface density $e/3^{1/2}R^2$, these planes being alternately # and $\beta$. In this way we have substituted for the original point distribution an equivalent laminar one. We can now treat the problem of recombination of ions as one of leakage in our laminar distribution. Writing the intensity of the electric force between two laminæ as $4\pi e/3^{1/2}R^2$, we consider the rate of leak proportional to this force and to the mobility $u_1$ or $u_2$ of the ions, and to $N_1$. But $N_1R^3 = 1$, so with $A$ a parameter we have finally

$$dN_1/dt = -AN_1^{5/3}. \ldots \ldots (17)$$

This factor of proportionality $A$ is proportional to $u_1 + u_2$,\n
\[\text{Fig. 1.}\]
\[\text{Fig. 2.}\]
and to the rate at which unsymmetrical distributions arise to produce the motion which we have treated as a leak. This equation can be written

$$dN_t^{-2/3}/dt = -\frac{2}{3}A(N_t^{-2/3})^2,$$  \hspace{1cm} (18)

and its integral is

$$N_t^{-2/3} = C + 2At/3,$$  \hspace{1cm} (19)

where C is a constant. Thus we have $N_t^{-2/3}$ a linear function of the time, whereas the integral of (15) makes $N_t^{-1}$ a linear function of the time. From the tabulated data of Barus for ions in air, I find with second for unit $t$

$$10^8 N_t^{-2/3} = 52 + 6t,$$  \hspace{1cm} (20)

with the following comparison:

<table>
<thead>
<tr>
<th>Seconds</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>60</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}N_t\exp$</td>
<td>83</td>
<td>38</td>
<td>27</td>
<td>14</td>
<td>9</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>$10^{-3}N_t\cal$</td>
<td>84</td>
<td>35</td>
<td>27</td>
<td>14</td>
<td>9</td>
<td>4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Barus gives five other sets of data in graph form, and in these $10^8 \times 2A/3$ has a value about 4.5. The comparison just given covers a range of $N_t$ large enough to show that (17) is to be preferred to (15). But as (15) has been taken by J. J. Thomson to be proved by various experiments originating in the Cavendish laboratory, it is necessary to look rather more closely into the evidence. In the paper of J. J. Thomson and Rutherford on the passage of electricity through gases exposed to Röntgen rays (Phil. Mag. [5] xlii. 1896, p. 392), the experimental results can be expressed with a slightly smaller average error by the $N_t^{-2}$ formula than by the $N_t^{-2/3}$ one, but they can be expressed with a still smaller average error by a formula using $N_t^{-6/2}$. These early experiments are therefore not suitable for deciding between the two formulæ. In Rutherford's paper on the rate of recombination (Phil. Mag. [5] xliv. 1897, p. 422) the experimental results are represented with the following average errors per cent. :

<table>
<thead>
<tr>
<th>On page</th>
<th>423</th>
<th>427</th>
<th>429</th>
</tr>
</thead>
<tbody>
<tr>
<td>With the $N_t^{-2}$ formula</td>
<td>5.7</td>
<td>6.0</td>
<td>6.7</td>
</tr>
<tr>
<td>&quot; &quot; $N_t^{-5/3}$</td>
<td>2.2</td>
<td>3.5</td>
<td>7.7</td>
</tr>
</tbody>
</table>

