The Electric Origin of Molecular Attraction.

By William Sutherland.*

Introduction.

By molecular attraction we understand intermolecular forces whose effects are not appreciable at distances of a larger order than molecular, thus excluding ordinary gravitation and ordinary electric and magnetic force. But the law of molecular attraction which I have discussed (Phil. Mag. [5] xxxv., xxxix., and other volumes), namely, that of the inverse fourth power, can be most readily accounted for by tracing it to the electric polarity which the electron theory of chemical valency necessarily ascribes to molecules, because the theory of magnetism familiarizes us with an inverse fourth power force between magnets at distances great compared with their lengths. In applying this known magnetic result to account for molecular attraction we are at the outset confronted with the difficulty that in the case of magnets the force is as often repulsive as attractive, the nature of the force depending on the relative direction of polarities in the magnets, whereas the molecular forces required to account for cohesion must be preponderatingly attractive.

We have to investigate how, if the electric axes of molecules are distributed at random, and repulsive forces would therefore seem to be as common as attractive, it is possible for the attractive so to prevail over the repulsive as to leave a final balance of attraction, as if on the average all the forces were

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Mr. W. Sutherland on the attractive. There is this fundamental distinction in the effects of attractive and repulsive forces whose strength decreases with increasing distance, that the attractive forces by their own operation tend to increase themselves, while the repulsive tend to decrease themselves. Consider, for example, a diatomic gas in which each molecule contains a single electric doublet formed by the opposite electrons holding its two atoms together. If two neighbouring molecules are approaching one another with their electric axes similarly directed in the straight line of relative motion, then the attractive force acts with strength increasing to the maximum possible value at the instant of collision. If their electric axes were oppositely directed in the line of motion the forces would be repulsive, and could reverse the motion before their maximum possible strength had been attained. In general there is the same tendency for attractive forces to increase their strength and for repulsive to diminish. This causes attraction to preponderate. The idea that molecular polarity might account for the inverse fourth power law of molecular attraction encouraged me when first investigating that law, though I failed to see how the attractive forces due to polarity could on the average be of more importance than the repulsive. It therefore seemed better at that time to work inductively at the accumulating mass of experimental material on molecular force, than to follow out a deductive theory of molecular attraction founded on molecular polarity, of which until recently we have had little convincing evidence. But with recent developments of the electron theory, which forces on our consideration electric doublets as a prominent feature in molecular structure, it becomes imperative to follow the deductive path. For if with Helmholtz we regard every chemical bond as consisting of a $\text{=}^1$ and a $\text{=}^2$ electron (Phil. Mag. [6] iii. Feb. 1902), we see that every junction of atom to atom involves the existence of an electric doublet $\text{=}^3$, analogous to a magnet and exercising on every other such doublet a force of attraction or repulsion varying inversely as the fourth power of the distance between them. The electron theory supplies us therefore with a true cause of molecular attraction on a very simple basis, namely, the inverse square law of electric force and the existence of the two sorts of electrons in equal numbers. The results to be interpreted in the light of the electron theory are contained in the following communications in the Phil. Mag.: series [5] “A Kinetic Theory of Solids,” vol. xxxii., “The Laws of Molecular Force,” xxxv., “The Viscosity of Gases and Molecular Force,” xxxvi., “The Attraction of Unlike Molecules,” xxxviii., “Further Studies on Molecular Force,” xxxix., “The Fundamental Atomic
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1. Statement of the theory, consideration of difficulties, and a short digression on the Maxwell-Faraday stresses in the æther and cohesion of the æther.
1a. The range of molecular force.
2. Comparison of results with known laws of molecular attraction.
4. Period of rotation of an electric doublet.
5. Electric doublets in different classes of chemical substances.

1. Statement of the Theory.

Briefly it is this:—That the electric doublets in molecules exercise mutual directive actions as do magnets, so that the nearer two neighbours approach the more do their electric axes tend to take the same direction, and therefore on this account they exercise a stronger attraction on one another; and also because attracting forces varying inversely as the fourth power of the distance produce motion which increases their strength, there are two causes which make the attractive forces amongst a number of moving doublets of more dynamical importance than the repulsive. To fix ideas we must look more closely into the system of forces between two magnets.

In Maxwell's 'Electricity and Magnetism' (2nd edit.) art. 387, we have Tait's results for the forces of magnets on

\[
\begin{align*}
H_1 & \\
H_2 & \\
R & \\
C & \\
\alpha & \\
D & \\
A & \\
B & \\
\end{align*}
\]

magnets translated from quaternion into ordinary expressions. Let \( AB \) and \( CD \) be two magnets of moments \( m_1 \) and \( m_2 \) in
different planes with their centres at distance $r$ apart. Through the centre of CD draw a b parallel to AB, and let $\mu_{12}$ be the cosine of the angle between CD and a b, and $\lambda_1$, $\lambda_2$ the cosines of the angles made by AB and CD with $r$, then the action of AB on CD consists of forces $R$, $H_1$, and $H_2$ given by the equations

$$R = (\mu_{12} - 5\lambda_1\lambda_2)3m_1m_2/r^4,$$

$$H_1 = \lambda_23m_1m_2/r^4; \quad H_2 = \lambda_13m_1m_2/r^4;$$

and also of two couples one of which acts in the plane of a b and CD with a moment $\sin(H_1H_2)m_1m_2/r^3$, where $(H_1H_2)$ is the angle between $H_1$ and $H_2$ which the couple tends to increase, while the second couple acts in the plane of $R$ and $H_2$ and tends to diminish the angle between these directions with a moment $\cos(RH_1)\sin(RH_2)3m_1m_2/r^3$.