ions in gases under different pressures has been subjected to some criticism in the Phil. Mag. (see G. W. Walker, viii. 1904, p. 206, Robb, x. 1905, p. 237), and by Langevin (Journ. de Phys. [4] iv. 1905, p. 322), who shows that on the basis of the \( N^2 \) formula it can be proved that in the experiments at a pressure of one atmo diffusion would cause one-tenth of the effect recorded as recombination by McClung, while at one-eighth of an atmo at least eight-tenths of the recorded effect is to be credited to diffusion. Diffusion must also have produced a large effect in the large apparent variation of \( \alpha \) with temperature in later experiments of McClung's. We can take McClung's experiments at 1, 2, and 3 atmo to be complicated with not more than 10 per cent. of diffusion effect. I find that his results can be represented as well by the \( N^{5/3} \) formula as by the \( N^2 \). The reason for this fact is that the residual experimental error in these difficult measurements is such that when \( N_1 \) is graphed as ordinate with \( t \) as abscissa, the points lie on an area which is traversed just as well by the curve which makes \( N_1^{-2/3} \) linear in \( t \) as that which makes \( N_1^{-1} \) linear in \( t \). Thus I think I have shown that the experimental evidence upon which J. J. Thomson relies for verification of the \( N^2 \) formula (15) is on the whole a little more favourable to the \( N^{5/3} \) formula (17). But (15) fails to apply to the experiments of Barus given previously in verification of (17), which is therefore the better approximation to the truth. In this connexion it would be important to make a full review of Langevin's own experiments, which, on account of wide variations of the conditions, he considers to verify the two laws that ionic velocity is proportional to strength of electric field, and that the rate of recombination of the two sorts of ions is proportional to the product of their numbers per c.c., or the two electrical densities which he denotes by \( p \) and \( n \). Thus Langevin holds that his experiments verify the \( N^2 \) formula. The theory of his method of experimenting is rather elaborate, so he contents himself with giving only final results and samples of his data which are not sufficient to allow me to investigate how the \( N^{5/3} \) formula would apply to his experiments directly. But the theory by which the \( N^{5/3} \) formula is established receives indirect support from Langevin's results, if we work it out in greater detail. We must investigate \( A \) in (17) more closely. Imagine the two sorts of ions for an instant uniformly distributed, alternately at the corners of a uniform cubical subdivision of the volume which they occupy. On account of its thermal velocity each ion will move away from this imaginary position, and the amount
by which it moves away will determine the degree of irregularity which causes the recombination which we suppose to go on as a sort of leak. To determine $A$ as a function of the density of the gas containing the ions is a problem in the calculus of probabilities known as that of the random walk. A man walks a distance $l$ in any direction from an origin $O$, then he walks the same distance in any other direction, and so on till he has taken $n$ walks. It is required to find the probability that his final distance from $O$ lies between $r$ and $r + dr$. Evidently this is the same as our ionic problem, for the ion after $n$ free paths of average length $l$ is at some required average distance from $O$, its original position in the initial imaginary uniform distribution. The solution has been given by Rayleigh ('Nature,' lxxii. 1905, p. 318; Phil. Mag. [5] x. 1880, p. 73, xlvii. 1899, p. 246) for the case when $n$ is large. The required probability is, when $l = 1,$

$$\frac{2}{n} e^{-r^2/n} r dr \ldots \ldots (21)$$

and the probability that the distance from $O$ is greater than $r$ is $e^{-r^2/n}$. If we introduce $l$ explicitly the exponent becomes $-r^2/l^2 n$. In comparing results for different substances or for the same substance at different pressures, we ought to take $n$ to be the number of paths described in unit length, because, though the departures from uniformity recur with a frequency proportional to the molecular velocity, each lasts a time inversely proportional to the velocity. For this reason the element of time does not enter into the comparison. Thus $nl$ is to be constant for the same substance at different pressures and also for different substances. We have now to find how $r$ is to be chosen in order that the comparison may be statistically correct. The agencies maintaining uniformity are proportional to $l$ the mean free path, for instance, $D$ the coefficient of diffusion is proportional to $l$. But the same agencies produce departures from uniformity temporarily, while they are maintaining average uniformity, just as the thermal velocities, which keep the average pressure of a gas constant and also its average density constant, at the same time cause those temporary local variations of pressure and density which occur when two molecules collide. As regards departures from uniformity, then the proper unit for measuring its amount linearly is the mean free path of a molecule. Thus $r$ must be proportional to $l$. Accordingly $r^2/l^2 n$ takes the form $cl$ where $c$ is a constant. Let $l_0$ be the value of $l$ when the
pressure is \( p_0 = 760 \) mm. of Hg, then \( l = l_0 p_0 / p \), and we now have \( A \) in (17) proportional to \( (u_1 + u_2)e^{-e l_0 p_0 / p} \),

\[ \therefore \log A / (u_1 + u_2) \text{ is linear in } 1/p. \quad \cdot \quad (22) \]

If we compare (15) and (17), and suppose them applied to the same set of experiments over a certain range of values of \( N_1 \), we see that for the average value of \( N_1 \) we must have approximately \( A = \alpha N_1^{1/3} \). But in Langevin’s experiments \( N_1 \) was the number of ions generated by a single flash from a Röntgen bulb, so that on the average for gas at different pressures we may take \( I_0 = p \). Thus then \( A \) is proportional to \( \alpha p^{1/3} \), and so from (16) \( A / (u_1 + u_2) \) is proportional to \( \varepsilon p^{1/3} \), and so from (22) \( \log \varepsilon p^{1/3} \) is linear in \( 1/p \). Thus from Langevin’s experiments I find with \( p \) in mm. of Hg

\[ \begin{align*}
\text{for air} & \quad \log_{10} \varepsilon p^{1/3} = 1.35 - 745/p, \\
\text{for CO}_2 & \quad \log_{10} \varepsilon p^{1/3} = 1.35 - 509/p,
\end{align*} \quad \cdot \quad (23) \]

which furnish the following comparison with experiment:

\[
\begin{array}{ccccccc}
\text{Air.} & \\
\hline
p & 152 & 375 & 760 & 1550 & 2320 & 3800 \\
\varepsilon \text{ exper.} & .01 & .06 & .27 & .62 & .80 & .90 \\
\varepsilon \text{ calcul.} & .00005 & .03 & .26 & .64 & .81 & .91 \\
\hline
\text{CO}_2. & \\
\hline
p & 135 & 352 & 550 & 758 & 1560 & 2380 \\
\varepsilon \text{ exper.} & .01 & .13 & .27 & .51 & .95 & .97 \\
\varepsilon \text{ calcul.} & .0007 & .11 & .32 & .50 & .91 & .92 \\
\end{array}
\]

It is to be remembered that the whole theory and working out of Langevin’s experiments is based upon (15) and (16) with the condition that \( \varepsilon \) must be less than 1. In these circumstances the very simple law \( e^{-e t} \), which has been worked out above for comparing departures from uniformity of distribution favourable to recombination, is verified as well as possible.

From the values found for \( \alpha \) in (15) for various gases it is easy to obtain \( A \) in (17). For instance, Townsend (Phil. Trans. exciii. 1900, p. 129), by an electrical method, in which during 0.93 second \( N_1 \) diminished in the ratio 77 to 46 for air, found \( \alpha = 3420e \), where \( e \) is the electron charge \( 3 \times 10^{-10} \). So by this electrical method \( A = 0.0000832 \).
the Ions of Gases.

We have already seen that the experiments of Barus by the entirely independent condensation method yield 6 and 4.5 for $10^3 \times 2A/3$, so that the mean value of $A$ is 0.0000787, with which the result obtained from Townsend's work is in excellent agreement. With the $N^2$ formula Barus found that in his experiments $\alpha$ ranged from 3 to 10 times that given by Townsend's and similar experiments. McClung and Langevin found values for $\alpha$ in air in close agreement with that of Townsend, though they used entirely different electrical methods. The experiments of McClung when used to give $A$ yield for air the value 0.000176, which is about double those just calculated. The data of Langevin do not contain all the particulars necessary for a calculation of $A$ absolutely. We shall now consider the values of $A$ for the four gases of Townsend's experiments, obtained from his data

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\alpha/e$</th>
<th>$10^7A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>3420</td>
<td>832</td>
</tr>
<tr>
<td>$O_2$</td>
<td>3380</td>
<td>769</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>3500</td>
<td>800</td>
</tr>
<tr>
<td>$H_2$</td>
<td>3020</td>
<td>922</td>
</tr>
</tbody>
</table>

It is remarkable that each parameter has a value that changes but little from one gas to another. McClung and Langevin by their independent methods get nearly the same value as Townsend for $\alpha$ for $CO_2$, and McClung's value in the case of $H_2$ agrees with that of Townsend. We have now to see how the values just given for $A$ accord with the theory of it. In (23) the coefficient of $1/p$ is to be proportional to the mean free path of an ion through the gas at a pressure of 760 mm., which is inversely proportional to the square of the molecular diameter with appropriate allowance for the attraction between ion and molecule. Thus we have the coefficient of $1/p$ in (23) inversely proportional to

$$(2a)^2(1+C'/288),$$

which can be calculated from the data of Table II., which yield the following value for the coefficient:—air 745, $O_2$ 860, $CO_2$ 462, and $H_2$ 908. The value 462 thus obtained for $CO_2$ is to be compared with 509 obtained in (23) from Langevin's experiments. These enable us to calculate for each gas at 760 mm. this coefficient divided by 760 which is the part of $log e^{p^{1/3}}$ we require. The corresponding factor of $e^{p^{1/3}}$ multiplied by $u_1 + u_2$ or by $u$ from Table II., according to the theory of $A$, is to be proportional to $A$. Here are the values of $A$ divided by this product:—air 50, $O_2$ 65, $CO_2$ 41,
and H₂ 20. If with CO₂ we use the coefficient 509, the result is 47. If in \((2a)^2(1+C'/288)\) the effective diameter of H₂ were increased by 16 per cent., the low value 20 for H₂ would be brought up to 50. Such uncertainties must be cleared up by new experiments and by fresh interpretations of those already on record, which have been worked out by their authors on the basis of the insufficient N₁² formula. The foregoing theory of A may be summarised by its results in the following way. Let \(l\) be the mean free path of an ion in the gas, being \(0.000004\), then

\[
A = 0.002484(u₁ + u₂)e^{-2.2565/l₀} \quad \ldots \quad (24)
\]

where \(l₀/2.2565\) is the constant length 0.000001754, which seems to be a fundamental constant in the physics of ions, related to a similar one in the statistics of molecules. In concluding the present discussion of the recombination of ions it may be helpful to notice that the formula (16) of Langevin can be derived from our method of laminae in the following way. Suppose the ions in cubical order at distance \(R\) apart. In a laminar distribution we get density \(e/R²\) and force \(4πe/R²\) between the laminae. A pair of oppositely charged ions experiencing this force would acquire relative velocity \(4πe(u₁ + u₂)/R²\) and would travel \(R\) in time

\[
R^3/4πe(u₁ + u₂).
\]