The more important standard case for our present purpose is that in which the two magnetic axes are in the same plane with the join of the middle points of the magnets. This can be further simplified for the discussion of a typical case by assuming the two magnetic axes to be parallel with one another and making an angle $\theta$ with the join. Then the forces reduce to a central repulsion

$$- (2\cos^2 \theta - \sin^2 \theta)3m_1m_2/r^4, \quad \ldots \ldots \quad (1)$$

and a component $2\sin \theta \cos \theta \cdot 3m_1m_2/r^4$ acting at right angles to the join. These latter rotational forces and the couples equilibrate one another if the two magnets are part of a rigid system. We shall neglect them for the present, and confine our attention to the central force. When $\theta=0$ this becomes

$$-6m_1m_2/r^4,$$

the minus sign denoting that it is an attraction; and when $\theta=\pi/2$ the force is repulsive of amount $3m_1m_2/r^4$.

This well-known case of the attraction in one standard position being double the repulsion in another might lead to an erroneous conception of how attractive force might preponderate over repulsive. For example, we might determine the average force acting between two magnets as one moves in a quarter circle of radius $r$ from $\theta=0$ to $\theta=\pi/2$, namely,

$$\frac{2}{\pi} \int_0^{\pi/2} 3m_1m_2/r^4(2\cos^2 \theta - \sin^2 \theta)d\theta = \frac{3m_1m_3}{r^4} \cdot \frac{1}{2};$$

and imagine that, if a number of magnets or electric doublets direct their axes to parallelism, they will exert forces on one another which are preponderatingly attractive. It is important to expose the fallacy of this incomplete reasoning, because in doing so we can touch upon a matter germane to the present inquiry.
If the electric properties of matter are to be explained in terms of electrons, so also must the electric and magnetic properties of the ether. I have proposed to call the molecule of electricity formed in the ether by the union of the atoms $\#$ and $\gamma$ of electricity the neutron, and to denote it by $\#\gamma$. In an electrostatic field we must suppose the electric axes of the neutrons so turned in the direction of the field that each has a positive component of electric moment in that direction. This acquisition of a common direction by the axes of the neutrons constitutes what is called the polarization of the ether regarded as a dielectric. The amount of the component electric moment is proportional to what Maxwell calls the electric displacement, which we can thus realize as a veritable displacement to be specified by an actual distance, namely, the component of the vector joining the centres of the two electrons in a neutron in the direction of the electric field. We thus come into contact with an important point in the dynamics of the ether bearing also on the subject in hand. We shall therefore glance at the problem: What is the virial of the force of a set of doublets uniformly distributed with parallel axes through any space?

Take a spherical shell of radius $r$ and thickness $dr$, and take the ring cut out by cones whose axis passes through the centre parallel to the axes of the doublets, and whose semiveritical angles are $\theta$ and $\theta + d\theta$; then if there are $n$ doublets per unit volume, and if $R$ denotes the central force between a doublet at the centre and any doublet in the shell, we have for the part of $\frac{1}{2}\Sigma Rr$ due to the doublets in the ring and at the centre, using the value of $R$ given by (1), the expression

$$\frac{n}{2} \cdot \frac{3m_1m_2}{r^3} (2\cos^2 \theta - \sin^2 \theta)2\pi r^2 \sin \theta d\theta dr = f(\theta) d\theta,$$

say;

and for the whole shell

$$2\int_0^{\pi} f(\theta) d\theta = 0.$$

Thus the tendency is for the virial $\frac{1}{2} \cdot \frac{1}{2}\Sigma Rr$ for all the doublets in a large space to vanish. Neither attractive nor repulsive forces predominate in the virial; and thus we see how it would not be correct to argue from elementary considerations that in parallel doublets uniformly distributed attractive forces could be assumed to preponderate.

Moreover, we see that if to the neutrons of the ether we apply Clausius's equation of the virial, as in the kinetic theory of matter, the production of an electrostatic field does not cause any variation of the virial of the internal forces. Now
the Maxwellian specification of the Faraday stress in the æther, when acting as an electrostatic field of intensity \( F \), is a tension \( F^2/8\pi \) along the lines of force, and a pressure of equal amount in every direction at right angles. Thus the change of the external virial for a volume \( v \) occupied by neutrons is \(-vF^2/16\pi\) on account of the tension, and \(2vF^2/16\pi\) on account of pressure. But by Clausius’s equation, if there are no other forces this must represent the change of the kinetic energy in volume \( v \); so that we find half the energy \( F^2/8\pi \), which Maxwell considers to be stored in each unit volume of the electrostatic field, is stored there as kinetic energy of the neutrons, if our simple conception of the action of the neutrons is correct. The other half of the energy must be that which has been put into the field in turning the electric axes of the neutrons so that they have all a positive component of moment in the direction of the field.

When the æther is not a field of force and the neutrons have their electric axes disposed at random, two cases will arise according as the neutrons have velocities of translation or not. If they have, then on account of the nearer approach of those attracting one another there will be a preponderance of attraction, which will give cohesion to the æther. If, on the other hand, the neutrons have no translatory velocities, but only rotate, then attractions and repulsions will act with the same strength, and there will be no cohesion in the æther on account of its neutrons. Having indicated how the principles of electric doublets must be applied to the æther as well as to matter, we had better now analyse some of the known laws of molecular force to test, before we proceed farther, whether they are compatible with an origin in the properties of electric doublets. But first to fix ideas we must interpose the following section.

1a. The Range of Molecular Force.

For the central force between two small magnets no range can be assigned, and similarly none can be specified for that between two electric doublets by themselves. But in considering a large number of such doublets we find conditions arise which practically fix the range of molecular attraction as a distance of the same order of magnitude as the average distance between two neighbour molecules. We have seen that there are two reasons for the preponderance of attractions over repulsions, namely, an effect analogous to induction by which two approaching doublets tend to pull one another’s electric axes into the straight line joining their
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centres, and an effect due to the large departure from average conditions when a pair of neighbours collide. For example, two molecules A and B, separated by a large number of others, may have their axes so directed that they have the maximum mutual inductive effect and maximum attraction at that distance, but it will be possible to find near A a molecule C whose effect on B is nearly equal and opposite to that of A, and a molecule D near B which neutralizes the effect of B on A. But if A and B are on the point of collision it is not in general possible to find another pair C and D capable of neutralizing the mutual effects of A and B. For molecules whose distance apart is several times the mean molecular interval, the preponderance of the attractive over the repulsive forces diminishes rapidly with increasing distance. To take account of the average effect of this phenomenon we can replace the perpetually varying actual forces by a fictitious molecular attraction \( f(r)/r^4 \), in which \( f(r) \) can be assigned a form which best represents the average facts, and introduces a fairly definite range beyond which molecular attraction is negligible. A speculation of van der Waals (Ann. d. Ph. Beibl. xviii, p. 734) suggests one form that \( f(r) \) might conveniently have assigned to it provisionally. He assumes that molecules attract one another according to Newton's law of gravitation, but that the lines of force are absorbed by the medium in such a way that the potential energy of two molecules may be written \(-f_0 e^{-r/\lambda}/r\), where \( \lambda \) is a parameter characteristic of the substance and is equal to \( H/K \), the ratio of Laplace's two capillary parameters. But we shall see immediately that molecular attraction has no direct connexion with gravitation. Moreover, the absorption of lines of force would be difficult to reconcile with the absence of any known gravitational property corresponding to the electric one of dielectric capacity. But van der Waals' factor \( e^{-r/\lambda} \) becomes intelligible if taken as representing our \( f(r) \). In the absence of knowledge as to the form of \( f(r) \) perhaps the simplest way of taking account of it is to remove it and assume that the force \( 1/r^4 \) acts from a distance \( r=\nu \), where \( \nu \) is of the order of the distance between contiguous molecules, up to a distance \( r=\nu \) and not beyond, \( \nu \) being so chosen that the effects due to distances greater than \( \nu \) are allowed for by exaggerating the effects up to distance \( \nu \) through treating the function \( f(r) \) as 1. This simple method of treating the unknown \( f(r) \) has the temporary advantage of agreeing with that which I have already adopted in investigating the law \( 1/r^4 \) while providing a more definite meaning for \( \nu \) than that formerly suggested. In one place
I proposed that $L$ might mark the linear dimensions of molecular swarms, but according to the present line of reasoning the idea of a molecular swarm gives place to that of a range limited to a small multiple of the average distance between two neighbours. Thus the range for an ordinary vapour would be different from that in its liquid. In steam over boiling water the average distance between neighbour molecules is about twelve times that in the water, but we cannot assert that because steam still shows measurable effects of molecular attraction therefore the range of molecular attraction in water extends to at least twelve times the distance between two neighbour molecules. The correct deduction according to the principles under discussion would be that in steam the range of molecular attraction must be taken to be about twelve times as large as in water. In the next section we shall introduce a great simplification by treating the range of molecular attraction as the average distance between two neighbour molecules, thereby expressing that attractions which eventuate in collisions are by far the most important of the forces we are now considering.

2. Comparison of Results with known Laws of Molecular Attraction.

It will now be shown that the laws of force so far discovered satisfy the conditions required by the electron theory. In the first place, although the force between two molecules was on the analogy of gravitation written by me in the form $3\lambda m^2/r^4$, it soon appeared from its application to experimental data that $3\lambda m^2$ ought to be regarded as a single parameter of molecular force $3\alpha^2$ which had no direct dependence on the mass $m$ of a molecule. This marks a strong contrast to the law of gravitation, and satisfies the first condition of the electron theory, namely, that molecular mass does not enter into the expression for molecular attraction. In the second place it has been proved (xxxviii.) that the force between two unlike molecules 1 and 2 is $3\alpha_1\alpha_2/r^4$, $\alpha_1$ and $\alpha_2$ being characteristic constants of 1 and 2. In the third place an almost direct proof of the electronic origin of molecular attraction is furnished by the law of the parameter $\alpha^2$ for binary molecules of the type $RS_n$ (Phil. Mag. [5] xxxix. pp. 25 & 45), namely,

$$\frac{\alpha^2}{\rho} = (\rho/\rho + \sigma)^{\alpha_2}$$

$\rho$ and $\sigma$ being parameters having definite values for each element $R$ and each element $S$, because, to quote from the
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Paper just referred to (p. 45), it "means that the mutual energy of two molecules of this type divided by the number of equivalents in each can be obtained by regarding each equivalent as a separate attracting entity." For if each pair of electrons forming a chemical bond attracts each other one, then in Clausius's equation of the virial if, neglecting for the present purpose external pressure, we write

\[ \frac{1}{2} \mathcal{N} m v^2 = \frac{1}{2} \cdot \frac{1}{2} \mathcal{S} \mathcal{S} 3a^2 r/r^4, \]

where the double summation \( \mathcal{S} \mathcal{S} \) is to be effected for all the \(\mathcal{N}\) molecules, we have really to sum for the electric doublets which produce the molecular attraction. In the first place, then, we have to evaluate \( \mathcal{S} 3a^2 r/r^4 \), where \( r \) represents the distance of any one definite molecule from any other, and the summation is to be effected for all molecules within a distance \( L \). Now if there are \( n \) doublets in each molecule and \( a \) is the value of \( a \) appropriate to a doublet, this would take the form \( n^2 \mathcal{S} a^2 r/r^4 \), if each doublet were associated with a molecule entirely its own. But as there are \( n \) doublets in each molecule, it is clear that in general the parameter \( a \) cannot be equal to \( na \). But there is an important exception to this, namely, when the axes of the doublets are all directed the same way, so that their moments are simply added together and then \( a = na \). We shall see in section 5 that complex molecules show a tendency towards this state of identical direction in the doublets which they contain. But the case of the simpler types of binary compounds is one where considerations of symmetry do not favour the hypothesis of similarly directed doublets in the molecule. For example, the structure of \( \text{CaCl}_2 \) would be best represented by the formula \( \text{hClhCa} \text{hClb} \), where the two doublets are oppositely directed. In the case of \( \text{SnCl}_4 \) we should expect the four doublets to be pointing from the centre to the corners of a regular tetrahedron. The collision of molecules carrying doublets directed in such ways as these can be regarded in the following manner. The circumstance chiefly directing the occurrence of attraction between two molecules is that the doublet in one which is nearest to a doublet in the other should have its axis in nearly the same direction as that of the latter. It is true that there are \( n^2 \) ways of arranging two molecules so that they may have a pair of doublets in the most favourable position for attraction. But out of every \( n \) chances which the \( n \) doublets give a molecule of being attracted by another only one eventuates in attraction, because it happens to be the strongest and ultimately leads to
a collision. Thus on the average the attracting power of molecules containing $n$ symmetrically arranged doublets each is only $n^2/n = n$ times that due to a single doublet. In this way the remarkable equation (A) may be explained.