The ions begin to move so that N per unit volume would disappear in this time. In the actual process the N positive and the N negative ions do not suddenly disappear by coming together simultaneously, but their instantaneous rate \(dN/dt\) is \(4πe(u₁ + u₂)N/R²\) and since \(NR² = 1\), this is (16) with \(ε = 1\). This brings out the assumption involved in (15) and (16).

2. The Large Ion without Liquid or Solid Nucleus.

If the small ion investigated in the previous section is placed in a gas whose molecules it attracts so strongly that it carries its immediate neighbours with it as satellites, some profound changes in the conditions are brought about. The induced viscosity \(θ\) almost disappears, because the central small ion has but little relative motion to its immediate neighbour molecules in which it has induced electrization, and the molecules relative to which it is moving are so far away that the induced electrization in them is small. We have here a beautifully simple instance of the way in which a rigidity may merge into a viscosity. It is probable that a
small ion in a moist gas tends to attach molecules of H₂O to itself as satellites and to surround itself with an envelope of vapour of H₂O. To such an ion we shall now apply equations (11) with the supposition that θu can be neglected and also Fu as a separate term, though Fu, as the cause of ζu, will be investigated immediately.

In large ions it has been found that \( u_2 = -u_1 = -u \), so that the two equations reduce to

\[
e^{-\frac{dE}{dx}} = 2\zeta uq^{-1/3} \quad \ldots \quad (25)
\]

ζ is proportional to \( q \), so that when \( dE/dx = \text{volt/cm} \), the last equation makes \( uq^{2/3} \) constant for different values of \( q \) at a given temperature. This is the result discovered by Moreau in his experiments on the cooled gases of flames sprayed with electrolytic solutions (Ann. de Ch. et de Ph. [8] viii. 1906, p. 201, Compt. Rend. cxxli. 1905, p. 1225). He found that in the cooled gases the number of ions per cm.² varies as the square root of the concentration of the electrolyte in the solution, in agreement with the law of Arrhenius for uncooled gases of flames at ordinary flame temperatures. H. A. Wilson has pushed the temperature up till the ionic dissociation in gases sprayed with electrolyte is complete.

If in Moreau’s experiments we denote the concentration of the sprayed electrolytic solution by \( n \), we have \( q \propto n^{1/2} \) and so from (25) we get \( un^{1/3} \) constant at a given temperature. He found \( u_1 = -u_2 \) and \( q \) of the order \( 10^5 \). We shall take his results with solutions of KCl as typical, their strengths being normal N, N/4, and N/16, which we shall express by putting \( n = 1, 1/4, \) and \( 1/16 \), giving his values of \( u \) in cm./sec. for \( dE/dx = \text{volt/cm} \).

<table>
<thead>
<tr>
<th>Temp. C</th>
<th>170°</th>
<th>110°</th>
<th>100°</th>
<th>70°</th>
<th>30°</th>
<th>15°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n=1 )</td>
<td>39 39</td>
<td>16 16</td>
<td>10 10</td>
<td>4.5 4.5</td>
<td>1.5 1.5</td>
<td></td>
</tr>
<tr>
<td>( n=1/4 )</td>
<td>65 41</td>
<td>27 17</td>
<td>15 9.4</td>
<td>— —</td>
<td>2.4 1.5</td>
<td></td>
</tr>
<tr>
<td>( n=1/16 )</td>
<td>90 36</td>
<td>47 19</td>
<td>24 9.5</td>
<td>7.2 2.9</td>
<td>5.1 2.0</td>
<td></td>
</tr>
</tbody>
</table>