The attraction of such molecules depends on the number of equivalents in each in a way that points suggestively to the doublet origin of molecular attraction.

The most important point now is to determine the definite connexion between the electric properties of doublets and the experimental parameters of molecular attraction. If we write Clausius's equation of the Virial as adapted for the kinetic theory of $N$ molecules in a volume $v$ we have

$$3pv/2 = Nmu^2/2 + \frac{1}{2} \cdot \frac{1}{2} \Sigma Rr,$$

where the last term, which is the virial of the internal central forces $R$ (different from Maxwell's $R$ for magnets), includes the virial of the preponderating attractive force as well as that of the repulsive forces coming into play during molecular collisions. These latter give a virial proportional to the kinetic energy, so that the last equation may be cast in the form

$$pv = RTv_f(v) + v\phi(v), \ldots$$

(2)

where $v\phi(v)$ represents two-thirds of the virial of the attractive forces, and $R$ is now the usual gas constant. Now according to the law of attraction $3Am^2/r^4$, or better $3a^2/r^4$, I have shown (xxxv.) that if the $N$ molecules form a sphere of radius $R$ (still another signification for $R$, but the context prevents confusion), and if $b$ is a length of the order of the distance between neighbour molecules,

$$\frac{1}{2} \cdot \frac{1}{2} \Sigma 3a^2/r^3$$

$$= 6\pi r^2 s^3 \left\{ \frac{1}{3} (R-b)^3 \log \frac{2R-b}{b} - \frac{2}{3} (R-b)^3 \right\}$$

$$- \frac{2}{3} R^2 (R-b) + \frac{R^2}{3} \log \frac{2R+b}{b} \right\}, \ldots$$

(3)

where $p$ is the density of the substance formed by the $N$ molecules.

But according to what we have stipulated about the origin of our preponderating attraction and the range of molecular force we can evaluate $\frac{1}{2} \cdot \frac{1}{2} \Sigma Rr$ in a far simpler manner. Let $es_1$ and $es_2$ be the electric moments of any two doublets, where $e$ is the numerical value of the charge $e$ or $b$ and $s_1$ and $s_2$ are the distances between $e$ and $b$ in the doublets, then, if $r$ denote the average distance apart of two neighbours
which have their axes so directed as to attract one another with the maximum force at that distance, we may consider the total attraction in which these two take part at a given instant to be expressed on our magnetic analogy by \(6e^2s_1s_2/r^4\), all other forces in which these two are involved cancelling one another. Thus, as in the theory of the viscosity of gases and molecular force (xxxvi.), we replace the almost intractable medley of nature by a simple representative pair of molecules. The part contributed to the first summation in the internal virial by this pair is \(3e^2s_1s_2/2r^3\), which stands for \(\frac{1}{2}\Sigma Rr\), and then

\[
\frac{1}{2}\cdot\frac{1}{2}\Sigma Rr = 3Ne^2s_1s_2/2r^3.
\]

In a homogeneous substance \(s_1=s_2=s\), and we may write \(r^3=v/N\), obtaining for the virial of the attractions \(3N^2e^2s^3/2v\).

The expression (3) may be written

\[
6a^2\pi (N^2/v^3) (4\pi R^3/3) f(b/R) = 6\pi f(b/R) a^2N^2/v,
\]

making it evident that \(a\) is proportional to \(es\). The simplest way of comparing the results of the two methods of calculating the virial of the attractive forces, namely that which treats the attractions as operating between each molecule and all the rest within a sphere of radius \(R\), and that which treats them as on the average acting only between immediate neighbours taken in pairs, is to calculate numerical values for \(f(b/R)\) when \(R/b=2, 10, \text{ and } 100\), namely 0.60, 2.69, and 7.78, which give (3) the three values (0.94, 4.2, and 12.2) \(a^2N^2/v\). By increasing \(R\) from 2\(b\) to 100\(b\), that is by increasing the number of molecules included in the first summation of \(\Sigma\Sigma\) from 8 to 100,000, the value of the internal virial of the attractions is increased only 13-fold. This illustrates how the effect of molecular attraction depends mostly on the mutual actions of immediate neighbours, as we indicated in discussing the range of molecular force.

In the papers referred to, the internal virial term \(v\phi(v)\) in (2) is proved for the element gases to take the form \(-l/v\), while for compounds at small enough values of \(v\) it also takes the form \(-l/2v\), passing at larger values of \(v\) through a very interesting transition to be discussed in section 5. In these communications values of \(l\) have been found for many substances, though mostly given indirectly by the tabulation of \(M^l\), where \(M\) is the molecular mass referred to that of the hydrogen atom as 1, and \(l\) is given for unit mass of the substance in terms of 10\(^{12}\) dynes as unit of force. Then, since \(l\) is \((2/3)6\pi f(b/R) N^2\alpha^2\) or \(N^2\varepsilon\sigma\), and if \(N\) refers
to unit mass it is $1/m$ where $m$ is the actual mass of a molecule, and so $N = 1/Mh$ where $h$ is the actual mass of an atom of hydrogen, the tabulated values of $M^2l$ are really values of $e^2s^2/h^2$. But $e/h$ is a standard electrolytic constant. Hence it follows that in investigating the laws of $(M^2l)^{1/2}$, as in some of the communications referred to, we were really studying the law of $s$ the distance between $#_1$ and $#_2$ in the doublets which form the chemical bonds. The electric theory of molecular attraction leads thus to the simplest possible physical interpretation of the parameters of molecular force, and invests their laws with a more immediate interest.