The departures from constancy in \( un^{1/3} \) are irregular. Moreau sought to give a different explanation for the origin of the constancy of \( un^{1/3} \) in his various solutions.
The main feature of (25) being verified, we shall now apply it to investigate the remarkable variation of \( u \) with temperature. So we must consider \( \xi \) more closely. The first business is to find the number of \( \text{H}_2\text{O} \) molecules kept captive by an electron, or rather by our nucleolus. We have already seen that an electron in air increases the density of the air round it. In the same way, but to a greater extent, it increases the density of the \( \text{H}_2\text{O} \) round it, because \( \text{H}_2\text{O} \) has an exceptionally large electric moment \( e_s \). For this reason an electron can constrain molecules of \( \text{H}_2\text{O} \) to describe orbits of finite range round it. In the sequel, as before, let suffix 1 refer to the nucleolus, 3 to the gas such as air in which the ion is moving, and 2 to \( \text{H}_2\text{O} \). The electric moment of \( \text{H}_2\text{O} \) is \( e_s \), and if an electron \( e \) is at distance \( r \) along the axis from the centre of \( \text{H}_2\text{O} \), their mutual potential energy is \( e^2s_2/r^2 \). Now when the nucleolus has captured one or two \( \text{H}_2\text{O} \) molecules, its velocity of translation may be neglected in comparison with that of the air molecules and of the free \( \text{H}_2\text{O} \). So we treat the electron as at rest, and the free \( \text{H}_2\text{O} \) molecules as if moving with velocity \( v_2 \) past it. The dynamical condition that a molecule of \( \text{H}_2\text{O} \) with velocity \( v_2 \) at distance \( r \) should just be able to travel to infinity is \( m_2v_2^2/2 = e^2s_2/r^2 \). Within this radius \( r \) the electron gathers a number of \( \text{H}_2\text{O} \) molecules whose axes all tend to pass through it, so that radially these molecules will attract one another, while each will repel its lateral neighbours which are at the same distance from the electron. Thus we have a highly characteristic field of force in our cluster of \( \text{H}_2\text{O} \) molecules. The lateral repulsions will nearly equilibrate one another, so that we can treat all the \( \text{H}_2\text{O} \) molecules as revolving round the centre with constant average linear velocity \( v_2 \). So it is necessary to take account of the radial cohesion. The cohesional potential energy of a molecule of \( \text{H}_2\text{O} \) just retained on the outer surface of radius \( r \) by the combined effect of attraction from electron and of cohesion may be assumed to be approximately constant and be written in kinetic form \( m_2w_2^2/2 \). Hence to determine \( r \) we have the more complete equation

\[
m_2(v_2^2 - w_2^2)/2 = e^2s_2/r^2.\]  

(26) 

Now that we have taken account of the cohesional energy, we can make a correct enough average case by treating all the water molecules as gathered on the surface of this sphere of radius \( r \) round the nucleolus and all moving with the average velocity of the ion. We shall take the number of \( \text{H}_2\text{O} \) molecules per unit surface of this sphere to be propor-
tional to \(N_2\) the number per unit volume in the air. The total number on the sphere is proportional to \(N_2r^2\), say equal to \(AN_2r^2\). We wish to find the resistance \(F\) to the motion of this sphere through the air with unit velocity. Just as in the theory of the viscosity of gases we may say that on account of the electric force of the nucleolus and the cohesional force of the sphere, the number of molecules of air encountered by the sphere will be increased in the proportion \(1 + \left(2e^2s_2/r^2m_2 + w_2^2\right)/v_2^2 : 1\). Unless the number of \(H_2O\) molecules in the sphere is great, the tendency will be for each molecule to experience as much resistance as if the others were absent. It is not a case of a compact sphere of radius \(r\), but of \(AN_2r^2\) spheres of radius \(a_2\). If the \(H_2O\) liquefies into something like water, we shall have to deal rather with a single large sphere formed by the liquid. For the resistance to one molecule of \(H_2O\) moving with unit velocity through the air we get from the kinetic theory of diffusion

\[
\frac{4}{3}N_3(a_2 + a_3)^2 \left\{ 2\pi(v_2^2 + v_3^2)/3 \right\} m_2m_3/(m_2 + m_3)
\]

Strictly we ought to write down the resistance offered to the nucleolus, but, as it would be quite similar to this, we shall merge it in the resistance offered to the \(AN_2r^2\) molecules. Thus

\[
F = \frac{4}{3}AN_3N_2r^2\left\{ 1 + \left(2e^2s_2/r^2m_2 + w_2^2\right)/v_2^2 \right\} (a_2 + a_3)^2
\]

Replacing \(m_2v_2^2/2\) by \(T\) the temperature and \(m_2w_2^2/2\) by \(T_a\) a constant temperature, we find from (26) that \(x^2 \propto 1/(T - T_a)\) and \(1 + \left(2e^2s_2/r^2m_2 + w_2^2\right)/v_2^2 = 2\), while \((v_2^2 + v_3^2)^{3/2} \propto T^3\). Returning to (25) remembering that \(\zeta\) is proportional to \(Fq\), we get

\[
e \frac{dE}{dx} = Cq^{2/3}N_2N_3T^4u/(T - T_a) \quad \ldots \quad (27)
\]