The best test to apply to the theory at this stage is to calculate the order of magnitude of $s$ to see whether it is consistent with what we know of molecular sizes. The linear dimensions of molecules are of the order $10^{-8}$ cm., and of electrons (Phil. Mag. [5] xlvii.) of the order $10^{-14}$, and these are limits for the size of $s$. Let us take the simplest type of binary molecule such as NaCl, for which the tabulated value of $(M^2l)^{1/2}$ (xxxix.) is 5.6, which is to be multiplied by $10^6$ to give the value when the dyne is the unit of force. Now

$$es/h = (M^2l)^{1/2} \quad \text{and} \quad h/e = 345 \times 10^{-17},$$

$$\therefore \quad \text{for NaCl} \quad s = 1.93 \times 10^{-8}.$$

To determine the linear dimensions of the NaCl molecule we can proceed as for that of the Li atom in “Ionization &c.” (Phil. Mag. [6] iii. p. 176) where the radius of the Li atom is found from its ionic velocity in water to be $2 \times 10^{-9}$. The volume of the Na atom is $7.4/2$ times that of Li, and of Cl is $19/2$ times (see Table III. of that paper), so that the mean radius of NaCl will be $(26.4/2)^{1/2} \times 2 \times 10^{-9} = 7.26 \times 10^{-9}$ cm. The diameter $d$ of the NaCl molecule is thus found to be $1.45 \times 10^{-8}$. The fact that we have found $s$ a little larger than $d$ indicates that we have overshot the mark in reducing molecular attraction so that it operates between only immediate neighbours at their average distance apart. But from the nature of the case we can expect to obtain only the order of magnitude of $s$, which is about equal to that of molecular diameters.


It is of great importance in chemical dynamics that we should be able to find accurately the ratio of $s$ to $d$ in order to push farther with Helmholtz’s theory that the chemical forces between atoms are identical with the forces between the electric charges constituting their valencies. Richarz
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(Wied. Ann. ii.), to test this theory in the simplest concrete way, treats the dissociation of $\text{N}_2\text{O}_4$ into $2\text{NO}_2$ and of $\text{I}_2$ into $2\text{I}$ as the performance of work $\varepsilon^2/r$ against electric force for each molecule of $\text{N}_2\text{O}_4$ or $\text{I}_2$ dissociated, $r$ being the distance apart of the charges $\sharp$ and $\flat$ which hold the two parts of $\text{N}_2\text{O}_4$ or $\text{I}_2$ together. Richarz, assuming $10^{20}$ to be the number of molecules in a c.c. of gas at $0^\circ$ C. and 1 atmo, and $r$ to be $10^{-8}$, finds for $\varepsilon$ a value agreeing with that derived from other sources. In order to make his results more definitely comparable with those of this paper, I will carry out his reckoning in the following manner:—Let $\mu$ be the mass of 1 c.c. of $\text{H}_2$ at $0^\circ$ C. and 1 atmo, then the number of molecules in a c.c. of any gas under standard conditions is $\mu/2h$, and the work of dissociating such a c.c. of $\text{N}_2\text{O}_4$ is

$$W = \frac{\mu}{2h} \cdot \varepsilon^2 = \frac{\mu}{2} \left(\frac{\varepsilon}{h}\right)^2 \cdot \frac{1}{r} \cdot \frac{m}{M \cdot \tau}.$$ 

But if $\rho$ is the density of the molecule $m = 4\pi pr^2/3$, taking $r$ to be its radius,

$$W = \frac{\mu}{2} \left(\frac{\varepsilon}{h}\right)^2 \cdot \frac{1}{M} \cdot \frac{4\pi \rho r^2}{3},$$

$$W = 25 \times 10^6 \text{ ergs}, \quad M = 92,$$

$$\rho = 92/49 \text{ (Phil. Mag. [5] xxxix, p. 7).}$$

$$\mu = 0.096 \times 10^{-8}, \quad h/\varepsilon = 345 \times 10^{-17}.$$ 

$$r = 8.8 \times 10^{-9} \text{ cm.}$$

We have followed the method of Richarz in identifying $r$, the distance apart of the charges, with the radius of $\text{N}_2\text{O}_4$. Strictly, according to our reasoning, the electrical work per molecule $\varepsilon^2/r$ ought to be written $\varepsilon^2/s$, and the previous reasoning would give us an equation for $\varepsilon^2/s$. But the important point at present is that the distance apart of the electric charges forming chemical valencies in molecules is found to be of the same order of magnitude as molecular diameters both from the electric theory of molecular attraction and from the simple cases to which Helmholtz's electric theory of chemical forces has been applied. Of course Richarz's simplifying assumptions require that when $\text{N}_2\text{O}_4$ is dissociated into $2\text{NO}_2$ the mass of gas should consist of a mixture of $\text{NO}_2$ ions, namely $\sharp\text{NO}_2$ and $\flat\text{NO}_2$ evenly mixed and forming a conductor for any difference of potential. In the same way, when iodine is dissociated to the atomic state it ought to be a good conductor of electricity if Richarz's calculation applies to it. Now J. J. Thomson's experiments on the passage of electricity through hot gases (Phil. Mag. [5] xxix.) proved that the specific conductivity of gaseous
iodine at about 1100° C. is about the same as that of glass at 300° C., and enormously less than that of ordinary electrolytic solutions. But the vapour-density measurements of Crafts and Meier show that at this temperature about a quarter of the I₂ is dissociated into 2I, and therefore if Richarz's simplifying hypothesis were true for iodine the conductivity ought to have been found enormously greater by J. J. Thomson than it was. Until this difficulty with I₂ and the corresponding one with N₂O₄ has been cleared up, we do not know what becomes of the electric charges which Richarz assumes to be separated, and are therefore not entitled to write \( \frac{e^2}{r} \) or \( \frac{e^2}{s} \) as the electrical work done in dissociating a molecule such as I₂ or N₂O₄. To account for the facts with iodine we shall have to assume a rearrangement of doublets rather than the splitting of them into separate electrons. Moreover, we have in Helmholtz's theory to take account of changes in the mutual potential energy of electrons and atoms in any change of relative positions caused by rearrangement of doublets. Therefore at present we must not attach too much importance to the agreement in order of magnitude between our \( s \) and Richarz's \( r \) as derived from Helmholtz's theory in a form which is the simplest possible and is apparently too simple for the facts of nature. There is obviously room for immediate further experimental and theoretical work in this interesting department.

4. Period of Rotation of an Electric Doublet.

If we carry out the Richarz simplification to one of its logical consequences we shall consider the two electrons of a molecule like NaCl, when giving the line spectrum of Na, to be revolving round one another with their relative path (perhaps entirely in the Na atom) a circle of such size that centrifugal force and electric attraction are in equilibrium. Let \( i \) be the inertia of an electron, then

\[
\frac{iv^2}{s} = \frac{e^2}{s^2} \cdot \frac{1}{K} = \frac{e^2}{s^2N^2},
\]

where \( K \) is dielectric constant and \( N \) index of refraction for NaCl (preferably perhaps for Na), and for the period of revolution we have

\[
\frac{2\pi s}{v} = \frac{2\pi Ns^3i^3}{e},
\]

with the values \( s \) of order \( 4 \times 10^{-9} \), \( i/e = 345 \times 10^{-17} + 500 \) (J. J. Thomson), \( e \) of order \( 3 \times 10^{-10} \), and \( N = 1.5 \), this gives
a period $36 \times 10^{-17}$. It is worth noting that this period corresponds to a frequency $28 \times 10^{14}$ which is about ten times as large as that of the visible part of the spectrum, and is nearly equal to the $33 \times 10^{14}$ which in "The Cause of the Structure of Spectra" (Phil. Mag. [6] ii. p. 273) was found to be the value of a fundamental spectral constant denoted by $1/A = VB$, where $V$ is the velocity of light in free æther and $B$ the parameter in Balmer's formula, which Rydberg assumes to be a constant of nature in his modified form of it, namely $n = n_0 - B/(m + \mu)^2$

We shall now resume the study of the Laws of Molecular Force in the light of the electron theory.

**5. Electric Doublets in different classes of Chemical Substances.**

Before considering in some little detail the laws of $(M^2l)^4$, which are those of $s$, for different chemical types, we must discuss the remarkable contrast shown (xxxv.) between the characteristic equations of element and compound gases. For the element gases $H_2, N_2, O_2$ and also for the compound $CH_4$ the equation of van der Waals represents the experimental facts down to nearly two-thirds of the critical volume. It can be written

$$pv = RT + RT \frac{k}{2(v-k/2)} - \frac{l}{v} \quad \ldots \ldots \ldots \ldots (4)$$

where the terms are respectively two thirds of the following, the virial of the pressure, the kinetic energy, the virial of the collisional forces, and the virial of the molecular attractions. For compound gases in general the type is

$$pv = RT + RT \frac{2k}{v+k} - \frac{l}{v+k} \quad \ldots \ldots \ldots \ldots (5)$$

Ethylene was found to have an intermediate form of equation, and probably other substances could be investigated to show different stages of transition from (4) to (5). Evidently (5) could be made more general by replacing $k$ in each of the three places where it occurs by a different parameter, but, as in xxxv., we will continue to use it in its more convenient simple form. When we contrast the collisional virial term for element gases $RT(k/2(v-k/2)$ with $RT2k/(v+k)$ for compounds, we see that in the first case $v$ is diminished by $k/2$, and in the second $v$ is increased by $k$. Now, according to the kinetic theory, the $-k/2$ comes in because the molecular free path is shortened by an amount depending on the
molecular radius on account of the mutual impenetrability of molecules. According to the kinetic theory $k/2$ stands for 4 times the volume of the molecules which occupy $v$. Then in compounds we must regard the $v + k$, which comes in instead of volume minus 4 times the actual volume of the molecules, to represent a lengthening of the mean free path, that is to say a diminution of the number of collisions. In the case of compounds then a collision is an event which, instead of shortening the interval between two successive ones from what it would be if the molecules could penetrate one another, actually prolongs it, so as not only to neutralize the term $-4$ times volume of molecules) but to add on $k$. In ethylene we meet with a transition case where the negative term is only neutralized, and the collisional virial is $RTk/v$. In compounds in general then, a collision is an entanglement of the parts of the molecules which lasts long enough to produce an appreciable effect on the dynamics of the molecules, namely a diminution of the collisional virial below what it would be if the molecules collided like hard spheres.

But in the present connexion the contrast between the virials of the attractive forces in element and compound gases is most important. From $v=\infty$ to $v=k$ (nearly) in element gases it is $-l/v$, and in compounds $-l/(v+k)$. For volumes less than $k$ the form for compounds is $-l/2v$. For compounds then we write the virial of the attractions

$$-\frac{l}{v+k} = -\frac{l}{v} + \frac{k}{v(v+k)},$$

and so see in it the general attractional virial $-l/v$ numerically reduced because a repulsional virial, which is a fraction $k/(v+k)$ of it, enters into the equation. When $v=k$ the fraction takes the value $\frac{1}{2}$, which it retains for smaller values of $v$, the virial then being $-l/v + l/2v = -l/2v$. Evidently then the entanglement during a collision of two compound molecules, which diminishes the virial of the collisional repulsive forces, introduces the virial $(l/v)[k/(v+k)]$ of repulsive forces of electrical origin.