where \(C\) is constant. This is the general equation for the motion of an ion consisting of nucleolus and \(H_2O\) molecules in an electric field. To apply it to the case of Moreau's experiments we put \(n^{1/3}\) for \(q^{2/3}\) and have \(N_3\), \(N_3\), and \(n\) all varying inversely as \(T\), so that \(u\) the mobility when \(dE/dx = \text{volt/cm.} \propto T^{1/6}(T - T_a)\). From Table IV. the mean value of \(un^{1/3}\) at each temperature gives a useful mean value of \(u\) for the case in which the solution sprayed into the flame was normal, and from these I find that \(T_a = 270\). In the next Table the first row gives temperatures, the second
mean values of \( u \) in cm./sec. for \( dE/dx = \text{volt/cm.} \), and in the third \( 10^{10}u/T^{11/6}(T-270) \) which by (27) is to be constant.

**Table V.**

<table>
<thead>
<tr>
<th>Temp. C.</th>
<th>170°</th>
<th>110°</th>
<th>100°</th>
<th>70°</th>
<th>30°</th>
<th>15°</th>
</tr>
</thead>
<tbody>
<tr>
<td>100( u )</td>
<td>39</td>
<td>17</td>
<td>16</td>
<td>10</td>
<td>3.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

This theory of the slower ion in gases leads to the revelation of an error in the ordinary experimental method of measuring their mobilities, the true values in the limit being only half of those assigned. Let AB and CD be two electrodes giving an electric field from AB to CD between which a stream of ionized gas is led in the direction of the arrow. It is assumed that, when all the ions are just caught as the stream flows uniformly, a positive ion entering at A travels along AD, and a negative ion entering at C travels along CB. But, if this were so, the positive ion after it had crossed the intersection of AD and CB would have no neighbour negative ions, and would be free from the viscous resistance \( \zeta \) of electric origin, it would finish its path more swiftly under the resistance \( F \) only. The paths of electrons entering at A and C are AOD and COB. If \( u_a \) is the mobility along AO and \( u_d \) along OD at right angles to AB, we have \( AC/u = AC/2u_a + AC/2u_d \) or \( 2/u = 1/u_a + 1/u_d \). Thus when \( u_d \) is large, \( u_a \) the desired mobility is only half of \( u \) which is usually assigned as the experimental measure of \( u \). Moreau’s values of \( u \) quoted in this paper should be divided by 2, as should also Langevin’s mobility for the very slow ion in air, namely about 1/3000, which should be nearly 1/6000, and a similar remark applies to many other determinations of \( u \). Since, so far, we have been considering only relative values of \( u \) this correction is not needed for the purposes of the previous part of this section. It is important in absolute calculations concerning these ions. This error does not affect the velocities of the small ions considered in section 1.

3. The Large Ion with Liquid or Solid Nucleus.

To account for the very small mobility of the large ion of Langevin I have imagined the structure already described,
namely a nucleus of \((H_2O)_3\) or \((H_2O)_2\) or both in a state very similar to that of a liquid surrounded by an envelope of \(H_2O\) vapour which is kept highly concentrated close to the nucleus. This envelope is similar to the surface film of vapour of \(H_2O\) deposited on the grains of fine powders. The number of \(H_2O\) molecules per cm.\(^3\) close to the nucleus will have a value \(N_3\) like a saturation value, and the number will diminish with increasing distance from the nucleus till it becomes \(N_2\) where its influence has ceased. The thickness of this transition layer may be taken to be constant for a given value of \(N_3\), or we can replace it approximately by a constant length \(l\) such that \(4\pi r^2 l\) is the volume of the transition layer, in which the mean value of \(N_2\) is not \((N_{2s} + N_2)/2\) but \(E'N_{2s} + H'N_2\) where \(E'\) and \(H'\) are constants. The resistance to the motion of all the vapour with unit velocity through the air will be \(4\pi r^2 l (E'N_{2s} + H'N_2)\) times \((26a)\). We can use \((26a)\) also to give the resistance to the motion of the nucleus by replacing \(a_2 + a_3\) by \(r\). We neglect the resistance of the nucleolus and write the total resistance to unit velocity in the form

\[
r^2N_2T^{1/2}(E'N_{2s} + G' + H'N_2)
\]

(28)

where \(G'\) is the constant for the nucleus. This is \(F\), and neglecting it in comparison with \(\xi q^{-1/3}\) which is proportional to \(Fq^{2/3}\) we obtain from \((25)\)

\[
e \frac{dE}{dx} = e^2q^{2/3}N_3T^{1/2}(EN_{2s} + G + HN_2)u
\]