We must briefly inquire into the probable cause of the contrast between the behaviour of element and compound gas-molecules during collision. In an element gas like $H_2$ we have $\#$ attached to $H$, and also $\varphi$ attached to $H$, whereas in a compound gas like $HCl$ $\#$ is associated only with $H$, and $\varphi$ with $Cl$. We can imagine then that in $H_2$ or $\#H\varphi$ it is possible for $\#$ and $\varphi$ to change places so as to form $\varphi H \#$ without displacing the atoms, whereas in the case of $\#HCl\varphi$
Electric Origin of Molecular Attraction.

it is impossible to get the electrons to change places without the atoms doing so also. When NaCl is giving the spectrum of Na perhaps both $\xi$ and $\eta$ are in Na. In a compound molecule, then, an electric doublet has less freedom of motion than in the molecule of an element gas. On this account the collision of molecules of an element gas is a simpler event than that of compounds. Moreover, in all compounds but the simple binary ones there are several doublets in each molecule, and during a collision a variety of possible combinations of positions of the doublets will succeed one another, causing an alternation of attractions and repulsions, which leave a different average preponderance of attraction at close quarters than at a distance. Thus below volume $k$ the preponderance of attraction is expressed by a virial $-l/2v$, and above $k$ by a virial $-l/(v+k)$, which, when $v$ is large, can be identified with the standard form $-l/v$. Now this contrast between the behaviour of compound and element gas-molecules at close quarters was verified in the Viscosity of Gases &c. (xxxvi.), where it was found that at close-quarters the mutual potential energy of two compound molecules is only half of what it would be if they behaved as the molecules of element gases.

In this way I have sought to explain the most important difficulty in the way of the electric theory of molecular attraction, namely that the attractive virial for compounds appears in the form $-l/(v+k)$ instead of $-l/v$, which is required by the general theory. Previously (xxxv.) I suggested that this phenomenon in compounds might be due to the pairing of compound molecules. This explanation must be withdrawn to be replaced by that of molecular entanglement here suggested, an entanglement being only a temporary sort of pairing.

We proceed now with the investigation of the laws of $s$.

In the case of the haloid compounds of the alkali metals it was shown in "Further Studies" (xxxix.) that to $(M^2)^1$, which is proportional to $s$, the metallic and halogen atoms contribute parts as follow:

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>2.4</td>
<td>3.5</td>
<td>4.6</td>
<td>6.0</td>
<td>7.3</td>
<td>0.9</td>
<td>2.1</td>
<td>2.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

For the Li family these can be written 1.2 (2, 3, 4, 5, 6), and for the F family 0.9 (1, 2, 3, 4). With the haloid compounds of the ‘dyad’ metals of the Be family, we must remember that $(M^2/2)^4$ now consists of a part $F$, due to the halogen atom as given above, and a part $F/2$ due to the

equivalent of metal, the latter having the values

\[
\begin{array}{ccccc}
\text{Be} & \text{Mg} & \text{Ca} & \text{Sr} & \text{Ba} \\
2.1 & 2.7 & 3.2 & 3.7 & 4.2
\end{array}
\]

which can be written 0.53 (4, 5, 6, 7, 8).

These simple laws for \( s \) lead to the following statement in regard to the Periodic Classification of the elements:—In successive columns the valency charges form the arithmetical progression \( e, 2e, 3e \) and so on, while in the successive rows the values contributed by atoms to \( s \), which is the other component factor of electric moment, form arithmetical progressions such as are exemplified above. In conjunction with these simple numerical relationships amongst the elements we must take the corresponding ones demonstrated in “A New Periodic Property of the Elements” and “The Cause of the Structure of Spectra” (Phil. Mag. [5] xxx. and [6] ii.). The volumes of the gramme-atom \( B \) of the alkali metals as given in “Further Studies” are subject to a simple numerical law, being given by

\[
2 + (n-1) n 2.7 = 2.7 \left( \frac{(n-\frac{1}{2})^2 + \frac{1}{2}}{1} \right)
\]

where \( n \) has the values 1, 2, 3 and so on, as the following comparison shows

\[
\begin{array}{cccccc}
\text{Li} & \text{Na} & \text{K} & \text{Rb} & \text{Cs} \\
\text{B found} & 2.0 & 7.4 & 18.6 & 34.4 & -- \\
\text{B calc.} & 2.0 & 7.4 & 18.2 & 34.4 & 56.0
\end{array}
\]

The volumes of the gramme-atom of the halogens in compounds run as 1, 2, 3, 4. But in the Be family there is no such simple relation discoverable. But in “Further Studies” it was shown that the following relations hold approximately between \( F \) and \( B \), namely in the Li family \( F^2 = 0.9B + 4.4 \), and in the Be family \( F^2/4 = 0.9B + 3.0 \). From formule just given we see that for the Li family a more accurate relation is

\[
B = 2 + 2.7 (F/1.2 - 1) (F/1.2 - 2).
\]

For the uncombined metals the following results are established by Tables XXIX. and XXX. of “Further Studies.” First that \( (M/\rho)/M^2l \) or \( B/M^2l \) is the same for the members of one chemical family, and second that for families of different valency \( n \) the values of \( nB/M^2l \) are nearly 2.8, except in the case of the Be family, for which it is 2.0. Thus, then, for the metals we have the relation that \( e^2s^2 \) is proportional to the volume of the atom with which the doublet is associated. To assign a simple meaning to this formula let us assume a doublet in a metallic atom, and use
for it the formula we used in calculating the period of rotation
of \( \# \) in NaCl, namely,

\[
\frac{i^2}{s} = \frac{e^2}{s^2} \cdot \frac{1}{N^2} ;
\]

\[ \therefore \quad e^2 s^2 = N^2 i^2 s^2. \]

Now \( i \) is constant; and if \( Nv \) is constant for the metals, then \( e^2 s^2 \propto s^3 \); and if \( s \) is equal or proportional to the linear
dimension of the atom, the remarkable proportionality between
\( e^2 s^2 \) and volume of atom in the uncombined metals would be
accounted for. It would seem as though the \( \# \) and \( \# \) in a
metallic atom moved out till centrifugal force balanced elec-
trical attraction, and so determined the linear dimensions of
the atom. If we remember that \( N \) varies inversely as the
velocity of light through the atom, the condition that \( Nv \) is
to be constant makes the ratio of \( v \) the linear velocity of \( \# \) or
\( \# \) to that of light through the atom constant, a result already
made probable in the 7th section of "The Cause of the
Structure of Spectra."