(29)

where \(E, G,\) and \(H\) are constants. Thus the reciprocal of the mobility for \(dE/dx = \text{volt/cm.}\) is linear in \(N_3\) which is proportional to the humidity. This is one of Pollock's results for the Langevin ion. He finds \(1/u = 1200 + 107.5h\), where \(h\) is the humidity in grams/m\(^3\). The constant term 1200, being not far from half the 2500 to 3000 usually found for the Langevin ion in ordinary air, shows that the resistance associated with \(N_{2s}\) is about equal to that associated with \(N_3\), a result which necessitates the stipulation above that the mean value of \(N_2\) takes the form \(E'N_{2s} + H'N_2\). Equation \((29)\) shows that the mobility of a Langevin ion in a gas should be inversely proportional to the density, so that refined observations in the atmosphere ought to be reduced to values for standard atmospheric pressure. But the most striking result in \((29)\) is that \(1/u\) should be proportional to \(q^{2/3}\), varying rapidly with change of concentration of the large ions. Moreover, as before in \((27)\), \(r^2\) is probably proportional to \(1/(T-T_b)\), so that \((29)\) gives a fairly complicated dependence of \(u\) upon the natural variables.
Further experiments must elucidate many of the points raised in the foregoing sketch of a theory. According to the theory the experimental values of the velocities found hitherto for the large Langevin ion ought to be doubled for the same reason as that for doubling the ionic experimental mobilities discussed in section 2. Very interesting questions present themselves as to the equilibrium of these three orders of the ion in the atmosphere. Radioactive substances generate the small ions, most of which disappear through recombination in such a way as nearly to keep the number of small ions constant under a given set of conditions. But some of the small ions will gather envelopes round them and so build up the ion of the intermediate type. This will be liable to destruction through neutralization of its charge by a small ion. The difficulties of building up the large Langevin ion must be great, but once it is formed, the following principle will act favourably to its permanence. The ionizing power of water comes into play. Consider a very small drop of water in which there is one molecule of NaCl. This will be ionized into Na⁺ and Cl⁻, which will be driven as far apart as possible by the ionizing action of the water, whose tendency is favourable to the splitting of the drop into two parts charged with the opposite ions. Thus then the nucleus of a large Langevin ion by its ionizing action will tend to keep its charge unneutralized by opposite ionic charges. So we can account for the permanent existence of the Langevin ion in the atmosphere. These large ions sometimes carry 50 times as much electricity as the small ions in the atmosphere at the same time. Lusby has shown that when the Langevin ions are removed from air, 22 minutes are required for the formation of the same number. If the large ion contains a nucleus of quasi-liquid H₂O, its structure merges into that of the drop of water in cloudy condensations. Something similar to the large ion ought to appear in the condensation of H₂O on small ions, and in the evaporation of a drop surrounding an ion. The theory of large ions is closely connected with that of cloudy condensation. Now J. J. Thomson in 'Conduction of Electricity through Gases' and Langevin (Bloch, Ann. de Ch. et de Ph. 1905, iv. p. 25) have given a theory of cloudy condensation upon ions, which in both cases seems to furnish a remarkably successful explanation of the experimental fact that fourfold saturation is needed in vapour of H₂O to produce cloudy condensation on small ions. But they use quite different expressions from those developed here concerning the potential energy of an electron and surrounding molecules. It seems to me that
their expressions are not the right ones for the purpose to which they apply them. For example J. J. Thomson writes $e^2/2Ka$ for the electrical potential energy of an electrified drop of radius $a$ surrounded by a medium of dielectric capacity $K$, which is put $=1$, and Langevin also uses $e^2/2a$. They then apply this to an electron surrounded by water. But, unless the electron spreads itself over the surface of the drop in much the same way as a large number of like electrons would, this expression is no longer valid. The electrical energy of an electron and an envelope of molecules is a mutual affair, tending to take the form $e^2s/a^2$ for a central electron and a molecule at distance $a$, so the total electric energy of electron and drop must be expressed by a form quite different from the $e^2/2a$ used by both authors. Then again they carry the conception of surface tension and surface energy even into the dynamical specification of the smallest drops. The directive effect of the central electron on the few molecules of the smallest drop must profoundly modify their cohesion forces. For these reasons the theory of Thomson and Langevin appears to me to be quite illusory in its details and to give its remarkable result concerning fourfold saturation by a concealed compensation of errors. They give a theory of what is essentially a molecular affair by means of purely molar considerations and data. Their theory applies to drops which are large enough to have a surface tension like that of ordinary water and which carry a surface charge of electricity. It can give no account of the real happenings when vapour of water begins to gather round a small ion.

**Summary.**

In a dynamical theory of the ions of gases the two new types of viscosity previously investigated for ions in electrolytic solutions are found to be of paramount importance. The induced viscosity, namely that which arises from the electric action of the ion upon surrounding molecules, produces in all gases about 7.6 times as much resistance to the motion of the small ion as ordinary gaseous viscosity does. The other type of viscosity, namely that which arises from the mutual energy of oppositely charged ions, is not of large enough amount to make its appearance in the experimental study of small ions at the low concentrations in which these are usually employed. In the case of the small ion there is another result of the electric action between it and surrounding molecules, for this causes collisions to occur more frequently, as cohesion force does in the theory of the effect of temperature on the viscosity.
of gases. In a gas above the critical temperature and at ordinary pressures the mobility of a small ion varies with temperature according to the formula \( u = A'T^{1/2}/(1 + C'/T) \) in which \( A' \) is a parameter characteristic of each gas, and \( C' \) is proportional to the mutual potential energy of ion and molecule when in contact during a collision, being similar to \( C \), the corresponding quantity in the theory of the viscosity of gases. On the principles of the kinetic theory of gases \( A' \) is found for any gas in terms of the number, diameter, mass, and velocity of its molecules, by an analysis which leads finally to (12). The theory is verified by means of the experiments of Phillips on the effect of temperature on the mobility of small ions in air, and by means of the data so far obtained experimentally for the mobility of small ions in gases and vapours. It leads to values of the potential energy of ion and molecule in contact which are given in Tables II. and III., and these furnish evidence of the presence in \( \text{H}_2 \), \( \text{He} \), \( \text{N}_2 \), and \( \text{O}_2 \) of an electric doublet of constant electric moment. By taking account of the new induced type of viscosity and also of \( C' \) it is shown that the small ion has no molecules attached to it. It is like the ion of electrolytic solutions. The smallness of the coefficients of diffusion of ions is traced to the induced viscosity, the hypothesis of molecular clusters being unnecessary. As regards the rate of recombination of small ions in gases it is necessary to replace the first approximation expressed in the formula of J. J. Thomson, namely \( \frac{dN}{dt} = -aN^2 \), by a second approximation \( \frac{dN}{dt} = -AN^{5/6} \), which is deduced theoretically by regarding recombination as a leak in laminar distribution of the ionic charges. This formula is verified over a wide range of values of \( N \) by the experiments of Barus and also by the experiments adduced by J. J. Thomson in support of the \( N^2 \) formula. From statistical considerations formula (24) is established for \( A \) and verified by the experiments of Langevin on the effect of pressure on the rate of recombination of ions in air and \( \text{CO}_2 \).

But although the small ion is not associated with molecular clusters, there are cases in which the small ion attaches molecules to itself and becomes a large ion. These are divided into two classes, the large ion consisting of an envelope of vapour, such as that of \( \text{H}_2\text{O} \), surrounding a small ion which is the central nucleolus, and the larger ion in which a liquid or solid nucleus forms round the ionic nucleolus, the whole being surrounded by an envelope. With these large ions the induced viscosity becomes of negligible importance, because the moving electric charge is too far from the molecules of the surrounding gas. But the direct electric
viscosity arising from the rigidity belonging to the evenly mixed ions becomes of paramount importance because of the greatly increased time of relaxation for large ions. The theory of the large ion without nucleus leads to (27), an equation connecting the mobility of this kind of large ion with concentration and temperature. This is verified in Tables IV. and V. by means of the experiments of Moreau on the slow ions formed by spraying solutions into flames and cooling the resulting gaseous mixture. For the large ion of Langevin, on the supposition that it has a nucleus of water, equation (29) is worked out to show the connexion of mobility with concentration of the ions, density of the air, humidity and temperature. This shows general agreement with the results of Pollock as to the effect of humidity on the mobility of the large ion of Langevin. Experimental data are lacking to test it otherwise. To account for the permanence of this large ion it is pointed out that the ionizing power of water tends to keep it intact. Certain objections are raised to the theory of J. J. Thomson and Langevin to account for cloudy condensation of H₂O vapour on small ions at fourfold saturation.

During the working out of the foregoing I have had the advantage of correspondence with Prof. Pollock while engaged in his experimental inquiries on large ions.

Melbourne, June, 1909.


Thesis approved for the Degree of Doctor of Science in the University of London †.

[Plates X.-XII.]

Part I.—The Echelon Spectroscope.

The Echelon and its Mounting.

The echelon spectroscope described in this paper was constructed by Messrs. Adam Hilger for Professor Schuster, a modification, which has proved to be very valuable, being made in the usual design. A front elevation,  

* Communicated by the Physical Society; read June 11, 1909.
† The following alterations have been made:—Equations 2, 3, 4, 9, 9†, and the section on the spectrum given by a hot lamp have been added; also the faint lines previously described as doubtful are shown to have their origin in the echelon.