On passing from the simple cases of metals and binary
compounds, where we are dealing with only a few regularly
arranged doublets in each molecule, to typical organic com-
ounds where the atoms are built up to molecules by means
of elaborate ramifications of doublets, we must expect to pass
through intermediate types, where the simplicity of the
binary compounds is lost without being replaced by the other
sort of simplicity which we may expect on account of the
law of averages coming into play in the complex organic
compounds. We had better then study the case of the typical
complex organic molecule first. We must expect the doublets
in such a molecule to exercise a mutual directive action on
one another, so that the whole molecule may be considered
to have an electric moment obtained in the following way.
It is known that with a uniformly magnetized sphere the
external field of force is the same as that of a small magnet
at its centre with a magnetic moment equal to the intensity
of magnetization multiplied by the volume of the sphere.
Therefore for a number of magnetic spheres of different
sizes uniformly magnetized with the same intensity the mag-
netic moment of each will be proportional to its volume. Now
in a complex molecule we must on the average expect the
doublets to arrange themselves so as to correspond as nearly
as possible to the case of uniform magnetization. For the
electric doublet I have already proposed the name neutron,
so the proposal we are considering might be called that of an
average uniform neutration in complex molecules or an approximation to it. The electric moment of such a molecule must then be proportional to its volume. But this is one of the main results obtained in "Further Studies," being expressed as follows at the end of section 1:—"As a subsidiary result, it has been shown that the attracting powers of the atoms of Cl, Br, I, O, S, N, and C (C unattached to H) are approximately proportional to their volumes in the combined state."

In the complex organic molecule the different atoms and radicals contribute to the limiting volume of the gramme-molecule parts which are, on the average, 10 times the part which they contribute to \((M^2l)^{1/3}\), \(l\) being the virial parameter expressed for a gramme of the substance with \(10^{12}\) dynes as the unit of force. But the fundamental radical \(\text{CH}_2\) has a limiting volume which is 19 times the part it contributes to \((M^2l)^{1/3}\). On the other hand, the two terminal hydrogen atoms of the paraffin molecule \(\text{C}_n\text{H}_{2n+2}\) seem to possess a ratio 4 instead of 10. For the great majority of gaseous compounds such as \(\text{CO}_2, \text{SO}_2, \text{C}_2\text{N}_2\), and the simpler volatile liquids the ratio \(B/(M^2l)^{1/3}\) is nearly 10. For a few such substances the ratio is small; thus for \(\text{H}_2\text{O}\) it is 6, for \(\text{H}_2\text{S}\) it is 7, and for \(\text{NH}_3\) also 7. It is worth noticing that these are substances possessing remarkable powers of ionizing electrolytes. This power would thus seem to be due to a high intensity of neutration. In the case of electrolytes of the simplest binary type we have \(B/(M^2l)^{1/3}\) ranging from 3.3 for \(\text{LiF}\) to 7.3 for \(\text{RbI}\). On the other hand, the element gases \(\text{H}_2, \text{O}_2, \text{N}_2\), and the compound \(\text{CH}_4\) have values for this ratio near 19.

Now when dissolved in water these are not electrolytes; and this fact would seem to be due to their small intensity of neutration. In these gases also the attractional virial is \(-l/v\), molecular entanglement during collision is slight. Obviously then intensity of neutration and the related magnitude of electric moment of doublets are important physical properties of substances, requiring detailed study.


As to the couples which doublets like magnets exercise on one another, their chief action appears to be that of giving similarity of direction to the electric axes of neighbouring molecules. The question as to whether they may appear in a kinetic theory of solids will require special examination; but as molecular attraction in liquids is of the same order as in solids, and yet the rigidity of liquids is very small indeed, it
Vibration of Ferromagnetic Wires in a Magnetizing Field. 645

would appear that molecular couples do not enter directly into the molecular theory of rigidity. But the existence of similarly directed electric axes in neighbouring molecules is suggestive of the existence of similarly directed axes of rotation in neighbouring molecules; and this would bring in gyrostatic properties of molecules as an element in rigidity. In "A Kinetic Theory of Solids" (Phil. Mag. [5] xxxii.) the ascription of independent kinetic energies in the directions of three rectangular axes amounts to the same thing as taking account of gyrostatic energy.

It is obvious that a logical deduction from the above principles must be the formulation of a dynamic theory of dielectric capacity in which electric doublets and molecular gyrostatic properties will play the most important part, and also the systematic development of an electrical theory of thermochemistry on Helmholtz's lines.

Melbourne, August 1902.

LXXI. Note on the Vibration of Ferromagnetic Wires placed in a Varying Magnetizing Field. By K. Honda and S. Shimizu*.

It is well known that ferromagnetic bodies emit an audible sound at the moment of making and breaking the magnetizing current. Page † first heard the sound in the magnet, when an electric current passed through a copper spiral placed between the poles of a horse-shoe magnet. The sound was more intense at the break than at the make. A similar phenomenon was also observed by Delezenne ‡. Marrian § placed iron and steel wires in a coil, and by making and breaking the magnetizing current, he heard a sound due to the longitudinal fundamental vibration of the wires. Matteucci ¶ examined the effect of tension, and found that the pitch of the sound was independent of the tension, but that the intensity was decidedly increased. The investigation with iron bars of different lengths led Wertheim ¶ to the conclusion that each bar vibrated in its fundamental mode. By passing an intermittent current through the magnetizing coil, he heard a continuous sound, the pitch of which was the same as that

* Communicated by the Authors.
§ Marrian, Phil. Mag. vol. xxv. p. 382 (1844).